Inter- and Intra-molecular Ligand-exchange and -rearrangement Reactions of Tetra-azadiene Complexes of Nickel, Platinum, and Cobalt

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Tetra-azadiene-exchange and -rearrangement reactions have been observed for both $[Ni(R_2N_4)_2]$ and $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ (R_2=1,4-diaryl) complexes. The reactions of $[Ni(R_2N_4)_2]$ or $[Co(R_2N_4)(\eta^5\text{-}C_5H_5)]$ with aryl azides lead to substitution of the tetra-azadiene ligands. Reactions of $[Pt(R_2N_4)(cod)]$ or $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ with aryl azides $R'N_3$ produced platinum and nickel complexes with non-symmetrical RN_4R' ligands. All products arising from these reactions were identified by field desorption mass spectrometry and/or h.p.l.c. Four mechanisms which can account for the nature of the observed products, the product distributions, and reaction times are discussed. Transient aryl-nitrene species are proposed as key intermediates in these reactions.

RECENTLY we reported the reactions of aryl azides with $[Ni(cod)_2]$ (cod = cyclo-octa-1,5-diene), $[Ni(\eta^5\text{-}C_5H_5)_2]$, and $[Pt(cod)_2]$ leading to $[Ni(R_2N_4)_2]$, $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$, and $[Pt(R_2N_4)(cod)]$, respectively.[1] A characteristic property of these and other [2] tetra-azadiene-metal complexes is their thermal stability and relative inertness towards substitution. Up to now only a few reactions involving the tetra-azadiene ligands have been reported. These comprise (*i*) the reaction of $[Ni(R_2N_4)_2]$ with Bu^tNC, leading to the formation of $[Ni(R_2N_4)(Bu^tNC)_2]$;[1] (*ii*) ligand-transfer reactions under mild conditions in which a complete R_2N_4 ligand is transferred from $[Ni(R_2N_4)_2]$ to another nickel or platinum centre *via* an isolable intermediate;[3] (*iii*) decomposition reactions with HCl;[4] and (*iv*) the photochemical rearrangement of $[Co\{1,4\text{-}(C_6H_4)_2N_4\}(\eta^5\text{-}C_5H_5)]$ to yield $[Co\{HN(C_6H_4)NC_6H_5\}(\eta^5\text{-}C_5H_5)]$.[5]

In this paper we report the first evidence for the occurrence of intermolecular ligand exchange processes and intramolecular rearrangements of tetra-azadiene metal complexes at high temperatures. Four separate mechanisms which are most likely to be operative in these reactions are discussed.

EXPERIMENTAL

Syntheses of the tetra-azadiene complexes $[Ni(R_2N_4)_2]$, $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$,[1,6] $[Pt(R_2N_4)(cod)]$,[7] and $[Co(R_2N_4)(\eta^5\text{-}C_5H_5)]$ [8] have been described elsewhere. All reactions were carried out in boiling toluene under a dry, oxygen free nitrogen atmosphere unless otherwise stated. The toluene used was carefully dried and distilled prior to use.

After evaporation of solvent *in vacuo* the residues of all reaction mixtures were analyzed by field desorption (f.d.) mass spectrometry without prior separation. The f.d. mass spectra were obtained with a Varian MAT 711 double focusing mass spectrometer equipped with a combined EI/FI/FD ion source and coupled to a spectro system MAT 100 data acquisition unit. Field desorption emitters with an average length of 30 μm for the carbon microneedles were used. The samples were dissolved in tetrahydrofuran (thf) and then loaded onto the emitters with the dipping technique. In all experiments emission-controlled f.d. was used at a threshold of (3—5) × 10^{-9} A, measured between the field anode and the slotted cathode, 1.5 mm distance apart. Mass spectra were obtained with emitter currents of 10 mA.

The h.p.l.c. (high performance liquid chromatography) separations were performed with an apparatus assembled from commercially available elements,[9] with u.v. detection. The column packing material was octadecyl modified silica (Zorbax ODS, 5 μm). The eluant consisted of 90% MeOH, 10% H_2O unless otherwise stated.

The symmetric $[Ni(R_2N_4)_2]$ products were identified by comparison of the observed capacity factors (K) with those of the pure products. For full details on the behaviour of $[Ni(R_2N_4)_2]$ complexes in h.p.l.c. phase systems see ref. 9.

Reactions between Various Tetra-azadiene-metal Complexes.—(*a*) *Reactions of* $[Ni(R_2N_4)_2]$ *with* $[Ni(R'_2N_4)_2]$. The complex $[Ni(R_2N_4)_2]$ ($R = C_6H_4Me\text{-}4$) (100 mg, 0.19 mmol) was refluxed in toluene in air with $[Ni(R'_2N_4)_2]$ (0.19 mmol) for 18 d ($R' = C_6H_4OMe\text{-}4$) or 3 d ($R' = C_6H_3Me_2\text{-}3,5$ or $C_6H_4Cl\text{-}4$).

(*b*) *Reactions of* $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ *with* $[Ni(R'_2N_4)_2]$. The complex $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) (50 mg, 0.14 mmol) was refluxed in toluene with $[Ni(R'_2N_4)_2]$ (0.14 mmol) for 18 h ($R' = C_6H_3Me_2\text{-}3,5$) and 5 h ($R' = C_6H_4OMe\text{-}4$).

The following reactions (*c*)—(*f*) were carried out on the same scale and following the procedure described for reaction (*b*), applying the reaction times as indicated.

(*c*) *Reactions of* $[Ni(R_2N_4)_2]$ *with* $[Pt(R'_2N_4)(cod)]$ (8 h) ($R = C_6H_4Me\text{-}4$, $R' = C_6H_4Cl\text{-}4$ or $C_6H_4NO_2\text{-}4$).

(*d*) *Reaction of* $[Ni(R_2N_4)_2]$ *with* $[Co(R'_2N_4)(\eta^5\text{-}C_5H_5)]$ (1 d) ($R = C_6H_4OMe\text{-}4$, $R' = C_6H_4Me\text{-}4$).

(*e*) *Reaction of* $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ (1 d) ($R = C_6H_4Me\text{-}4$).

(*f*) *Reaction of* $[Co(R_2N_4)(\eta^5\text{-}C_5H_5)]$ *with* $[Co(R'_2N_4)(\eta^5\text{-}C_5H_5)]$ (3 d) ($R = C_6H_4Me\text{-}4$, $R' = C_6H_3Me_2\text{-}3,5$). For this reaction the residue isolated from reaction (*i*) (*vide infra*) was used.

Reactions between Tetra-azadiene-metal Complexes and Aryl Azides.—(*g*) *Reactions of* $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ *with* $R'N_3$. The complex $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) (50 mg, 0.14 mmol) was refluxed with $R'N_3$ ($R' = C_6H_4OMe\text{-}4$) (1 g, 6.7 mmol) in toluene (20 cm^3) for 45 min. The mixture was concentrated *in vacuo* to 4 cm^3 and chromatographed (in air) on a silica 60 column (20 × 2 cm) with toluene until the yellow band [unreacted azide and 4,4′-bis(methoxy)azobenzene] had been eluted. Further elution of the column with a 1 : 1 mixture of thf and toluene yielded a deep purple band. This fraction was concentrated to dryness. The reaction with $3,5\text{-}Me_2C_6H_3N_3$ was carried out similarly.

(*h*) *Reactions of* $[Ni(R_2N_4)_2]$ *with* $R'N_3$. The complex $[Ni(R_2N_4)_2]$ ($R = C_6H_4Me\text{-}4$) (100 mg, 0.19 mmol) was refluxed with $R'N_3$ ($R' = C_6H_4OMe\text{-}4$) (1 g, 6.7 mmol) in toluene (20 cm^3) in air for 5 h. Work-up of the reaction mixture followed the same procedure as described for the reactions of type (*g*). The reaction with 3,5-$Me_2C_6H_3N_3$ was carried out similarly, but in this case [$Ni(R_2N_4)_2$] (1 mmol) was refluxed with $R'N_3$ (30 mmol) in toluene (20 cm^3).

(*i*) *Reactions of* [$Co(R_2N_4)(\eta^5$-$C_5H_5)$] *with* $R'N_3$. The complex [$Co(R_2N_4)(\eta^5$-$C_5H_5)$] (R = C_6H_4Me-4) (50 mg, 0.14 mmol) was refluxed with $R'N_3$ (R' = $C_6H_3Me_2$-3,5) (1 g, 6.8 mmol) in toluene (20 cm^3) for 8 h. Work-up was as described for reaction (*g*) with the exception that the products were eluted as a dark brown band with pure thf. Analysis by f.d. mass spectrometry only showed a mixture of [$Co(R_2N_4)(\eta^5$-$C_5H_5)$] and [$Co(R'_2N_4)(\eta^5$-$C_5H_5)$]. [This mixture was used for reaction (*f*).]

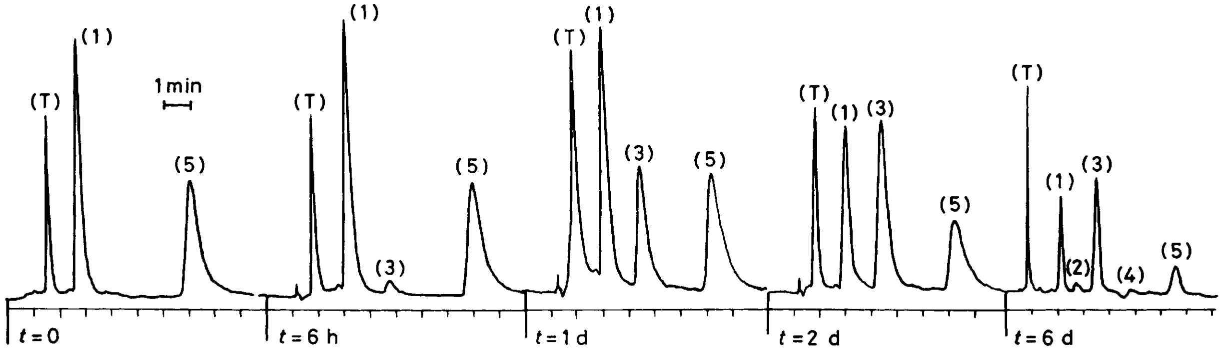

FIGURE 1 Chromatograms of the reaction between [$Ni(R_2N_4)_2$] (R = C_6H_4Me-4) and [$Ni(R'_2N_4)_2$] (R' = C_6H_4OMe-4) as monitored by h.p.l.c. (λ 274 nm): toluene (T); [$Ni(R'_2N_4)_2$] (1); [$Ni(R'_2N_4)(RN_4R')$] (2); [$Ni(RN_4R')_2$] and [$Ni(R_2N_4)(R'_2N_4)$] (3); [$Ni(R_2N_4)(RN_4R')$] (4); [$Ni(R_2N_4)_2$] (5). The chromatogram at t = 6 d was recorded using a freshly packed column

(*j*) *Reactions of* [$Pt(R_2N_4)$(cod)] *with* $R'N_3$. The complex [$Pt(R_2N_4)$(cod)] (R = C_6H_4Cl-4) (100 mg, 0.18 mmol) was refluxed with $R'N_3$ (R' = C_6H_4Me-4) (1 g, 6.7 mmol) in toluene (20 cm^3) for 8 h. After cooling the reaction mixture to room temperature, pentane (50 cm^3) was added and the mixture stored for 18 h at −20 °C. The resulting precipitate was washed with pentane (4 × 5 cm^3) and dried *in vacuo*. The reaction of $R'N_3$ with [$Pt(R_2N_4)$(cod)] (R = $C_6H_4NO_2$-4) was carried out similarly.

RESULTS

Reactions and Products.—The reactions between the symmetric tetra-azadiene metal complexes [$Ni(R_2N_4)_2$] and [$Ni(R'_2N_4)_2$] (R = C_6H_4Me-4, R' = C_6H_4OMe-4, C_6H_4Cl-4, or $C_6H_3Me_2$-3,5) [reactions (*a*)] resulted initially in the formation of [$Ni(R_2N_4)(R'_2N_4)$] products. After the reaction had run for between 2 to 6 d [$Ni(R_2N_4)_2$], [$Ni(R_2N_4)(R'_2N_4)$], and [$Ni(R'_2N_4)_2$] were present in an approximate 1 : 2 : 1 molar ratio [see Figures 1 and 2, products (5), (3), and (1) respectively]. Products containing one non-symmetric RN_4R' ligand [Figure 1, products (2) and (4)] were detectable after 6 d in the chromatogram and after 3 d in the f.d. mass spectra (see Table).* These products were not observed for R' = C_6H_4Cl-4.

The reaction of [$Ni(R_2N_4)(\eta^5$-$C_5H_5)$] with [$Ni(R'_2N_4)_2$] (R = C_6H_4Me-4, R' = $C_6H_3Me_2$-3,5) [reaction (*b*)] resulted in formation of five products: [$Ni(R_2N_4)(\eta^5$-$C_5H_5)$], [$Ni(R'_2N_4)(\eta^5$-$C_5H_5)$], [$Ni(R_2N_4)_2$], [$Ni(R_2N_4)(R'_2N_4)$], and [$Ni(R'_2N_4)_2$], after 2 h (see Table). It appeared that the [$Ni(R_2N_4)(\eta^5$-$C_5H_5)$] and [$Ni(R'_2N_4)(\eta^5$-$C_5H_5)$] complexes were no longer detectable after 18 h, owing to decomposition. For R' = C_6H_4OMe-4 only two products were observed after 5 h namely [$Ni(R_2N_4)(R'_2N_4)$] and [$Ni(R'_2N_4)_2$].

No reaction was observed in the mixtures (*c*)—(*f*) after refluxing for periods varying from 8 h to 3 d and only the starting materials were detected by f.d. mass spectrometry.

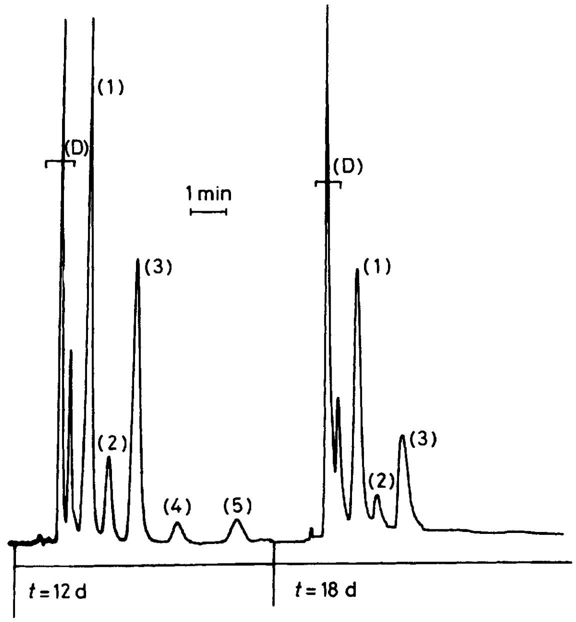

FIGURE 2 Chromatograms of the same reaction as in Figure 1, but the decomposition products have largely been removed by filtering through a silica 60 column. Organic decomposition products are marked (D) (detection at λ 350 nm)

The reactions of tetra-azadiene-metal complexes with aryl azides were faster than the reactions between the tetra-azadiene-metal complexes themselves. These reactions were not restricted to the nickel complexes, but were also found for [$Co(R_2N_4)(\eta^5$-$C_5H_5)$] (R = C_6H_4Me-4) and [$Pt(R_2N_4)$(cod)][7] (R = $C_6H_4NO_2$-4). Two types of reaction were observed, (*i*) reactions in which only complete tetra-azadiene units were substituted; and (*ii*) reactions in which

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* The Table containing the f.d. mass spectra and Figure 3 showing the chromatograms of the reaction of [$Ni(R_2N_4)_2$] with [$Ni(R'_2N_4)_2$] are available as Supplementary Publication No. SUP 23299 (10 pp.). For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

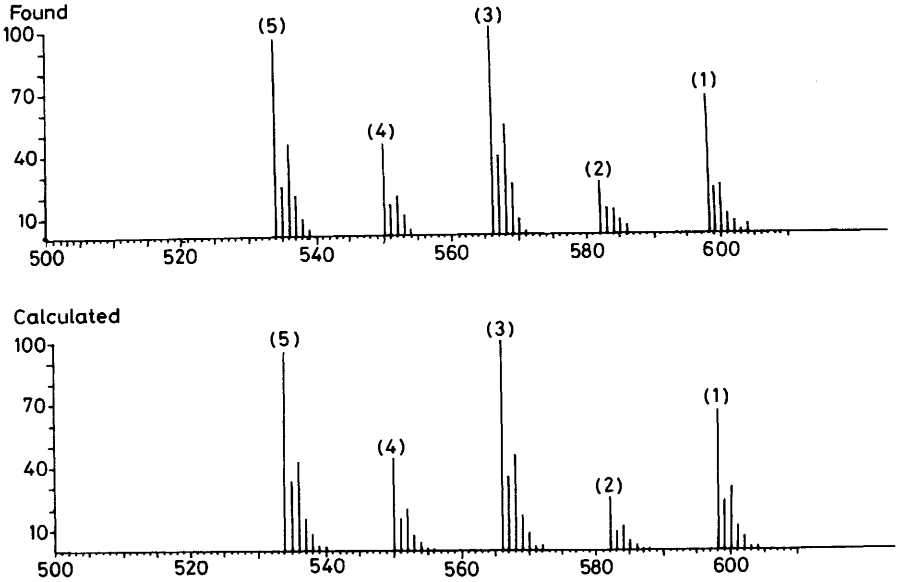

FIGURE 4 f.d. Mass spectra of the reaction mixture of $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ with $R'N_3$ ($R = C_6H_4Me\text{-}4$, $R' = C_6H_4OMe\text{-}4$) after removal of decomposition products over a silica 60 column, $t = 45$ min. For each $[Ni(R'_2N_4)_2]$ product the intensity of the highest peak is depicted equal to the corresponding measured peak

also complexes containing non-symmetrical (RN_4R') ligands were formed.

The f.d. mass spectra (Table) indicated that complete tetra-azadiene ligands were substituted in the reactions of excess azide ($R'N_3$) with $[Ni(R_2N_4)_2]$ ($R = C_6H_4Me\text{-}4$, $R' = C_6H_4OMe\text{-}4$ or $C_6H_3Me_2\text{-}3,5$) [reactions (*h*)] affording $[Ni(R_2N_4)(R'_2N_4)]$ and for $R' = C_6H_4OMe\text{-}4$ yielding $[Ni(R'_2N_4)_2]$. The similar reaction of $R'N_3$ ($R' = C_6H_3Me_2\text{-}3,5$) with $[Co(R_2N_4)(\eta^5\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) [reaction (*i*)] led to the formation of $[Co(R'_2N_4)(\eta^5\text{-}C_5H_5)]$.

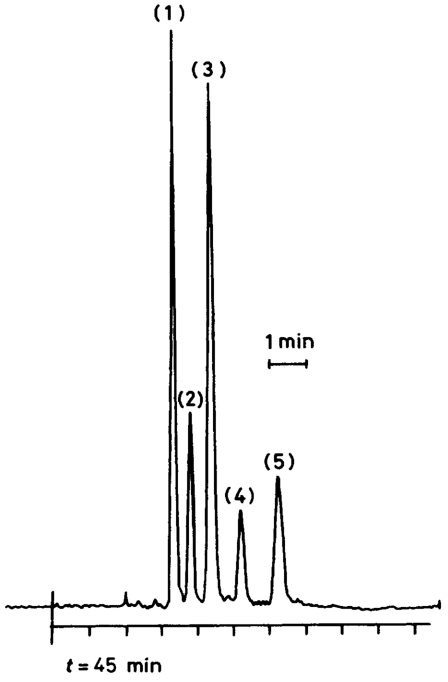

FIGURE 5 Chromatogram of the products of the reaction between $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ and $R'N_3$ ($R = C_6H_4Me\text{-}4$, $R' = C_6H_3Me_2\text{-}3,5$): $[Ni(R_2N_4)_2]$ (1); $[Ni(R_2N_4)(RN_4R')]$ (2); $[Ni(RN_4R')_2]$ and $[Ni(R_2N_4)(R'_2N_4)]$ (3); $[Ni(R'_2N_4)(RN_4R')]$ (4); $[Ni(R'_2N_4)_2]$ (5) (detection at λ 350 nm)

Complexes containing non-symmetrical ligands (RN_4R') were observed in: (*i*) the chromatograms and f.d. mass spectra of the reactions of $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$) with $R'N_3$ ($R' = C_6H_4OMe\text{-}4$ or $C_6H_3Me_2\text{-}3,5$) [reaction (*g*)] [see Figures 3(*b*),* 4, and 5, and Table]; and (*ii*) in the f.d. mass spectra of the reaction of $[Pt(R_2N_4)(cod)]$ ($R = C_6H_4NO_2\text{-}4$) with $R'N_3$ ($R' = C_6H_4Me\text{-}4$) [reaction (*j*)] (see Table).

The reactions of $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ with $R'N_3$ proceeded relatively fast (45 min), yielding a mixture of all five R–R′ permutation products ($[Ni(R_2N_4)_2]$, $[Ni(R'_2N_4)_2]$, $[Ni(R_2N_4)_2(RN_4R')]$ *etc.*). The reactions of $[Pt(R_2N_4)(cod)]$ with $R'N_3$ yielded no substitution products if R was $C_6H_4Cl\text{-}4$. However, for $R = C_6H_4NO_2\text{-}4$ the reaction yielded $[Pt(R'_2N_4)(cod)]$ and $[Pt(RN_4R')(cod)]$.

Analysis of the Residues obtained from Reactions (a)—(j) *by F.D. Mass Spectrometry and H.P.L.C.*—The f.d. mass spectra of the pure $[Ni(R_2N_4)_2]$ starting materials showed molecular ions with *m/e* values and isotope distributions as expected. For perfect correlation of calculated and measured isotopic patterns mean values of repetitive scans are necessary.[10] However, results with single scans were judged satisfactory (see Figure 4). The f.d. mass spectra give only a rough picture of the relative abundance of detected species in the reaction mixture. The volatility and the stability of their molecular ions is of main importance. Accordingly the absence of a $M^{\cdot+}$ or $(M + H)^+$ peak in the spectrum does not prove the absence of that product in the reaction mixture, but then fragments of the products should be detected. However, for closely related species ($[M(R_2N_4)_n(L)_m]$, differing only in R) similar properties can be anticipated. In these cases absence of one of the possible species was considered to be indicative of absence of that species in the reaction mixture. A good qualitative correlation was obtained between h.p.l.c. chromatograms and f.d. mass spec-

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* For Figure 3 see SUP No. 23299.

tra concerning the relative abundance of the constituents of the reaction mixtures as detected [*cf.* Figures 3(*b*) and 4]. The products from the reactions (*a*) and (*g*) were investigated by h.p.l.c. In each case the totally symmetric [Ni(R_2N_4)$_2$] complexes could be identified by their known capacity factors in these systems.[9] Other products visible in the chromatograms could be identified by correlation of the chromatograms with the f.d. mass spectra and for the products from the reactions between [Ni{1,4-(C_6H_4Me-4)$_2$-N_4}(η^5-C_5H_5)] with 3,5-$Me_2C_6H_3N_3$ and between [Ni{1,4-(C_6H_4Me-4)$_2N_4$}$_2$] and [Ni{1,4-(C_6H_4OMe-4)$_2N_4$}$_2$], by correlation of the capacity ratio *K′* with the number of carbon and oxygen atoms, respectively, in that product (see Figure 6). The expected relationship between *K* and the nature of the R ligands in the bis(tetra-azadiene)nickel complexes is clearly illustrated. As the separation of these mixtures on a preparative scale on the available columns was not possible, the products could not be characterized by other techniques and no precise yields were determined. However, as the molar absorption coefficients of [Ni{1,4-(C_6H_4-Me-4)$_2N_4$}$_2$] and [Ni{1,4-(C_6H_4OMe-4)$_2N_4$}$_2$] are nearly equal at 274 and 350 nm (the wavelengths used in the u.v. detection of the peaks in h.p.l.c.) and those of the other reaction products are expected to be approximately the same, the area of the peaks of the chromatograms can be used as a reliable measure for the relative abundance of the detected species. Comparison of the relative peak area ratios of the products and toluene reveals that in this case we are dealing with the principal reaction. The chromatograms of the reaction between [Ni{1,4-(C_6H_4Me-4)$_2N_4$}$_2$] and [Ni{1,4-(C_6H_4OMe-4)$_2N_4$}$_2$] (274 nm) showed that gradual decomposition of the reactants occurred, *i.e.* (C_6H_4Me-4)$_2N_2$ and (C_6H_4OMe-4)$_2N_2$ appeared in the chromatograms along with a decreasing intensity of the [Ni(R_2N_4)$_2$] peaks relative to the internal standard toluene [see Figure 1 (6 d) and Figure 2].

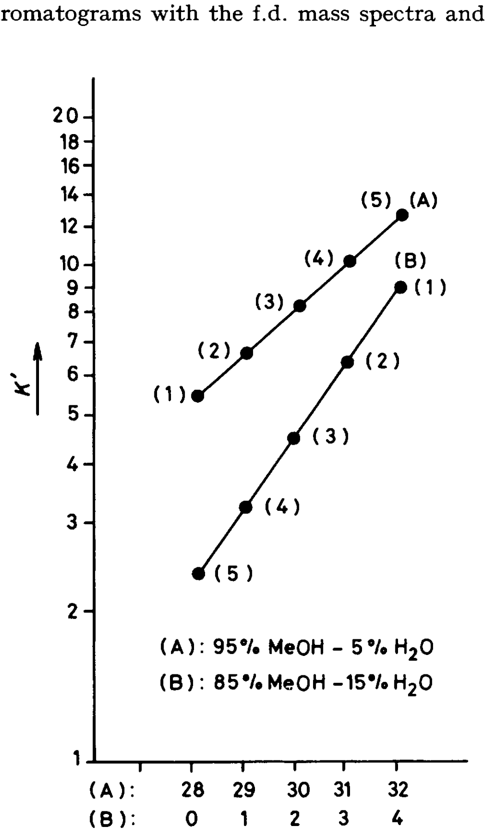


FIGURE 6 Relationship between *K′* and the structure of products from the reactions between [Ni(R_2N_4)(η^5-C_5H_5)] and R′N_3 (A) (R = C_6H_4Me-4, R′ = $C_6H_3Me_2$-3,5, see also Figure 5) and between [Ni(R_2N_4)$_2$] and [Ni(R'_2N_4)$_2$] (B) (R = C_6H_4Me-4, R′ = C_6H_4OMe-4, see also Figure 1). For reaction (A) capacity factors are correlated to the total number of carbon atoms in the complexes, for (B) they are correlated to the total numbers of oxygen atoms in the complexes. The numbers (1)—(5) correlate with the peaks in the chromatograms (see Figures 5 and 1, respectively)

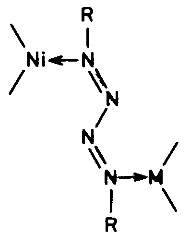
DISCUSSION

The exchange and rearrangement processes observed in reactions between tetra-azadiene-metal complexes and their reactions with aryl azides constitute a new and unexpected feature in this field. To date only a few examples are known of reactions in which a R_2N_4 (R = alkyl, aryl, or tosyl *etc.*) ligand participates.

On the basis of the nature of the observed products, the product distributions, and reaction times we discern four distinct mechanisms. Although the outcome of all these mechanisms can be clearly observed, proof of the mechanistic details will require further research. Before discussing the proposed mechanisms it must be noted that during the reactions decomposition of the products occurs. This is visible in Figures 1 and 2 where [Ni(R_2-N_4)$_2$] decomposes faster for R = C_6H_4Me-4 than for R = C_6H_4OMe-4. Although these decomposition reactions influence all final product distributions, product formation could easily be followed by f.d. mass spectrometry and h.p.l.c. techniques (see Results section).

Mechanism (I).—*Exchange of complete* R_2N_4 *ligands between complexes.* Exchange of complete R_2N_4 ligands is observed in the reactions between [Ni(R_2N_4)$_2$] and [Ni(R'_2N_4)$_2$] [reaction (*a*)] and between [Ni(R_2N_4)(η^5-C_5H_5)] and [Ni(R'_2N_4)$_2$] [reaction (*b*)]. A possible mechanism may be derived from the observations in the ligand-transfer reactions reported earlier.[3] In these reactions an R_2N_4 ligand is transferred under mild conditions from a [Ni(R_2N_4)$_2$] complex, *via* an isolable intermediate in which two metals are bonded to one R_2N_4 ligand, to another nickel or platinum centre. As the free tetra-azadiene moiety is unknown and probably unstable it must apparently be continuously stabilized by co-ordination to at least one metal.[3a]

The exchange reactions under vigorous conditions discussed now may also very well depend on a tetra-azadiene-bridged intermediate (see below). The rate



determining step in this case is the loss of an R_2N_4 ligand (which decomposes) from a $[Ni(R_2N_4)_2]$ complex. The resulting reactive $Ni(R_2N_4)$ species, which has two unoccupied co-ordination sites, would then react further according to equation (i). This would constitute a

$$\begin{aligned} &Ni(R_2N_4) + [(R'_2N_4)Ni(R'_2N_4)] \rightleftharpoons \\ &\quad [(R_2N_4)Ni(R'_2N_4)Ni(R'_2N_4)] \rightleftharpoons \\ &\qquad [(R_2N_4)Ni(R'_2N_4)] + Ni(R'_2N_4) \quad \text{(i)} \end{aligned}$$

random chain mechanism, which must be expected to work towards a 1 : 2 : 1 equilibrium for $[Ni(R_2N_4)_2]$, $[Ni(R'_2N_4)(R_2N_4)]$, and $[Ni(R'_2N_4)_2]$, respectively. In our experiments this distribution was observed after the reaction had run for 2—6 d [see products (1), (3), and (5) in Figure 1].

The reaction between $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ and $[Ni(R'_2N_4)_2]$ [reactions (*b*)] proceeds much faster (*cf.* Table). In this case the explanation is to be found in the relative lability of the nickel-cyclopentadienyl bond, which may dissociate more easily than a nickel-tetra-azadiene bond. Accordingly a $Ni(R_2N_4)$ fragment is produced much easier. Alternatively a free co-ordination site on the nickel centre may be created by the C_5H_5 ring, changing its bonding mode from η^5 to σ. Such rearrangements have been observed in mono(η^5-cyclopentadienyl)nickel complexes.[11,12]

Mechanism (II).—*Intramolecular rearrangement in* $[Ni(R_2N_4)_2]$ *complexes.* The observation of complexes containing non-symmetric ligands (RN_4R') among the products of reaction (*a*) cannot be explained by mechanism (I) alone. The fact that these products appear only after a relatively large amount of $[Ni(R_2N_4)(R'_2N_4)]$ has been formed (see Figure 1) suggests an intramolecular rearrangement taking place in this species to give $[Ni(RN_4R')_2]$. A possible mechanism may be the break-up of an R_2N_4 ligand as originally suggested by Cenini and coworkers,[13] into a co-ordinated nitrene species and a co-ordinated azide. If $[Ni(R_2N_4)(R'_2N_4)]$ breaks up in this way the fragments could then rearrange intramolecularly, *via* 1-*N*,3-*N'*-addition, giving rise to $[Ni(RN_4R')_2]$ (see Figure 7). The so formed bis(tetra-azadiene)nickel species containing non-symmetric ligands then also becomes part of the equilibrium outlined in mechanism (I). This works towards a 2 : 1 : 2 molar ratio for $[Ni(RN_4R')(R_2N_4)]$, $[Ni(RN_4R')_2]$, and $[Ni(RN_4R')(R'_2N_4)]$ respectively [see Figure 1, products (2), (3), and (4)] but full equilibrium is not reached because of decomposition of the bis(tetra-azadiene)nickel complexes at different rates, dependent on the nature of R. Figures 1 and 2 clearly show the onset of decomposition after 6 d.

It is interesting to note that no complexes containing only one non-symmetric ligand were observed among the products of the reaction between $[Ni\{1,4\text{-}(C_6H_4Me\text{-}4)_2N_4\}_2]$ and $[Ni\{1,4\text{-}(C_6H_4Cl\text{-}4)_2N_4\}_2]$. This may point to an influence of the aryl substituent upon the break-up of the R_2N_4 ligand.

A decomposition pathway, other than *via* $Ni(R_2N_4)$ fragments, involves intramolecular rearrangement to an aryl–azo compound *via* 1-*N*,1-*N'* coupling of the co-ordinated nitrene and azide fragments instead of 1-*N*,3-*N'* coupling, which forms the tetra-azadiene again. Co-ordinated aryl-azo ligands are expected to be unstable at 110 °C in air and have been reported to form free azo compounds.[12] Support for this decomposition mechanism is found in the presence of azo products in the reaction mixtures (see Figures 2 and 3).

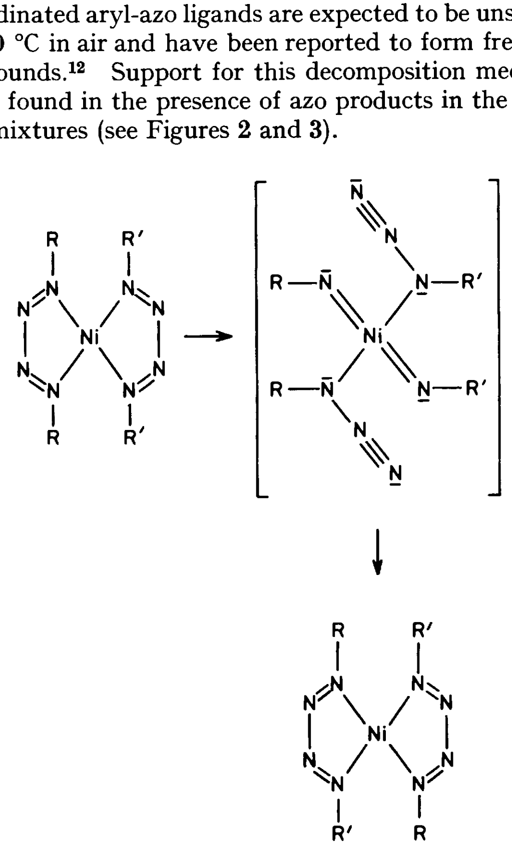


FIGURE 7 Proposed mechanism for the intramolecular rearrangement of co-ordinated R_2N_4 ligands [mechanism (II)]

Mechanism (III).—*Substitution of complete* R_2N_4 *ligands by reaction with aryl azide.* This process is observed in the reactions of excess aryl azide $R'N_3$ either with $[Ni(R_2N_4)_2]$ [reaction (*h*)] or with $[Co(R_2N_4)(\eta^5\text{-}C_5H_5)]$ [reaction (*i*)]. Attack of the azide on the metal in these complexes clearly leads to a destabilization and substitution of a complete tetra-azadiene unit. The attacking azide may then combine with another azide to form a new tetra-azadiene ligand. It is interesting to note that the reaction of $[Ni(R_2N_4)_2]$ ($R = C_6H_4Me\text{-}4$) with $R'N_3$ ($R' = C_6H_4OMe\text{-}4$) leads to formation of both $[Ni(R_2N_4)(R'_2N_4)]$ and $[Ni(R'_2N_4)_2]$ (see Table) while the reaction with $R'N_3$ ($R' = C_6H_3Me\text{-}3,5$) is slower and only produces $[Ni(R_2N_4)(R'_2N_4)]$.

Apparently an R_2N_4 ligand is more easily displaced in the order $R = C_6H_3Me_2\text{-}3,5 > C_6H_4Me\text{-}4 > C_6H_4OMe\text{-}4$. This is in line with our finding that the thermal stability of $[Ni(R_2N_4)_2]$ is greater for $R = C_6H_4OMe\text{-}4$ than for $R = C_6H_4Me\text{-}4$ (see Figures 1 and 2). So once a $[Ni(R_2N_4)(R'_2N_4)]$ species has been formed in the reaction between $[Ni(R_2N_4)_2]$ and $R'N_3$ the tetra-azadiene ligands will exhibit different stability, dependent on their aryl substituents. For $R' = C_6H_4OMe\text{-}4$ the reaction is expected to proceed *via* substitution of R_2N_4 to formation of $[Ni(R'_2N_4)_2]$, while for R′ = $C_6H_3Me_2$-3,5 the reaction is expected to proceed *via* substitution of R'_2N_4 to re-formation of $[Ni(R_2N_4)(R'_2N_4)]$. Furthermore the reaction of $R'N_3$ (R′ = $C_6H_3Me_2$-3,5) with $[Ni(R_2N_4)_2]$ (R = C_6H_4Me-4) is expected to be slower than the corresponding reaction involving R′ = C_6H_4OMe-4. These expectations are in line with our observations (see Table and Experimental section).

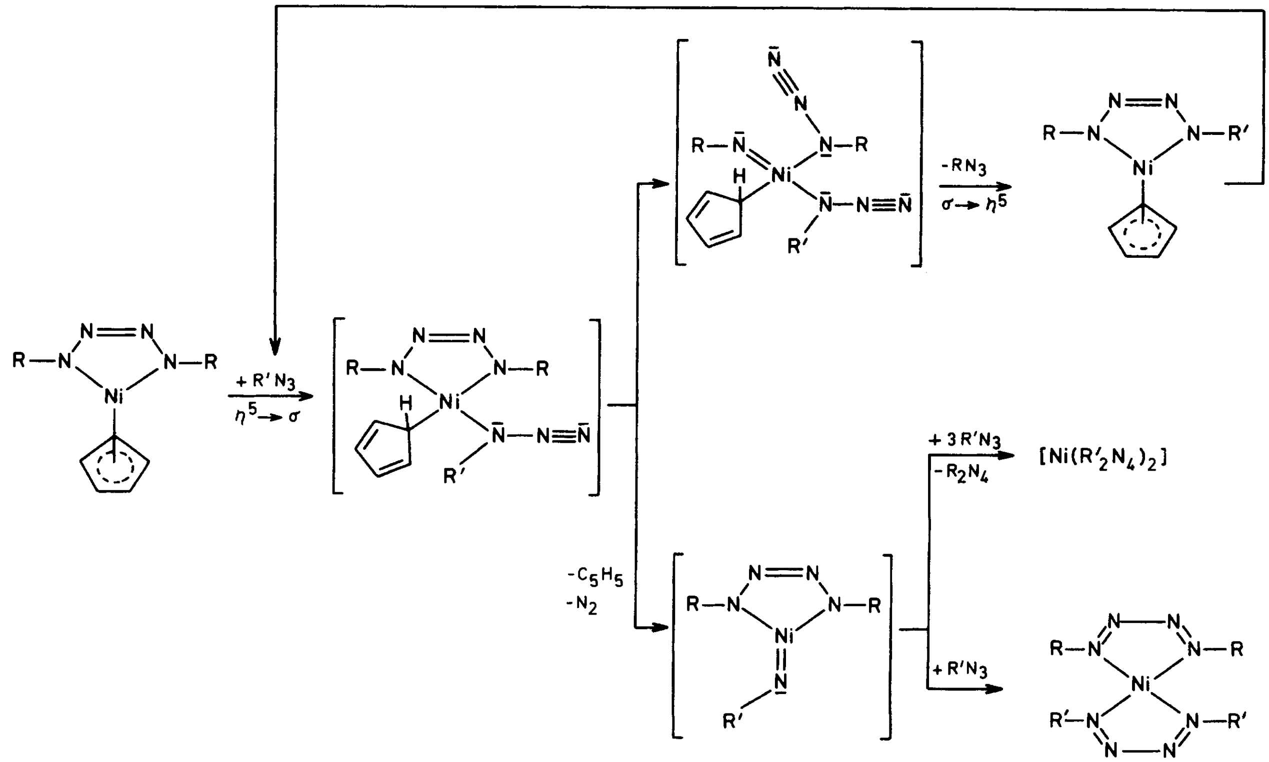


FIGURE 8 Reactions of $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ with $R'N_3$. Proposed pathways leading to all observed products

Mechanism (IV).—*Rearrangement of a tetra-azadiene with an attacking aryl azide.* The main difference for this mechanism compared to the proposed mechanism (III) is the possibility of a transition state in which the attacking azide is co-ordinated with initial retention of all ligands. In this transition state the break-up of the tetra-azadiene, which is slow in mechanism (II), could be induced by the attack of the azide on the metal centre. Intramolecular 3-*N*(azide)–1-*N*(nitrene) coupling leading to a non-symmetric tetra-azadiene is then possible (Figure 8). This mechanism can account for non-symmetric ligands in the reactions of $R'N_3$ with either $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ [reaction (*g*)*] or $[Pt(R_2N_4)(cod)]$ [reaction (*j*)]. In the reactions of $[Pt(R_2N_4)(cod)]$ with $R'N_3$ it is again the nature of the substituent on R which determines the outcome of the reaction. For R = C_6H_4Cl-4, no reaction is observed; for R = $C_6H_4NO_2$-4 intramolecular rearrangement of the R_2N_4 ligand with the incoming azide $R'N_3$ takes place leading to the formation of $[Pt(RN_4R')(cod)]$ and $[Pt(R'_2N_4)(cod)]$ species. This substituent effect is so strong that after 8 h the starting complex was no longer detected (see Table) whereas $[Pt\{1,4\text{-}(C_6H_4Cl\text{-}4)_2N_4\}(cod)]$ showed no reaction at all with $4\text{-}MeC_6H_4N_3$.

Mechanism of Formation of a Tetra-azadiene-metal Complex.—A mechanism for the formation of tetra-azadiene-metal complexes by the reaction of a metal centre with two azides has been proposed.[14] This proposal involves initial formation of a monodentate, σ-*N* co-ordinated R_2N_4 ligand which then becomes bidentate σσ-*NN′* bonded by attack of the second N^{α} atom on the metal. As 3-*N*(azide)–1-*N*(nitrene) coupling seems to be operative in mechanisms (II) and (IV), with both the nitrene[15] and the azide bonded to the metal before coupling, a similar mechanism for the formation of a tetra-azadiene-metal complex in the reaction of a metal centre with two azides cannot be excluded.

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* From reactions between $[Ni(R_2N_4)(\eta^5\text{-}C_5H_5)]$ with RN_3 on a preparative scale $[Ni(R_2N_4)_2]$ was isolated in at least 50% yields (*cf.* refs. 1 and 6).

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