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METAL COMPLEXES WITH ALLYLANILINES

IV *. SYNTHESIS AND REACTIVITY OF RHODIUM(I) COMPLEXES WITH 2-ALLYLANILINE AND *N*-ALLYLANILINE

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Summary

The reaction of 2-allylaniline (2aa) with $[Rh(C_2H_4)_2Cl]_2$ (I) in toluene or benzene at room temperature affords the dimer $[Rh(2aa)Cl]_2$ (II) in which the ligand acts as bidentate, being coordinated to the metal through the N atom and the olefinic group. II in CH_2Cl_2, isomerizes 2aa to *trans*-2-propenylaniline. This reaction goes also catalytically. Heating of II in benzene affords 2-methylindoline.

N-Allylaniline (naa) reacts with I to give the deep violet diamagnetic complex $Rh_2Cl_2(naa)_3$ (III), which is converted slowly into $[Rh(N\text{-phenylazetidine})ClC_7H_8]_2$. When III is heated with an excess of naa, the ligand is catalytically transformed into propene, azobenzene, *N*-n-propylaniline, *N*-i-propylaniline, *N*-allylideneaniline and aniline, as the more abundant products. Moreover, III reacts with diphenylacetylene to afford 2,5-dihydro-1,2,3-triphenyl-4-methylpyrrole. The reaction of III with methylacetylene follows a more complex path, and products of dimerization and trimerization of the alkyne have been isolated. Carbon dioxide influences the oligomerization reaction.

Introduction

Considerable attention has been given recently to the investigation of the rearrangement of amino olefins promoted by transition metals [1—3] which are able both to convert the unsaturated amines into five- or six-membered nitrogen heterocyclic compounds under mild conditions and to promote a C—N bond cleavage reaction [4].

* For part III see ref. 7.

We have shown that chelation of *N*-allylaniline to palladium(II) causes C—N bond cleavage at temperatures below 20°C [5,6] and that platinum(II) converts the ligand 2,6-diallylaniline into 1,2,4,5-tetrahydro-2,4-dimethylpyrrolo-[3,2,1-*h*,*i*]indole [7]. "$PtCl_2$" is not consumed during the reaction which can thus be considered as catalytic.

In extension of our work, we have studied the interaction of rhodium(I) with 2aa and naa in order to investigate the influence of the metal atom on the rearrangement of the ligand. Moreover, we have investigated the reaction of the coordinated ligand naa with substituted acetylenes as a possible route to sustituted 2,5-dihydropyrroles.

Experimental

The solvents used were dried by standard methods and distilled and stored under nitrogen. The reactions were carried out under purified nitrogen. The IR spectra were run with a Perkin—Elmer 577 spectrophotometer, gas-chromatographic analyses were performed with a Hewlett—Packard HP 5750 instrument, and ^1H NMR spectra were obtained on a Varian HA 100 instrument. The protons of the ligands are numbered as reported in Fig. 1 and τ values are referred to internal TMS. *N*-Allylaniline and 2-allylaniline were prepared and purified as previously reported [5,6].

Preparation of [Rh(2aa)Cl]$_2$

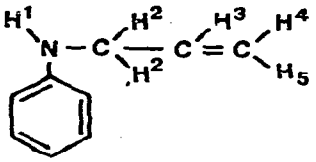
The ligand 2aa (0.17 g, 1.28 mmol) was added slowly with stirring to a filtered solution of $[Rh(C_2H_4)_2Cl]_2$ (0.25 g, 0.64 mmol) in toluene, and the solution was briefly pumped out in vacuum in order to remove the evolved ethylene. The yellow solid which separated was filtered, washed with pentane, and dried in vacuo (yield 0.30 g, 85%).

Isomerization of 2-allylaniline to trans-2-propenylaniline

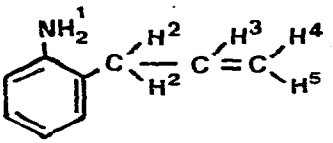
$[Rh(2aa)Cl]_2$ (0.20 g, 0.37 mmol) was dissolved in 20 cm^3 of CH_2Cl_2 and after addition of 2aa (2.00 g, 15.1 mmol) the solution was refluxed for 6 h. After cooling to room temperature, the solvent was distilled off in vacuo and pentane (20 cm^3) was added. The dark yellow solid was filtered off, washed with pentane, and dried in vacuo. Recrystallization from benzene/pentane gave 0.250 g (84%) of $[Rh(2pa)_2Cl]_2$. The pentane mother liquor after concentration to dryness left an oil, which, after purification by chromatography on a silica gel column with benzene/pentane (1/5) as eluant, afforded 0.85 g of pure *trans*-2-propenylaniline. The same isomerization, was carried out using $Pd(PCy_3)_2$. The starting Pd complex was recovered unchanged along with the isomerized ligand.

Preparation of $Rh_2(naa)_3Cl_2$ and [Rh(N-phenylazetidine)(C_7H_8)Cl]$_2$

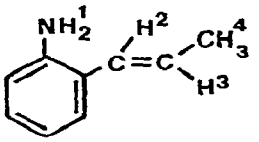
To a filtered solution of $[Rh(C_2H_4)_2Cl]_2$ (0.23 g, 0.59 mmol) in benzene (25 cm^3) the ligand naa (0.24 g, 1.8 mmol) was added, and the solution was briefly pumped out in vacuo. The solution changed in colour from orange to deep violet, and after one hour it was concentrated in vacuo to about 10 cm^3 and pentane was added. The deep violet compound which separated was fil-



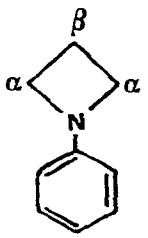
(n a a)



(2a a)

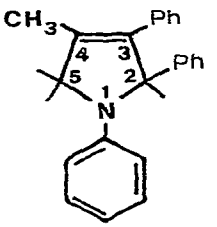


(trans - 2p a)



N- phenylazetidine

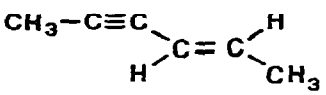
(npa)



2,5-dihydro-1,2,3-triphenyl-4-methyl-pyrrole

(hmp)

N-allylidenaniline



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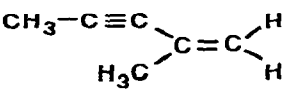

(B)

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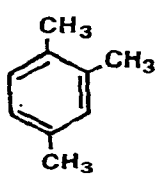

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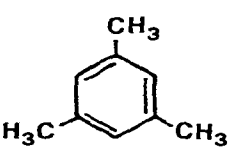

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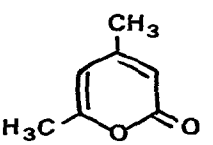

(D)

Fig. 1. Formulas and symbols of ligands and products of the oligomerization reactions.

tered off, washed with pentane, and dried in vacuo (yield 0.35 g, 90%).

Attempts to crystallize the complex from benzene, or other solvents, caused naa elimination, and a new orange complex was obtained which did not show any band attributable to the free or coordinated NH group, neither to double bonds. A new band was present in the IR spectrum of the solid complex (1950 cm^{-1}, Nujol mull). Crystallization from CH_2Cl_2 afforded a similar complex which IR spectrum showed a band at 1990 cm^{-1} (Nujol mull). The nature of this compound was dependent on the time it was kept in solution. Different

fractions, having different IR and ^1H NMR spectra, were isolated, but all analyzing for [$Rh(C_9H_{11}N)Cl$ · solvent].

From a dilute toluene/pentane solution stored for 25 days at a temperature around −20° C, an orange complex was isolated, and on the basis of the spectral features and analytical data this complex was formulated as [Rh(*N*-phenylazetidine)Cl]$_2$ · 2 C_7H_8. The yield ranged from 10 to 20% based on the starting complex.

Reaction of $Rh_2Cl_2(naa)_3$ with diphenylacetylene

Diphenylacetylene was added to a solution of $Rh_2Cl_2(naa)_3$ (0.50 g, 0.74 mmol) in benzene (50 cm^3) and the mixture was either stirred at room temperature overnight or refluxed for 1 h. After concentration in vacuo to small volume, pentane was added and the dark solid which formed was filtered off, washed with pentane, and dried in vacuo (yield 0.60 g, 90%).

Catalytic rearrangement of naa in the presence of $Rh_2Cl_2(naa)_3$

$Rh_2Cl_2(C_2H_4)_4$ (0.17 g, 0.44 mmol) and the ligand naa (1.0 g, 7.52 mmol) were placed in the two arms of an inverted Y tube and the system was stoppered, connected to a gas burette, and evacuated. The reagents were mixed and 41 cm^3 of gas were collected at 18° C and 756 mmHg. The gas was identified as pure ethylene (1.95 mol per Rh atom). After pumping in vacuo, the system was isolated and heated slowly: gas evolution started at ca. 80° C and lasted to 150° C. VPC showed that the gas collected (22 cm^3 measured in the above conditions) was propene (about one mol per Rh atom) accompanied by a small amount of ethylene (0.05 mol per Rh atom). The residual oil was analyzed by VPC and the more abundant products separated by chromatography on a silica gel column using pentane/benzene (5/1) as eluant.

Oligomerization of methylacetylene

Two procedures were used:

(a) The catalyst was dissolved in the solvent in a 40 cm^3 cell connected to a

TABLE 1

PHYSICAL AND ANALYTICAL DATA OF COMPOUNDS II AND III

Compound	Colour	M.p. (°C) [a]	Analyses (Found (calcd.) (%))			
			C	H	Cl	N
$Rh_2(2aa)_2Cl_2$ · 0.5 C_7H_8	yellow	150 (dec)	43.88 (44.0)	4.42 (4.50)	12.06 (12.0)	4.76 (4.69)
Rh_2(*trans*-2pa)$_4Cl_2$	dark yellow	144 (dec)	53.40 (53.3)	5.45 (5.50)	8.78 ((8.70)	6.92 (6.95)
$Rh_2(naa)_3Cl_2$ · 0.1 C_6H_6	deep violet	dec. from 175	48.42 (48.7)	4.91 (4.95)	10.38 (10.2)	6.14 (6.13)
$Rh_2(npa)_2Cl_2$ · 2 C_7H_8	orange	167 (dec)	52.82 (52.7)	5.26 (5.20)	9.76 (9.70)	3.84 (3.79)
$Rh_2(hmp)_2Cl_2$ · 2 C_6H_6	dark yellow	133 (dec)	65.98 (65.3)	5.16 (5.13)	6.72 (6.70)	2.65 (2.65)

[a] Uncorrected.

Abbreviations are reported in Fig. 1.

gas reservoir at constant pressure. (The concentration of the catalyst, the amount of solvent and the temperature are specified in Table 2) 0.1 cm^3 of the solution were withdrawn at fixed intervals of time and analyzed by VPC.

(b) The solution (10 cm^3) of the catalyst was added under nitrogen to the monomer which had been condensed at —78° C into a graduated glass vessel. The latter was then placed, with exclusion of air, into a rocking autoclave immersed in a thermostat oil bath. The conditions of the reaction are reported in Table 2. At the end of the run the solution was analyzed by VPC.

Rearrangement of the ligand trans-2-propenylaniline promoted by rhodium(I)

A solution of 0.30 g of $[Rh(2pa)_2Cl]_2$ (0.37 mmol) in benzene (20 cm^3) was refluxed for 3 h. To the dark orange solution obtained 1,2-bis(diphenylphosphino)ethane (0.60 g, 1.5 mmol) was added, and the solution heated gently for five minutes. A yellow solid separated. The solution was concentrated in vacuo to 5 cm^3 and pentane (5 cm^3) was added to complete the precipitation of the solid. This was filtered off, washed with pentane, and dried in vacuo. It was identified as $Rh(diphos)_2Cl$. The mother solution was evaporated to dryness and the residual oil dissolved in ether (3 cm^3) and analyzed by VPC.

Gas chromatographic analyses

The ethylene and propene were determined using a 1.5 m Cyano-Silicone + 1.5 m DMCS in Chromosorb column. The amines were determined using a 3 m Carbowax 20M column or Polyglycol 4000-KOH column. The products of dimerization and trimerization of the alkyne were determined using a Silicone/Chromosorb 3 m column. Alternatively an Apiezon L 3 m column was used as duplicate control.

Results and discussion

The addition of 2-allylaniline (2aa) to a solution of $Rh_2Cl_2(C_2H_4)_4$ (I) in toluene or benzene causes evolution of ethylene and a yellow complex, sparingly soluble in aromatic solvents, precipitates. It analyzes for $[Rh(2aa)Cl]_2 \cdot 0.5$ toluene (or benzene) (II). Its IR spectrum in Nujol mull shows bands at 3220, 3155 and 3090 cm^{-1} attributable to the $\nu(NH_2)$ of the ligand 2aa acting as a bidentate in the dimer complex II. The bands of the coordinated double bonds are at 1510 m (=CH_2 scissoring [8]), 1232 m and 1222 m (C=C stretching of the coordinated double bond [8]), 990, 978, 965, 942, 933 cm^{-1} (δ(C—H) out of plane of the coordinated olefinic group). The ν(Rh—Cl) is found at 288 cm^{-1}, in accordance with a Cl-bridged structure [9]. The ^1H NMR spectrum in DMSO-d_6 shows resonances at τ 2.98 (m, 4H, H(Ph)), 4.62 (broad singlet, 2H, NH_2), 6.10 (m, 1H, H^3), 6.81 (d, 2H, H^2, $J_{2,3}$ 6.0 Hz), 7.30 (dd, 1H, H^4, $J_{3,4}$ 8.0 Hz, $J_{4,5}$ 2 Hz), 8.36 (dd, 1H, H^5, $J_{3,5}$ 12.2 Hz, $J_{4,5}$ 2 Hz). Exchange with D_2O confirms that the signal at 4.62 is due to the NH_2 group. The VPC analysis of a solution of II in CH_2Cl_2 confirms the presence of toluene of crystallization in the ratio 0.25 mol of solvent per Rh atom. When a solution of II in CH_2Cl_2 is stirred at room temperature for a few hours under N_2 a new complex is isolated, and its IR spectrum shows that 2aa has been isomerized to *trans*-2-propenylaniline (2pa). Moreover, 2aa is easily converted catalytically

TABLE 2

OLIGOMERIZATION OF METHYLACETYLENE

Catalyst	Concentration [a]	Solvent	P (atm)	T (°C)	Molar ratio [c] of trimers	Molar ratio [d] of dimers A/B	% conversion of the alkyne, (time (h))	Other products formed
$Rh_2Cl_2(naa)_3$	9.6	benzene	1 [b]	20	6.6	6.5		
$Rh_2Cl_2(naa)_3$	32.6	toluene	1 [b]	25	7.6	7.0		
$Rh_2Cl_2(naa)_3$	20.0	Et_2O	1 [b]	25	6.5	6.2		
$Rh_2Cl_2(naa)_3$	34.5	toluene	1 [e]	25	2.0	1.8		
$Rh_2Cl_2(naa)_3$	3.1	Et_2O	65 [f]	60	2.3		35 (12) [g]	C [d, h]
$Rh_2Cl_2(naa)_3$	6.0	Et_2O	7 [b]	60	6.6		39 (12) [g]	
$Rh_2Cl_2(naa)_3$	19.0	CH_3CN	65 [f]	120	3.5		89 (80) [g]	C [d, h], D [d, i]
$Rh_2(C_2H_4)_4Cl_2$	27.0	benzene	1 [b]	20	6.7			

[a] As Rh (mmol l^{-1}). [b] $CH_3C{\equiv}CH$ alone. [c] 1,2,4-Trimethylbenzene/1,3,5-trimethylbenzene. [d] For the meaning of the symbols see Fig. 1. [e] 0.5 atm of $CH_3C{\equiv}CH$ and 0.5 atm. pf CO_2. [f] 7 atm of alkyne and 58 atm of CO_2. [g] In the autoclave were charged 2.0 g of condenseralkyne. [h] The amount of C ranged from 2 to 4 mol per Rh. [i] About three mol per Rh.

into 2pa by II in boiling CH_2Cl_2 and from this solution the complex $[Rh(2pa)Cl]_2$ is isolated, in this complex the ligand acts as monodentate, being coordinated to the metal through the NH_2 group ($\nu(NH_2)$ at 3200ms, 3140m and 3110 cm^{-1}; ν(C=C) not coordinated at 1650 cm^{-1}, δ(HC=CH) at 962 cm^{-1}, ν(Rh—Cl) at 290 cm^{-1}). The IR spectrum of the free 2pa ligand (isolated by chromatography on a silica gel column) shows bands at 3450 and 3370 $\nu(NH_2)$, 1655, ν(C=C), 966, δ(HC=CH) cm^{-1}, consistent with a *trans*-geometry of the propenyl group [6,10]. The ^1H NMR spectrum is coincident with that of *trans*-2-propenylaniline [6]. The isomerization of the ligand is also easily accomplished using $Pd(PCy_3)_2$, which is recovered unchanged. It is noteworthy that the isomerization of the allyl group to propenyl is readily promoted by transition metals [6,11,12] and can be accelerated by the presence of a weak base such as $NaHCO_3$ [6] or CH_3COONa [13], but requires a strong base ($NaNH_2$) [14] in the absence of transition metals.

When $Rh_2Cl_2(2pa)_4$ is heated in C_6H_6 under nitrogen a red solution results. After addition of 1,2-bis(diphenylphosphino)ethane, the VPC analysis of the solution shows the presence of 2pa and 2-methylindoline (20% based on the starting complex). From the solution the complex $Rh(diphos)_2Cl$ is isolated. Hegedus [2] has reported that $Pd(C_6H_5CN)_2Cl_2$ converts 2aa into 2-methylindole with Pd metal deposition and HCl elimination. In our experiments neither rhodium metal nor hydridorhodium species were formed.

The complex $Rh_2(2aa)_2Cl_2$ is very sensitive to oxygen, which attacks the coordinated double bond, possibly through a rhodium mediated oxygen transfer; the products of this reaction are under investigation *.

From the reaction of I with *N*-allylaniline (naa) in benzene at room temperature a deep violet complex is isolated, and this analyzes for $Rh_2(naa)_3Cl_2$ (III). In this reaction ethylene is quantitatively evolved (1.98 mol per Rh atom) and we have no evidence for an electrophilic attack by the amine on the coordinated ethylene in I. Complex III is diamagnetic (χ_M^{corr} —356 × 10^{-6}). The IR spectrum of III in Nujol shows bands at 3340 m, 3245 w and 3190 cm^{-1} due to the stretching ν(NH) of the coordinated ligand. The ν(Rh—Cl) is found at 315 cm^{-1}, and is more consistent with a terminal than with a bridged Rh—Cl stretch [9]. On the basis of these features we propose that two moieties "Rh(naa)Cl" are bridged by a *N*-allylaniline molecule. It is of interest that in $Pd(naa)_2Cl_2$, in which the ligand acts as bidentate [6], the ν(NH) bands are at 3100 and 3075 cm^{-1}. The comparison of the ν(NH) values for the rhodium(I) and palladium(II) complexes indicates that the N metal σ-donation is weaker in the rhodium complex, in accordance with the oxidation state. The higher energy ν(NH) stretching can be assigned to the two NH groups coordinated on the same Rh atom.

The ^1H NMR spectrum in DMSO-d_6, run soon after the solution is prepared, shows signals at τ 2.96 (m, 3H, H(Ph)), 3.43 (m, 2H, H(Ph)), 4.26 (broad singlet, 1H, NH), 5.24 (m, 1H, H^3), 6.42 (d, 2H, H^2, $J_{2,3}$ 6 Hz), 6.8 (d, 1H, H^5, $J_{5,3}$ 11.5 Hz), 8.37 (d, 1H, H^4, $J_{4,3}$ 7.0 Hz). This spectrum changes with time

* After treatment of the yellow $[Rh(2aa)_2Cl]_2$ with oxygen, displacement of the ligand with KCN/H_2O or with diphos, affords a rhodium complex containing an aromatic ligand and aliphatic products are found in the mother solution. These compounds are now under investigation.

and signals due to the free ligand appear, owing to dissociation, according to eq. 1:

$$Rh_2(naa)_3Cl_2 \xrightarrow{solvent} \text{“Rh(L)Cl(solvent)”} + naa \quad (1)$$

The ^1H NMR spectrum of the aged solution shows that the coordinated ligand undergoes rearrangement with time.

The UV and visible spectra of a freshly prepared solution of III in benzene show maxima at 280 (ϵ 11 600), 360 (sh) (ϵ 10 400), 408 (ϵ 3300), 470 (ϵ 2600), 515 (ϵ 2460) nm. These spectral figures, as well as the the colour of the complex, are unusual for rhodium(I) square planar complexes, either monomeric [15,16] or dimeric [17], which do not show absorption bands of noticeable intensity in the visible at energies lower than 430 nm. In the present case an increased importance of the metal spin-orbit coupling can be invoked to explain the high intensity of the low energy bands. In addition, an effect due to a conjugation of the coordinated double bonds through the metal atoms, which could give rise to a chromophore system must be considered. It must be emphasized that on aging the solutions for one hour the spectrum changes to that expected for a rhodium(I) complex (Fig. 2), and free naa (1 mol per Rh atom) can be detected in solution by VPC. This is in accordance with the ^1H NMR features. Moreover, we isolated several samples of orange complexes from concentrated solutions of III in benzene or CH_2Cl_2. The nature of the products is dependent on the time for which the original complex is kept in solution, and the IR spectra of these products in Nujol show the following features: (i) a medium band at 1950 cm^{-1} (from benzene) or at 1990 cm^{-1} (from CH_2Cl_2); (ii) the NH band is absent or very weak; (iii) no evidence for coordinated or free double bonds. Attempts to run the ^1H NMR spectrum of these intermediate fractions in DMSO-d_6 failed because decomposition of the complex occurred. Heating the solutions to accelerate or complete the conversion reaction was prevented by decomposition, which gave rhodium metal. Eventually, we isolated from a dilute toluene/pentane solution of III stored for more than three weeks at −20° C an orange complex analysing for $Rh(C_9H_{11}N)Cl \cdot C_7H_8$. Its ^1H NMR in DMSO-d_6 shows, in addition to a multiplet centered at ca. τ 3 (5H, H(Ph)), a triplet centered at τ 6.4 (4H, J 6.5) and a quintet centered at τ 8.22 (2H). These features are in agreement with a formulation of the ligand as *N*-phenylazetidine. For comparison, free *N*-phenylazetidine shows the signal due to the α protons at τ 6.10 (triplet) and that due to the β protons (quintet) at τ 7.70 *, and *N*-ethylazetidine shows signals at τ 6.70 (triplet, α protons) and τ 7.78 (quintet, β protons) in benzene [19] (for the numberation of the protons see Fig. 1). Displacement of the ligand with diphos affords an oil which, after purification by thin layer chromatography on silica gel, gives the pure *N*-phenylazetidine, n_D^{24} 1.5696 (literature n_D^{24} 1.5695 [20]).

Intramolecular cyclization of amino olefins promoted by transition metals to afford five- or six-membered heterocyclic rings is well documented [1—3]: this is the first example of a formation of a four-membered ring. Attempts to optimize the yields of the intramolecular ring closure of naa is under way, since at

* The authors do not specify the solvent used. The spectrum was recorded at 60 MHz [18].

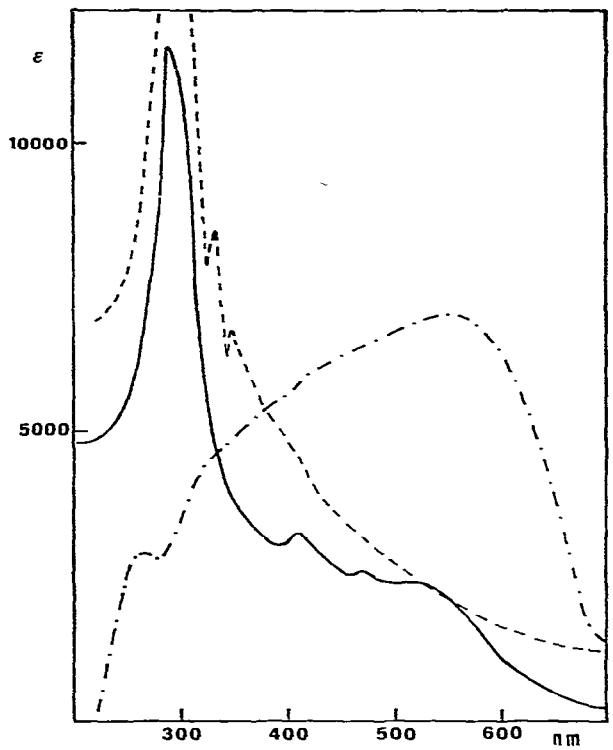

Fig. 2. UV and visible spectrum of $Rh_2(naa)_3Cl_2$. ——— 8×10^{-4} *M* solution of $Rh_2(naa)_3Cl_2$ in benzene under nitrogen; - - - - - - the same solution aged for 1 h; · — · — · reflectance spectrum of $Rh_2(naa)_3Cl_2$ in MgO,MgO as reference.

present *N*-phenylazetidine is obtained in yields ranging from 10 to 20%. It is noteworthy that it has been reported that, in the preparation of *N*-phenylazetidine by alkalyne cyclization of *N*-(3-halopropyl)aniline (halogen = Cl, Br) [18,20,21], *N*-allylaniline is often obtained as a side product [18,20].

The cyclization reaction we have observed can be conveniently represented in terms of an electrophilic attack of the nitrogen atom on the double bond coordinated to the metal and, thus, the reaction depends on the availability of the lone pair on the N atom. The presence of the band at 1950—1990 cm^{-1} in the IR spectra of the orange intermediate complexes suggests an alternative route, viz. formation of an hydrido complex formed through hydrogen transfer from the NH or olefinic groups. These possibilities are under investigation.

When an excess of the ligand naa is heated in the presence of III, it is catalytically converted into propene (the only gaseous product), aniline, azobenzene, *N*-n-propylaniline, *N*-i-propylaniline or *N*-allylideneaniline. The amounts of the various products are as follows:

$$18\ naa + III \rightarrow CH_3CH{=}CH_2 + 0.5\ C_6H_5N{=}NC_6H_5$$
$$3\ C_6H_5NH(CH_2CH_2CH_3) + 3\ C_6H_5NH|CH(CH_3)_2|$$
$$x\ C_6H_5N{=}CH{-}CH{=}CH_2 + y\ C_6H_5NH_2 + \text{minor products.}$$

The products were determined by VPC or isolated by chromatography on a silica gel column. The amount of *N*-allylideneaniline and of aniline are dependent on the treatment of the mixture, as the former is converted into the latter and acroleine. The combined amount of the two products is about 10 mol from 1 mol of III.

From the reaction of $Rh_2(naa)_3Cl_2$ with diphenylacetylene in benzene at room temperature (or at 80°C) the complex $Rh(L)Cl(C_6H_6)$ is obtained, where L = 2,5-dihydro-1,2,3-triphenyl-4-methylpyrrole. Its IR spectrum in Nujol does not show any band attributable to ν(NH), to the free or coordinated double bond of the naa ligand, or to triple bonds. The ^{1}H NMR spectrum in $CDCl_3$ shows signals, at τ 2.5 (m, 15H, H(Ph)), 7.25 (s, 1H, H^2), 8.12 (m, 2H, H^5), 8.46 (m, 3H, CH_3), which are consistent with the proposed structure.

The intermolecular 1,3-addition of amino olefins to triple bonds may be useful route to substituted 3-pyrrolines, which are usually obtained from 2-vynilaziridines [22,23], the reaction of aniline with 1,4-dihydro-2-butene [24], or the reaction of acetates with *N*-butylazides [25]. The old method, involving the reduction of pyrrole with HI/P [25] affords mixtures of 3- and 2-pyrrolines.

As an attempt to extend the reaction to other substituted acetylenes we investigated the reaction of III with methylacetylene, and found that III catalyses the oligomerization of the alkyne, the products being the dimers A, B, C and 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene (see Fig. 1, 3 and Table 2). We observed that at room temperature the rate of consumption of the alkyne decreases with time as a sparingly soluble product is formed *.

The mechanism of alkyne oligomerization proposed by Meriwether et al. [26] can be used in order to explain the formation of the linear dimers (*cis* addition of two molecules of the monomer). A molecular model shows that in the addition of the third molecule of the monomer, *trans* addition permits a favored conformation in which the 1 and 6 carbon atoms approach within bond distance to afford the cyclic trimers. The linear trimers are not present. Conversely, the nickel(0) catalysed reaction [26,27] gives the linear trimers, the cyclic trimers and the linear dimers concurrently. The former are produced through a *cis-trans* addition only: *cis-cis* products were not detected.

Furukawa et al. [28] investigated the influence of the basicity and steric hindrance of the phosphorus ligands on the rhodium(I) catalysed dimerization of substituted acetylenes, and found that the formation of the linear dimer (A) is favored by the more basic and less hindered ligands. In comparing our results with Furukawa's, it must be emphasized that compound III produces the dimers A and B (and also 1,2,4- and 1,3,5-trimers) in a molar ratio which would be expected for a system formed by rhodium(I) and a phosphine more basic and less hindered than P-n-Bu_3. In our case log (B/A) = —0.82, compared with the value —0.6 reported by Furukawa for the Rh^I—P-n-Bu_3 system. We find that the dimers are the first products formed at room temperature, but they are not formed at high temperature (see Table 2). Moreover, if a system made up at room temperature and, thus, containing the dimers, is heated at 80°C under 7 atm of the monomer, the dimers are converted into the cyclic trimers. This

* The products of the reaction of III with acetylene, methylacetylene and phenylacetylene will be described in a forthcoming paper.

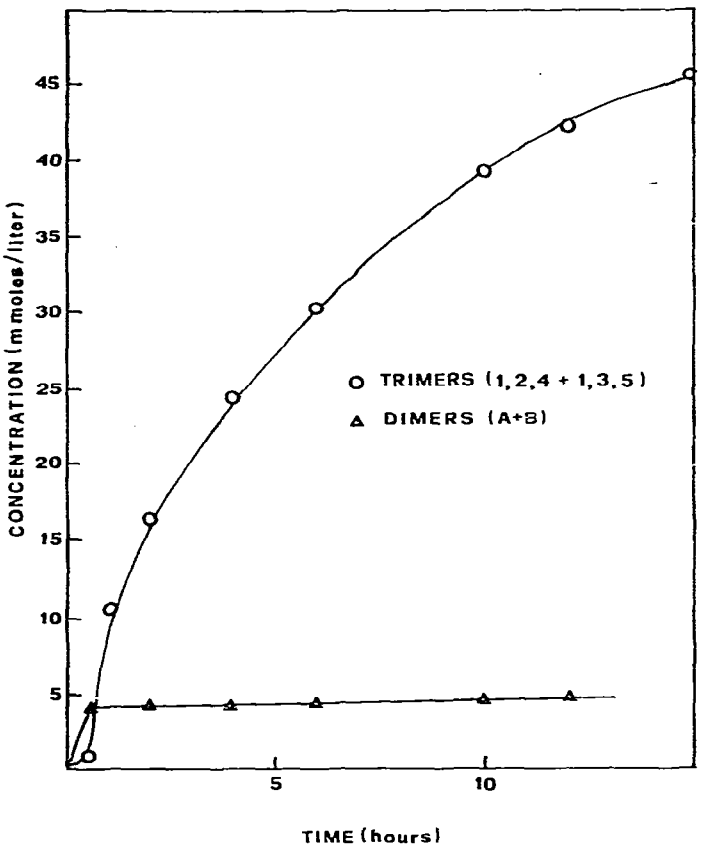

Fig. 3. Concentration-time plot of oligomerization of methylacetylene (P = 1 atm) with $Rh_2(naa)_3Cl_2$ (9.6 mmol s l^{-1}) in benzene (20 cm^3) at 20°C.

suggests that the dimers A and B are the parent compounds of 1,2,4- and 1,3,5-trimethylbenzene, respectively.

Addition of CO_2 to the system produces an effect comparable with that found by Furukawa on replacing P-n-Bu_3 by 1,2-bis(diphenylphosphino)-ethane: log (B/A) = —0.3 for both systems. The formation of the cyclic dimer 1,4-cyclohexadiene under CO_2 was not repeated for either the nickel(0) nor the rhodium(I)-phosphine catalysed system [26—28]. It is known that CO_2 can modify the activity of the catalysts [29,30], and clearly it can affect the basicity of the catalyst. In our reactions one would expect that the interaction of CO_2 with the metal center, or preferably with the amino group, would reduce the basicity of the catalyst. On this basis, the variation of the molar ratio B/A is well accounted for, but further investigation is necessary in order to gain an insight into the mechanism of the formation of the cyclic dimer.

Use of CH_3CN as solvent under CO_2 at >110°C, (III) promotes the reaction of methylacetylene with CO_2 to afford small amounts of 4,6-dimethyl-2-pyrone. It is relevant to recall that nickel(0) catalyses the reaction of 1-hexyne with CO_2 to afford 4,6-dibutylpyrones [31].

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