Transition metal complexes of diazenes XXXIX [1]
Stilbenylazobenzene derivatives by cobalt-catalysed addition of diphenylacetylene to 1,2-diaryldiazenes and their acid-catalysed rearrangement to N-anilinoindoles [2]

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Abstract

$CoH_3(PPh_3)_3$ catalyses the regioselective double and monoinsertion of tolan into the *ortho*-CH bonds of several 1,2-diaryldiazenes at room temperature. When halogenated azobenzene derivatives are involved, only the substituted phenyl ring is attacked. The structure of 2-(*trans*-stilbenyl)-3,5-dichloroazobenzene was determined by single crystal X-ray analysis. Depending on the substitution pattern the stilbenyl derivatives may isomerize to 2,3-dihydrocinnolines. These 1:1 adducts are identified as the intermediates previously postulated in the rhodium-catalysed synthesis of N-anilinoindoles from alkynes and 1,2-diaryldiazenes. The rearrangement of 2,3,4-triphenyl-2,3-dihydrocinnoline to N-anilino-2,3-diphenylindole was studied at 70–90 °C; it is catalysed by acetic acid and the rate law reveals reaction orders of 1.0 and 0.6 for the dihydrocinnoline and HOAc respectively. While the activation enthalpies of 56 ± 9 and $54 \pm 3 \, kJ \, mol^{-1}$ are the same within experimental error, the activation entropy of the catalysed reaction, $\Delta S^{\ddagger}_{298K} = -136 \pm 7 \, J \, K^{-1} \, mol^{-1}$, is more positive than the $-191 \pm 14 \, J \, K^{-1} \, mol^{-1}$ value measured in the absence of HOAc. © 1997 Elsevier Science S.A.

Keywords: Cobalt catalysis; Hydride complexes; Diaryldiazene; Alkyne insertion; Stilbenylazobenzene; 2,3-Dihydrocinnoline; Indoles

1. Introduction

Recently we have reported that in refluxing 1-PrOH–HOAc solution $RhCl(PPh_3)_3$ catalyses the 1:1 addition of alkynes to 1,2-diaryldiazenes affording hitherto unknown N-anilinoindoles [2]. It was proposed that a key step of the catalytic cycle is the rearrangement of an intermediate 2-alkenylazobenzene derivative formed by insertion of the alkyne into an *ortho*-CH bond of the diaryldiazene [3]. In attempts to isolate such an intermediate, a solvent-free reaction between diphenylacetylene and various azobenzene derivatives in the presence of catalytic amounts of $CoH_3(PPh_3)_3$ was investigated. In almost all cases 2:1 adducts of the type 2,6-distilbenylazobenzene were obtained as initial products which

usually undergo a thermal electrocyclic ring closure to the corresponding 2,3-dihydrocinnolines except when a methyl or chloro substituent is present at the 3-position (Scheme 1) [4,5]. Only when three out of the four *ortho*-CH bonds of the 1,2-diaryldiazene were blocked, as in the case of 2,4,6,2',4'-pentamethylazobenzene, could a 1:1 adduct be isolated in the form of the corresponding 2,3-dihydrocinnoline. In the following we report that upon conducting the cobalt-catalysed reaction in solution, isolation of labile 1:1 adducts becomes feasible although all four ortho-positions are unblocked. Kinetic parameters of the acid-catalysed and uncatalysed rearrangement of these postulated intermediates to the corresponding N-anilinoindoles were also determined.
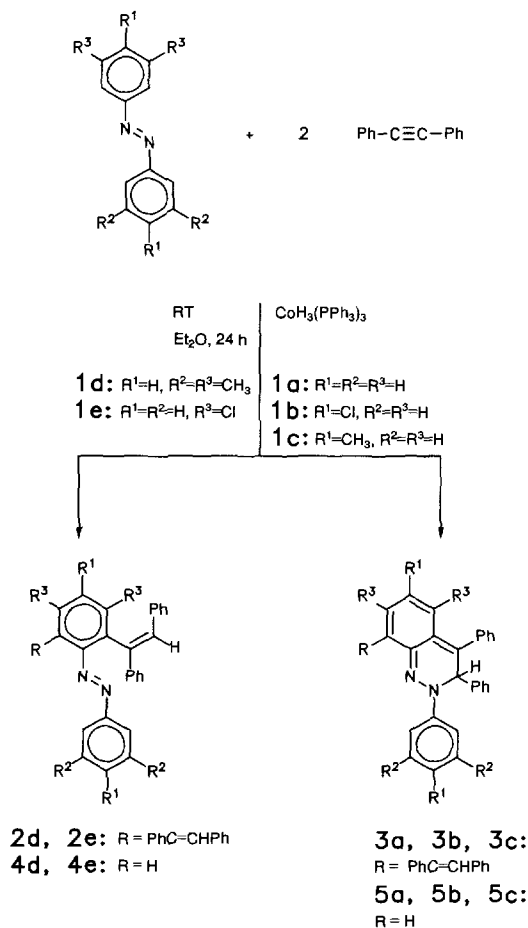
2. Results

When the reaction between diphenylacetylene and azobenzene derivatives in the presence of $CoH_3(PPh_3)_3$ was performed in diethyl ether or THF at room tempera-

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Scheme 1.

Fig. 1. Molecular structure of **4e**; hydrogen atoms are omitted for clarity.

ture, H$_2$-evolution occurred and a dark red solution was obtained. Product isolation by column chromatography and preparative HPLC afforded the known 2:1 adducts **2d, 2e, 3a–c** and the new 1:1 adducts **4d, 4e, 5a–c**. The latter formed orange (**4d**) or red (**5a–c**) oils which could be purified only by HPLC. In the case of **4e** an orange powder was obtained. In general 2,3-dihydrocinnoline compounds are dark red while the distilbenylazobenzene derivatives are orange [6]. Turnover numbers were in the range of 2–6. When toluene was used as solvent, only a very slow reaction took place.

Fig. 1 shows the molecular structure of **4e** based on a single crystal X-ray analysis. (A summary of the crystal data, data collection and structure refinement of **4e** is given in Table 1; bond lengths and angles are listed in Table 2 and atomic coordinates in Table 3.) The regioselective insertion of one molecule of diphenylacetylene in one of the four possible *ortho*-C–H bonds afforded the 2-*trans*-stilbenylazobenzene **4e**, an intermediate of the catalytic formation of the corresponding 2,6-di(*trans*-stilbenyl)azobenzenes. The N1–N2 distance of 124.4(2) pm is almost the same as in azobenzene (124.3 pm) [8] and the C3–C4 bond length (132.1(3) pm) of the *trans*-stilbenyl fragment agrees excellently with

that of *trans*-stilbene (131.8 pm) [9] or of the previously characterized **2e** (133.1 and 133.3 pm) [4,5]. The two phenyl rings of the azobenzene fragment (C11–C16 and C21–C26) are twisted slightly to each other forming an

Table 1
Crystal data and summary of data collection and structure refinement of **4e**

Molecular formula	C$_{26}$H$_{18}$Cl$_2$N$_2$
Molecular weight	429.32
Crystal system	triclinic
Space group	P$\bar{1}$
Wavelength (MoKα radiation) (pm)	71.073
a (pm)	876.5(3)
b (pm)	1071.4(4)
c (pm)	1267.3(3)
α (deg)	66.67(2)
β (deg)	81.79(3)
γ (deg)	76.54(3)
Cell volume (nm^3)	1.061(6)
Z	2
μ (mm^{-1})	0.32
d_{calc} (g cm^{-3})	1.344
Temperature (K)	200(2)
Crystal size (mm^3)	0.70 × 0.40 × 0.40
Colour	red
2θ-range (deg)	4–54
Scan rate (deg min^{-1})	3–30
Number of measured reflections	5684
Independent reflections	4672
Observed reflections [$F_o \geq 4\sigma(F)$]	2819
Structure solution	direct methods [6]
Structure refinement	full-matrix least squares on F^2 [7]
Number of parameters refined	343
R_1 [$F_o \geq 4\sigma(F)$]	0.045
wR_2 (all data)	0.114

Table 2
Bond distances (pm) and bond angles (deg) of **4e**

Cl(1)–C(13)	174.0(2)
Cl(2)–C(15)	173.6(2)
N(1)–N(2)	124.4(2)
N(1)–C(11)	143.2(3)
N(2)–C(21)	142.8(3)
C(3)–C(4)	132.1(3)
C(3)–C(31)	148.1(3)
C(3)–C(16)	150.0(3)
C(4)–C(41)	147.9(3)
N(2)–N(1)–C(11)	115.1(2)
N(1)–N(2)–C(21)	113.6(2)
C(4)–C(3)–C(31)	123.6(2)
C(4)–C(3)–C(16)	119.8(2)
C(31)–C(3)–C(16)	116.5(2)
C(3)–C(4)–C(41)	126.7(2)
C(16)–C(11)–N(1)	114.6(2)
C(12)–C(11)–N(1)	123.8(2)
C(15)–C(16)–C(3)	121.2(2)
C(11)–C(16)–C(3)	121.6(2)
C(22)–C(21)–N(2)	124.4(2)
C(26)–C(21)–N(2)	115.2(2)
C(36)–C(31)–C(3)	121.3(2)
C(32)–C(31)–C(3)	121.3(2)
C(42)–C(41)–C(4)	121.8(2)
C(46)–C(41)–C(4)	120.3(2)

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) of **4e**

|	x	y	z	U_{eq}
Cl(1)	−1488(1)	4320(1)	−1426(1)	53(1)
Cl(2)	−30(1)	2357(1)	2970(1)	45(1)
N(1)	−1898(2)	−680(2)	1377(2)	33(1)
N(2)	−2524(2)	−770(2)	595(2)	39(1)
C(3)	−925(3)	−337(2)	3222(2)	28(1)
C(4)	−1993(3)	−236(2)	4047(2)	31(1)
C(11)	−1491(3)	634(2)	1115(2)	29(1)
C(12)	−1623(3)	1709(2)	33(2)	34(1)
C(13)	−1269(3)	2943(2)	−102(2)	35(1)
C(14)	−774(3)	3150(2)	791(2)	34(1)
C(15)	−641(3)	2073(2)	1853(2)	32(1)
C(16)	−1020(2)	801(2)	2051(2)	27(1)
C(21)	−2951(3)	−2082(2)	896(2)	35(1)
C(22)	−2600(3)	−3201(3)	1914(2)	41(1)
C(23)	−3108(3)	−4406(3)	2131(3)	50(1)
C(24)	−3973(3)	−4500(3)	1345(3)	54(1)
C(25)	−4320(4)	−3393(3)	332(3)	56(1)
C(26)	−3807(3)	−2171(3)	94(2)	47(1)
C(31)	467(3)	−1474(2)	3402(2)	30(1)
C(32)	445(3)	−2779(2)	4264(2)	39(1)
C(33)	1756(4)	−3822(3)	4441(2)	47(1)
C(34)	3114(4)	−3611(3)	3757(2)	47(1)
C(35)	3167(3)	−2335(3)	2891(2)	43(1)
C(36)	1851(3)	−1284(3)	2717(2)	36(1)
C(41)	−3441(3)	835(2)	3925(2)	30(1)
C(42)	−4464(3)	1189(3)	3059(2)	37(1)
C(43)	−5814(3)	2186(3)	2956(2)	43(1)
C(44)	−6173(3)	2850(3)	3713(2)	41(1)
C(45)	−5199(3)	2502(3)	4584(2)	44(1)
C(46)	−3838(3)	1503(3)	4699(2)	37(1)
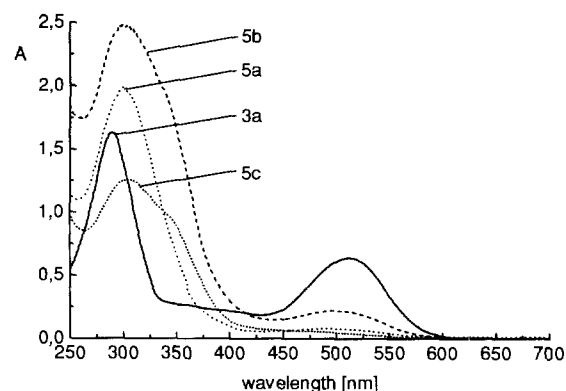
Fig. 2. UV–vis spectra of **5a**, **5b**, **5c** and **3a** in CH_2Cl_2.

interplanar angle of 14.4°. There is no significant electronic interaction of the stilbenyl substituent with the azobenzene system as evidenced by the C16–C3 distance (150.0(3) pm) and the interplanar angle of 75.6° between the planes C11–C16 and C3–C4–C31–C41. Finally, the phenyl rings C31–C36 and C41–C46, which form a dihedral angle of 76.8°, are twisted relative to the double bond plane by 27.4 and 49.4° respectively.

The red oil **5a** is a 1:1 adduct according to MS spectra. When comparing the UV–vis spectrum with that of the structurally known **3a** [10] one can conclude that **5a** is 2,3,4-triphenyl-2,3-dihydrocinnoline (Fig. 2). There is only a weak π,π^* band of the *ortho*-quinoid system of **5a** at 499 nm ($\varepsilon = 800\,M^{-1}\,cm^{-1}$) while **3a** gives rise to a more intensive π,π^* band at 511 nm ($\varepsilon = 13\,500\,M^{-1}\,cm^{-1}$). Generally, 2:1-adducts from alkynes and azobenzenes in the form of 2,3-dihydrocinnolines undergo a photochemical ring opening to the corresponding distilbenylazobenzenes [4,5]. The same is observed when a diluted solution of **5a** ($c < 10^{-3}\,M$, $\lambda > 375\,nm$) is irradiated for 90 s; the absorbance at 499 nm decreased but recovered to its original value upon standing in the dark for 80 min at room temperature (Fig. 3).

HPLC analysis revealed that **5a** contains about 3% of N-anilino-2,3-diphenylindole (**6a**) and 6% of two unknown impurities. The chromatogram was identical with that of the product obtained by a Wittig–Horner reaction from 2-benzoylazobenzene and diethyl-benzylphosphonate [5]. Multiple attempts to purify **5a** by HPLC failed due to rapid isomerization to **6a**; only at −20 °C could **5a** be handled without immediate isomerization. A mutual preparation at −30 °C was not successful since the substrates were only poorly soluble and CoH$_3$(PPh$_3$)$_3$ did not lose hydrogen. At −6 °C reaction occurred but the purity of **5a** was not improved. Rearrangement of **5a** to **6a** was accelerated when it was performed in 1-BuOH–HOAc at 100 °C, which were the experimental conditions of the rhodium-catalysed indole synthesis [3].
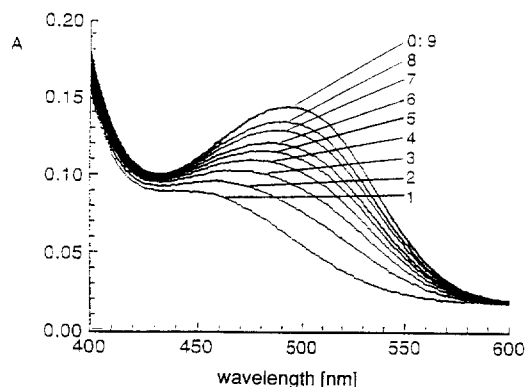
When 4,4′-dichloroazobenzene, 4,4′-dimethyl-

Fig. 3. Photochromic behaviour of 5a in CH_2Cl_2. Spectra 0 and 1 describe the situation before and immediately after 90 s of irradiation ($\lambda > 375$ nm, 12 V/20 W tungsten halogen lamp) respectively. Spectra 2 to 9 exhibit the increase of absorbance at $\lambda = 499$ nm upon standing in the dark for 5, 10, 15, 20, 25, 35, 45 and 80 min. Spectrum 9 is identical with the situation before irradiating.

Scheme 2.

azobenzene and 3,3',5,5'-tetra-methylazobenzene are used, the new 1:1 adducts 5b, 5c and 4d were obtained as red or orange oils in addition to the known 2:1 adducts 3b, 3c and 2d. The structural assignments for 4d is based on its UV–vis spectrum which resemble the spectrum of the structurally known 2d [5] and 4e (Fig. 4). Accordingly, these compounds do not exhibit photochromism. In contrast to that, 5b and 5c possess characteristic 2,3-dihydrocinnoline spectra (Fig. 2) and undergo the photochromic electrocyclic ring opening to 4b and 4c upon irradiation. In addition, 5b and 5c could be isomerized to their corresponding indoles 6b and 6c in 1-BuOH–HOAc solutions. The compounds 6a–c are easily obtained in rhodium catalysis, while in the reaction between either 1d or 1e with tolan no N-anilinoindole had been formed [3]. The stilbenylazobenzenes 4d and 4e obtained via cobalt catalysis could be isomerized to the new indole derivatives 6d and 6e in 1-BuOH–HOAc solution.

The structures of all new compounds follow from comparison of extensive NMR data (^{1}H, ^{13}C, ^{1}H–^{1}H-COSY, ^{1}H–^{13}C-COSY) with those of unsubstituted

azobenzene and stilbene and from calculation of the ^{13}C NMR data with the increment system for substituted benzenes and olefinic C-atoms described in the literature (for atom numbering see Scheme 2) [11].

The ^{13}C NMR spectra contain the peaks of the carbon atoms C-1, C-2, C-6, C-7, C-13, C-14, C-15 and C-15' in the range of 151 ppm, 140 ppm, 116 ppm, 152 ppm, 143 ppm, 132 ppm, 138 ppm and 137 ppm respectively (Table 4). The phenylazo-substituted atoms C-1 and C-7 exhibit only small deviations from the corresponding value for unsubstituted azobenzene (152.5 ppm); the ortho-stilbenyl group leads to a shift of C-1 to higher field of about 2 ppm except in the cases of 5b, 5c and 4e where the para-Cl and para-CH$_3$ substituents induce a shift to 149 ppm while the two meta-chloro substituents shift the C-1 signal to 152 ppm. Compared to azobenzene (123 ppm) the signals of C-2 and C-6 are shifted to lower and higher field at 140 ppm and 116 ppm respectively, except in the case of 5b and 4d where the meta-Cl and para-CH$_3$ groups induce for C-6 a low field and a high field shift to 117 ppm and 114 ppm respectively. The chemical shift differences of C-2 between 5a–c and 4d,4e reflect the structural difference between the ortho-quinoid and aromatic systems respectively. Since the phenyl group at C-13 interacts with the ortho-quinoid system, as evidenced by the molecular structure of 3a [10], a low field shift to 140 ppm results for the C-15 signals of 5a–c compared with the theoretical value of 138 ppm observed in unsubstituted stilbene.

Various experiments were performed in diethyl ether solution to examine the role of $CoH_3(PPh_3)_3$. It is likely that the catalytically active species results by loss of


Fig. 4. UV–vis spectra of 2d, 4d and 4e in CH_2Cl_2.

Table 4
Characteristic ^{13}C NMR data of 5a–c, 4d–e (chloroform-d_1) [a]

	C-1	C-2	C-6	C-7	C-13	C-14	C-15	C-15'
5a	150.8	140.1	116.3	152.8	143.9	131.9	140.2	137.3
5b	149.0	142.0	117.6	151.1	143.3	131.7	138.4	136.8
5c	148.8	141.4	116.0	151.1	144.0	132.0	140.8	137.4
4d	150.9	138.4	113.7	153.2	143.4	129.7	137.5	137.7
4e	152.4	135.9	115.1	152.3	141.7	131.7	136.9	137.3

[a] For atom numbering see Scheme 2.

dihydrogen, as indicated by EI-MS in the reaction be-
tween azobenzene and diphenylacetylene. In the reac-
tion between $CoH_3(PPh_3)_3$ and diphenylacetylene in the
absence of azobenzene only oligomerization products of
the alkyne in combination with the hydrogenation prod-
uct stilbene could be detected by FD-MS. The forma-
tion of various tetramers, trimers and dimers of the
alkyne is also observed in the reaction of
$P(CH_2CH_2PPh_2)_3CoH$ with 1-alkynes HCCR (R =
CO_2Et, Ph) [12]. In the corresponding reaction between
$CoH_3(PPh_3)_3$ and azobenzene in the absence of
diphenylacetylene no formation of an orthometalated
species occurred, but only the phosphazene $Ph_3P=NPh$
at $m/e = 353$ and traces of hydrazobenzene were de-
tected.

In a parallel experiment the addition sequence of the
substrates was reversed in order to investigate whether
alkyne insertion into the cobalt hydride bond or or-
thometalation of the azobenzene derivative represents
the first step of the catalytic cycle. 3,3′,5,5′-tetramethyl-
azobenzene 1d and 4-methoxytolan were selected, since
they react slower than the other substrates. The colour
of the suspension changed within 2 min from colourless
to reddish brown when 4-methoxytolan was added to
$CoH_3(PPh_3)_3$. After 40 min, FD-MS analysis revealed
formation of the linear trimer, the cyclic and linear
dimer of the alkyne and the hydrogenation product
4-methoxystilbene. The conversion was almost 100%.
Contrary to that, the orange colour remained for about
15 min and afterwards changed to black when 1d was
added initially. After 40 min only the phosphazene
$Ph_3P=N–C_6H_3(CH_3)_2$ and unreacted 1d were detected
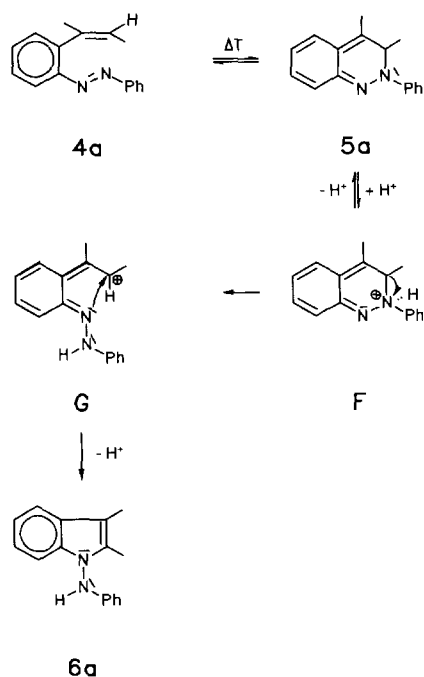
Scheme 3. Postulated isomerization mechanism of 5a to 6a.

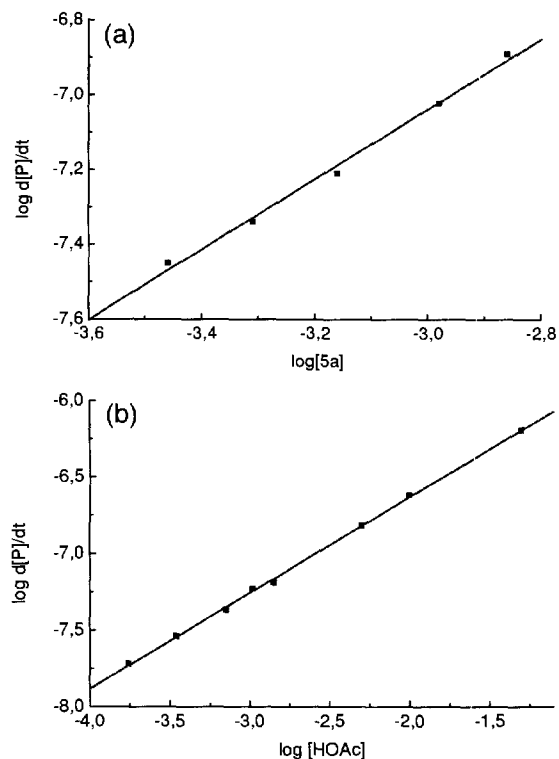
Fig. 5. Plot of log(d[P]/dt) vs. (a) log[5a] (correlation coefficient
0.997) and (b) log[HOAc] (correlation coefficient 0.998).

by MS-analysis. Immediately after the characterization
by FD-MS the second substrate was added and product
analysis was performed after 30 min. In both experi-
ments, the final molar ratio of catalyst:azobenzene:al-
kyne was 1:1:2. When the second substrate was 1d,
formation of 1:1 or 2:1 adducts of type 4 or 2 could not
be observed while that was possible when it was 4-
methoxytolan (see Section 4).

2.1. Kinetic measurements

The isolation of the stilbenylazobenzenes and 2,3-di-
hydrocinnolines, which were proposed to be intermedi-
ates in the rhodium-catalysed indole synthesis, opened
the possibility to study the kinetics of their rearrange-
ment to N-anilinoindoles. This was performed with 5a
in 1-BuOH solution at 80 °C. To determine the reaction
order, the initial formation rate of 6a (Scheme 3) was
measured as a function of increasing concentrations of
5a and HOAc at 15, 30, 45 and 60 min after mixing the
reactants.

From the slopes of the corresponding straight lines of
the logarithmic plots of rate vs. concentration (Fig. 5(a)
and Fig. 5(b)) reaction orders of 1 and 0.6 were ob-
tained for 5a and HOAc respectively. Accordingly, the
rate law for the acid-catalysed rearrangement is given
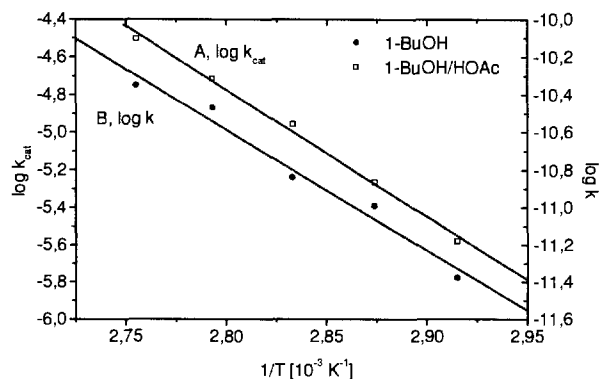by Eq. (1).

$$d[6a]/dt = k_{cat}[5a][HOAc]^{0.6} \qquad (1)$$

Fig. 6. Arrhenius plot for (A) the catalysed isomerization ([HOAc] = 6.94×10^{-4} mol l^{-1}, correlation coefficient 0.997) and (B) the uncatalysed isomerization (correlation coefficient 0.988) of **5a** (6.94×10^{-4} mol l^{-1}) to **6a** in 1-BuOH (70–90 °C).

When in the HOAc-catalysed reaction an equimolar amount of NaOAc was added, the rate decreased by about 20%. No change in rate, compared to the uncatalysed reaction, was observed upon addition of a 100-fold excess of 2,2,6,6-tetramethylpiperidine.

Activation parameters were determined by measuring the rate constants for the catalysed and uncatalysed reactions in the range of 70 −90 °C (Fig. 6). While the activation energies of 56 ± 9 kJ mol^{-1} and 54 ± 3 kJ mol^{-1} are the same within experimental errors for both the catalysed and the uncatalysed isomerizations respectively, the activation entropy of the catalysed reaction, $\Delta S^{\ddagger}_{298K} = -136 \pm 7$ J K^{-1} mol^{-1}, is more positive than the -191 ± 14 J K^{-1} mol^{-1} value measured in the absence of HOAc.

3. Discussion

The cobalt-catalysed addition reaction in solution can be rationalized by a modified version of the catalytic cycle previously formulated for formation of 2:1 adducts in a melt of tolan and azobenzene (Scheme 4) [5]. In the initial step loss of dihydrogen from the d^6 starting complex affords the d^8 intermediate **A**. This type of d$^6 \rightarrow$ d^8 transformation is typical for aromatic C–H activation [13]. Coordination of diphenylacetylene and insertion into the cobalt–hydride bond leads to the stilbenyl complex **B**. Substitution of a phosphine ligand by azobenzene and subsequent orthometalation affords the intermediate **C**. The sequence of these two steps of the catalytic cycle is corroborated by the parallel experiment described above. Since the catalytic active species **A** in the absence of azobenzenze converts tolan almost quantitatively to oligomerization products, while it does not react with azobenzene in absence of tolan, it seems likely that the insertion of the alkyne in the Co–H bond takes place before orthometalation. In presence of both
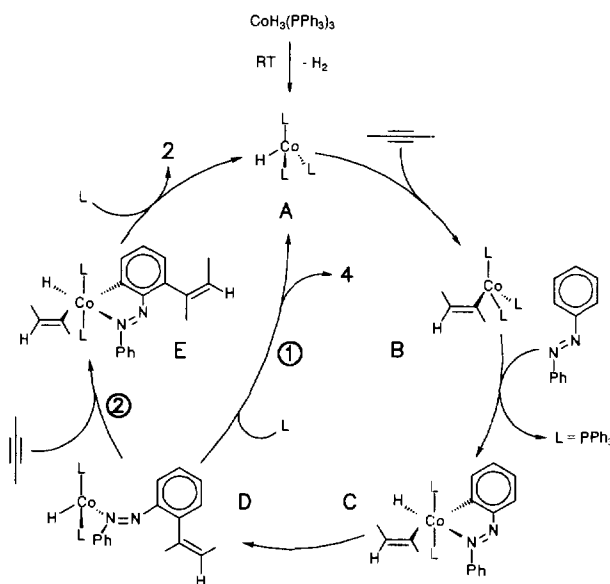
Scheme 4. Postulated catalytic cycle.

reactants, oligomerization of the alkyne and orthometalation of azobenzene are competitive reactions. That the latter leads to the adducts of type **4** and **2** is evidenced by the second part of the parallel experiment where addition of 4-methoxytolan to the solution of CoH$_3$(PPh$_3$)$_3$ and **1d** produced **4** and **2**. Because of the trans geometry of the σ-aryl and the σ-stilbenyl ligand in **C** [14], [3] isomerization to the cis-configuration has to occur before reductive C(sp^2)–C(sp^2) elimination to the key intermediate **D** can take place. Substitution of the stilbenylazobenzene by an incoming phosphine ligand affords **4** and **A** (path 1), while insertion of a second molecule of alkyne into the Co–H bond, orthometalation of the coordinated stilbenylazobenzene and reductive elimination followed by substitutional decomplexation of the double insertion product through PPh$_3$ produces **2** and regenerates **A** (path 2). It seems likely that the coordination and insertion of a second molecule of diphenylacetylene in the sterically crowded complex **D** (first step of path 2) requires a higher activation energy than substitution of the stilbenylazobenzene ligand by PPh$_3$ (first step of path 1). Therefore it becomes reasonable that path 2 is favoured in the melt reaction at 85 °C [5]. Finally, the initial products **4** and **2** undergo a thermal electrocyclic ring closure to the corresponding 2,3-dihydrocinnolines **3** and **5** except when a methyl or chloro substituent is present at the meta-position of the diazene.

There is a characteristic difference in the regioselec-

[3] The cis-position of the hydrido and aryl ligand is supported by the structure of the orthometalated product obtained from azobenzene and [RhCl(PCy$_3$)$_2$S] (S = solvent molecule) [14].

tivity of the $CoH_3(PPh_3)_3$- or $RhCl(PPh_3)_3$-catalysed reactions. In cobalt catalysis orthometalation also occurs in cases like **1d** and **1e**, where the meta-positions are substituted by steric-demanding methyl or chloro functions, and affords products of type **2** or **4**, while in rhodium catalysis in these cases no orthometalation and indole formation occurred. This opposite behaviour may originate in the different van der Waals radii of the meta-substituents. In the case of methyl and chloro they are 200 pm and 180 pm respectively, while for fluoro and hydrogen they are 135 pm and 120 pm respectively [15]. The two latter substituents allow orthometalation by both metals. In cobalt catalysis, 3,5-difluoroazobenzene **1f** affords both 2:1 adducts of type **2** and **3**, [4] while in rhodium catalysis two different indole derivatives are formed by orthometalation of the substituted or the unsubstituted phenyl ring. The higher steric selectivity of the rhodium-catalysed reaction reflects the sterically more demanding orthometalation step which occurs in the tolan complex $[RhCl(PPh_3)_2(PhC_2Ph)(PhN_2Ph)]$ [3]. In the case of cobalt catalysis the corresponding intermediate $[Co(PhC=CHPh)(PPh_3)_2(PhN_2Ph)]$ is less crowded. In the case of a halogenated azobenzene derivative always the substituted phenyl ring is orthometalated when the cobalt complex is used as catalyst. Contrary to that, the unsubstituted (**1e**) or both rings (**1f**) are attacked in the case of rhodium catalysis [3]. Upon performing the cobalt-catalysed reaction between azobenzene derivatives and diphenylacetylene in solution, formation of new 1:1-adducts bearing sterically demanding substituents becomes possible which afterwards can be easily isomerized to new indole derivatives which cannot be obtained by using $RhCl(PPh_3)_3$ as the catalyst.

A postulated mechanism for the rearrangement of the primary insertion product of type **4** to the *N*-anilinoindole **6** is summarized in Scheme 3, wherein the alkyne phenyl substituents are omitted for the sake of simplicity. Since in the rhodium-catalysed reaction indole formation was observed only when ring closure to the 2,3-dihydrocinnoline was not prevented by substituents at the meta-positions of the azobenzene derivative, [3] this step (**4 → 5**, Scheme 3) initiates the rearrangement. Noteworthy is the formation of the new *N*-anilinoindole derivatives **6d** and **6e** from the stilbenylazobenzenes **4d** and **4e** at 110 °C, although neither compound isomerizes to 2,3-dihydrocinnoline derivatives at 85 °C due to the presence of the sterically demanding methyl and chloro substituents respectively. It is likely that at the higher reaction temperature small amounts of the dihydrocinnoline are produced; a subsequent fast proton-catalysed rearrangement affords the *N*-anilinoindole isomer. Pro-
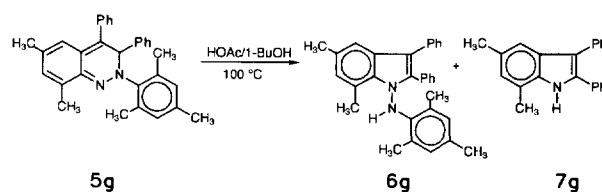
Scheme 5. Acid-catalysed isomerization of **5g** to **6g** and **7g**.

tonation of **5** should occur at the more basic 2-position affording the ammonium intermediate **F**. Similarly, only the 2-benzyl derivative is observed when 4-hydroxycinnolines are treated with NaOEt and $PhCH_2Cl$ [18]. This step is corroborated by the acid-catalysed rearrangement of **5g** [5] to a mixture of **6g**:**7g** = 1:4 (Scheme 5).

C–N bond cleavage leads to the delocalized intermediate allyl cation **G**. Nucleophilic attack of N1 at the terminal carbon and subsequent deprotonation affords **6**. This step is supported by the observation that upon reduction of 4-phenyl-[2-^{15}N]-cinnoline with Zn(Hg)–HOAc an indole is obtained which contains 93% [14]N, i.e. the N2 atom is eliminated during the rearrangement [19]. The nucleophilic attack of N1 at the carbon atom of the initial imine function **G → 6** resembles the mechanism of the Fischer indole synthesis wherein an acid-catalysed rearrangement of a hydrazone produces an indole and NH_3 [20]. Due to the acidic character of the α-H atom, in the case of 1,4-dihydrocinnolines this proton undergoes a fast H/D exchange in CH_3CO_2D–D_2O [19], and deprotonation of **G** should be a fast process. Accordingly, 2,2,6,6-tetramethylpiperidine does not affect the formation rate of **6** and NaOAc even slows it down.

The almost same activation enthalpies of the catalysed and uncatalysed rearrangements suggest that the protonation of **5** is not the rate-determining step of the isomerization mechanism. This seems to be rather the nucleophilic attack of N1 at the allyl cation, as evidenced by the negative values of the activation entropies.

4. Experimental section

All reactions were conducted under a nitrogen atmosphere, solvents were dried and purified by standard procedures and nitrogen-saturated after distillation. Acetonitrile (Ferak) used for the HPLC measurements was sonicated and stored under nitrogen. Column chromatography: Al_2O_3 (ICN, neutral, activity I); $l = 40$ cm, $\varnothing = 2.0$ cm; petroleum ether–tetrahydrofuran = 20/1 (v/v) as eluting agent. HPLC: Knauer HPLC pump 64 with analytical and preparative pump head, Knauer UV–vis filter photometer at $\lambda = 220$ nm as detector. *Analytical measurements*: pre-column (30 mm × 8 mm) attached to main column (250 mm × 8 mm) and both

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[4] For **2f** see Ref. [16]; for **3f** see Ref. [17].

filled with Spherisorb ODS2, 5 μm (RP C18), eluting with $CH_3CN-H_2O = 5/1$ (v/v) at a flow rate of 5.0 ml min^{-1}. *Sample preparation*: 500 μl of the reaction solution was withdrawn, evaporated to dryness, and redissolved in 0.5 ml of CH_3CN; 20 μl of this solution was then injected and the concentration was determined via a calibration curve. *Preparative isolations*: 1 ml of the acetonitrile solution was injected; identical elution agent and filling material were used while the size of pre-column and main column were 30 mm × 32 mm and 250 mm × 32 mm respectively; the flow rate was 35 ml min^{-1}.

^{1}H and ^{13}C NMR spectra were measured in chloroform-d_1 solutions at 400 or 270 MHz and 100 or 67 MHz respectively, and IR spectra in KBr unless otherwise noted. The following instruments were used: NMR, Jeol FT-JNM-LA 400 and Jeol FT-JNM-EX 270; IR, Perkin–Elmer 983 and FT IR 1600; UV–vis, Shimadzu UV-3101 PC; MS, Jeol MStation 700 and Varian MAT 212.

$CoH_3(PPh_3)_3$ was prepared according to the literature [21]. Azobenzene (Merck) and diphenylacetylene (Fluka) were commercially available. The symmetric diazenes **1b–d** were synthesized from the corresponding aniline derivatives [22], the non-symmetric **1e** from 3,5-dichloroaniline and nitrosobenzene [23].

4.1. Synthesis of 2,6-di(trans-stilbenyl)azobenzenes 2, 2,3-dihydrocinnolines (3 and 5) and the 2-trans-stilbenylazobenzenes 4

4.1.1. In general

The following reactions have all been performed in diethyl ether or THF. Unless otherwise noted, the general procedure for the synthesis of the mixtures of **2** and **4** or **3** and **5** is described in the following. Afterwards the isomerization of each 1:1-adduct to the corresponding *N*-anilinoindole **6** is described.

4.1.2. 2,3,4-Triphenyl-8-(trans-stilbenyl)-2,3-dihydrocinnoline 3a and 2,3,4-triphenyl-2,3-dihydrocinnoline 5a

728 mg (4.0 mmol) of azobenzene and 1426 mg (8.0 mmol) of diphenylacetylene were diluted under stirring in 20 ml of diethyl ether. Thereafter about 700 mg (0.82 mmol) of $CoH_3(PPh_3)_3$ were added in one portion whereby the colour of the solution changed within 5 min from orange over black-green and dark-brown to red. After stirring for another 24 h at room temperature, 5 g of Al_2O_3 were added; after removing the solvent, the dark red residue was chromatographed at Al_2O_3 with light petroleum ether–THF = 20/1 (v/v). The first orange-red fraction yielded 425 mg (1.18 mmol, 30%) of an orange oil of **5a** and some by-products, the following red fraction afforded 130 mg of a red powder of **3a** (0.24 mmol, 6%), turnover number (TON) (mmol **5** +

mmol **3**)/mmol catalyst = 1.7). The orange-red oil was purified by prep. HPLC yielding 100 mg (0.28 mmol) of **5a**.

3a. MS: EI (70 eV) m/z (%): 537 (90) $[M]^+$, 461 (46) $[M - Ph]^+$, 360 (74) $[M - Ph-C≡C-Ph]^+$, 268 (100) $[M - N-Ph, -Ph-C≡C-Ph]^+$, 180 (98) $[Ph-C≡C-Ph]^+$; FD m/z 537 $[M]^+$. ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm): 7.55–6.90 (m, 26H, Ph–H and Ph–C=C–HPh), 6.43 (d, 3H, 5-H, 6-H, 7-H), 1.35 (s, br, 1H, 3-H). UV–vis (CH_2Cl_2) $λ_{max}$ [nm] $(ε$ $[M^{-1} cm^{-1}])$: 511 (13 500), 293 (38 000). Calcd for $C_{40}H_{30}N_2$ (538.7): C, 89.19; H, 5.61; N, 5.20. Found: C, 88.27; H, 5.64; N, 4.33. **5a**. MS: EI (70 eV) m/z (%): 360 (24) $[M]^+$, 283 (100) $[M - Ph]^+$, 182 (44) $[M - Ph-C≡C-Ph]^+$, 178 (94) $[Ph-C≡C-Ph]^+$; FD m/z 360 $[M]^+$. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.75–6.97 (m, 20H, 3-H, 4-H, 5-H, 6-H, 8-H, 9-H, 10-H, 11-H, 12-H, PhC=CHPh (11H)). ^{13}C NMR (100.4 MHz, CDCl$_3$) δ (ppm): 116.3 (C-6), 122.9 (C-8 and C-12), 126.7 (C-18), 127.0 (C-16 and C-20), 127.2 (C-18'), 127.9 (C-17 and C-19), 128.2 (C-17' and C-19'), 128.6 (C-5), 128.7 (C-9 and C-11), 129.2 (C-16' and C-20'), 129.8 (C-3), 130.6 (C-10), 131.1 (C-4), 131.9 (C-14), 137.3 (C-15'), 140.2 (C-2), 140.4 (C-15), 143.9 (C-13), 150.8 (C-1), 152.8 (C-7). UV–vis (CH_2Cl_2) $λ_{max}$ [nm] $(ε$ $[M^{-1} cm^{-1}])$: 499 (800), 300 (23 500). HPLC $(CH_3CN-H_2O = 5/1$ (v/v), 5 ml min^{-1}) retention time [min] (integrated area): 5.1 $(6.5 × 10^4)$ **6a**, 7.9 $(6.5 × 10^4)$ unknown, 9.1 $(2.2 × 10^6)$ **5a**, 10.8 $(1.5 × 10^5)$ unknown. From these HPLC data one estimates for **5a** a purity of 90%; since only one peak $(m/z = 360)$ appears in the MS spectrum, one has to assume that the two unknown impurities are also (as is **6a**) isomers of **5a**.

4.1.3. Isomerization of 2,3,4-triphenyl-2,3-dihydrocinnoline 5a to N-anilino-2,3-diphenylindole 6a catalysed by HOAc

10 mg $(2.77 × 10^{-5}$ mol) of the orange-red oil of **5a**, dissolved in 3 ml of 1-BuOH and 1.6 μl of HOAc $([5a] = [HOAc] = 9.25 × 10^{-3}$ mol l$^{-1})$, were heated to 100 °C. The colour of the solution changed within 5 min from orange to yellow and an intensive blue fluorescence $(λ_{exc} = 366$ nm) was observed. The reaction was complete after 30 min. The HPLC-analysis indicated an increase of the indole **6a** (area = $4.7 × 10^6$) at the expense of **5a** (area = $1.8 × 10^4$).

4.1.4. 2-(4-Chlorophenyl)-3,4-diphenyl-6-chloro-8-(trans-stilbenyl)-2,3-dihydrocinnoline 3b and 2-(4-chlorophenyl)-3,4-diphenyl-6-chloro-2,3-dihydrocinnoline 5b

1004 mg (4.0 mmol) of 4,4'-dichloroazobenzene, 1426 mg (8.0 mmol) of diphenylacetylene and 235 mg (0.28 mmol) of $CoH_3(PPh_3)_3$ in 20 ml of THF were used. Yields after column chromatography were: 614 mg

of the red oil of **5b** (1.43 mmol, 36%) and by-products, 132 mg (0.21 mmol, 5%) of **3b** (TON = 5.9). After purification by prep. HPLC 150 mg of **5b** were obtained.

3b. MS: FD m/z 607 [M]$^+$. Calcd for $C_{40}H_{28}Cl_2N_2$ (606.7): C, 79.07; H, 4.65; N, 4.61. Found: C, 78.59; H, 4.73; N, 4.32. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 515 (11 400), 289 (44 700). **5b**: MS: FD m/z 429 [M]$^+$. ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm): 7.70–6.95 (m, 18H, 3-H, 5-H, 6-H, 8-H, 9-H, 11-H, 12-H, PhC=CHPh (11H)). ^{13}C NMR (67.7 MHz, CDCl$_3$) δ (ppm): 117.6 (C-6), 124.3 (C-8 and C-12), 127.0 (C-16 and C-20), 127.5 (C-18), 128.1 (C-17 and C-19), 128.3 (C-18′), 128.4 (C-17′ and C-19′), 128.5 (C-5), 129.0 (C-3), 129.1 (C-9 and C-11), 129.2 (C-16′ and C-20′), 130.0 (C-4), 131.7 (C-14), 136.8 (C-15′), 137.2 (C-10), 138.4 (C-15), 142.0 (C-2), 143.3 (C-13), 149.0 (C-1), 151.1 (C-7). UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 505 (2200), 309 (22 700). HPLC $(CH_3CN–H_2O = 5/1$ (v/v), 5 ml min^{-1}) retention time [min] (integrated area): 17.0 (5.3 × 10^4) unknown, 19.3 (2.1 × 10^6) **5b**, 20.4 (7.2 × 10^4) unknown.

4.1.5. Isomerization of 2-(4-chlorophenyl)-3,4-diphenyl-6-chloro-2,3-dihydrocinnoline 5b to N-(4-chloroanilino)-2,3-diphenyl-5-chloroindole 6b catalysed by HOAc

74 mg (1.72 × 10^{-4} mol) of the red oil of **5b**, dissolved in 3 ml of 1-BuOH and 9.85 μl of HOAc ([**5b**] = [HOAc] = 5.73 × 10^{-2} mol l^{-1}), were heated to 100 °C. The colour of the solution changed within 5 min from red to reddish brown and an intensive blue fluorescence at λ_{exc} = 366 nm was observed. The reaction was stopped after 1 h, and after removing the solvent a pale red residue was obtained. HPLC-analysis: **5b** (19.4 min, initial value: area = 6.8 × 10^5, final value: area = 4.0 × 10^4); **6b** (8.45 min, initial value: area = 1.4 × 10^5, final value: area = 7.3 × 10^5); analytically pure **6b** had a retention time of 8.48 min.

4.1.6. 2-(4-Methylphenyl)-3,4-diphenyl-6-methyl-8-(trans-stilbenyl)-2,3-dihydrocinnoline 3c and 2-(4-methylphenyl)-3,4-diphenyl-6-methyl-2,3-dihydrocinnoline 5c

841 mg (4.0 mmol) of 4,4′-dimethylazobenzene, 1426 mg (8.0 mmol) of diphenylacetylene and 350 mg (0.41 mmol) of CoH$_3$(PPh$_3$)$_3$ in 20 ml of diethyl ether were used. Yields after column chromatography were: 430 mg of an orange-red oil of **5c** (1.10 mmol, 28%) and by-products, 240 mg (0.42 mmol, 11%) of **3c** (TON = 3.7). After prep. HPLC purification 93 mg of **5c** were obtained.

3c. MS: FD m/z 567 [M]$^+$. Calcd for $C_{42}H_{34}N_2$ (566.8): C, 89.11; H, 6.05; N, 4.94. Found: C, 87.50; H, 6.90; N, 3.30. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 523 (14 000), 292 (52 100). **5c**. MS: FD m/z 389 [M]$^+$. ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm):

7.68–6.98 (m, 18H, 3-H, 5-H, 6-H, 8-H, 9-H, 11-H, 12-H, PhC=CHPh (11H)), 2.32 (s, 3H, 4-CH$_3$), 2.31 (s, 3H, 10-CH$_3$). ^{13}C NMR (67.7 MHz, CDCl$_3$) δ (ppm): 21.4 (C-21, C-21′), 116.0 (C-6), 122.8 (C-8 and C-12), 126.6 (C-18), 127.0 (C-16 and C-20), 127.1 (C-18′), 127.9 (C-17 and C-19), 128.1 (C-17′ and C-19′), 129.2 (C-9 and C-11), 129.4 (C-16′ and C-20′), 129.5 (C-3 and C-5), 132.0 (C-14), 137.4 (C-15′), 140.2 (C-4 and C-10), 140.8 (C-15), 141.4 (C-2), 144.0 (C-13), 148.8 (C-1), 151.1 (C-7). UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 305 (11 200), 460 (200). HPLC $(CH_3CN–H_2O = 5/1$ (v/v), 5 ml min^{-1}) retention time [min] (integrated area): 6.8 (2.3 × 10^4) **6c**, 13.0 (6.1 × 10^5) **5c**.

4.1.7. Isomerization of 2-(4-methylphenyl)-3,4-diphenyl-6-methyl-2,3-dihydrocinnoline 5c to N-(p-toluidino)-2,3-diphenyl-5-methylindole 6c catalysed by HOAc

25 mg (6.43 × 10^{-5} mol) of the orange-red oil of **5c**, dissolved in 3 ml of 1-BuOH and 3.86 μl of HOAc ([**5c**] = [HOAc] = 2.14 × 10^{-2} mol l^{-1}), were heated to 100 °C. The colour of the solution changed within 5 min from orange to yellow and an intensive blue fluorescence (λ_{exc} = 366 nm) was observed. The reaction was stopped after 1 h; a grey powder was obtained after solvent removal. HPLC-analysis: **5c** (11.3 min, initial value: area = 8.2 × 10^5, final value: area = 2.3 × 10^4); **6c** (5.76 min, initial value: area = 1.1 × 10^5, final value: area = 1.3 × 10^6); analytically pure **6c** had a retention time of 5.78 min.

4.1.8. 2,6-Di-(trans-stilbenyl)-3,3′,5,5′-tetramethylazobenzene 2d and 2-(trans-stilbenyl)-3,3′,5,5′-tetramethylazobenzene 4d

953 mg (4.0 mmol) of 3,3′,5,5′-tetramethylazobenzene, 1426 mg (8.0 mmol) of diphenylacetylene and 700 mg (0.82 mmol) of CoH$_3$(PPh$_3$)$_3$ in 20 ml of THF were used. The colour of the solution changed after addition of the catalyst, but only from orange to green-black and not to red because of the lower absorptivity in the region of about 500 nm of the distilbenylazobenzene **2** compared to the dihydrocinnoline **3**. Yields after column chromatography were: 890 mg of an orange oil of **4d** (2.13 mmol, 53%) and by-products, 134 mg (0.22 mmol, 6%) of an orange powder of **2d** (TON = 2.9). After purification by prep. HPLC 100 mg of **4d** were obtained.

2d. MS: FD m/z 595 [M]$^+$. Calcd for $C_{42}H_{34}N_2$ (594.8): C, 88.85; H, 6.44; N, 4.71. Found: C, 88.73; H, 6.57; N, 4.73. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 459 (1200), 295 (51 300). **4d**. MS: FD m/z 416 [M]$^+$ and 208 [M]$^{2+}$. ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm): 7.35–6.87 (m, 16H, 4-H, 6-H, 8-H, 10-H, 12-H, PhC=CHPh (11H)), 2.35 (s, 3H, 5-CH$_3$), 2.22 (s, 6H, 9-CH$_3$ and 11-CH$_3$), 2.06 (s, 3H, 3-CH$_3$).

^{13}C NMR (67.7 MHz, CDCl$_3$) δ (ppm): 19.5 (C-23), 21.2 (C-22 and C-22′), 21.3 (C-23′), 113.7 (C-6), 120.7 (C-8 and C-12), 126.5 (C-16 and C-20), 126.8 (C-18), 127.0 (C-18′), 128.1 (C-17 and C-19), 128.2 (C-17′ and C-19′), 128.5 (C-16′ and C-20′), 129.7 (C-14), 132.1 (C-10), 133.7 (C-4), 136.9 (C-3), 137.5 (C-15), 137.7 (C-15′), 138.0 (C-5), 138.3 (C-9 and C-11), 138.4 (C-2), 143.4 (C-13), 150.9 (C-1), 153.2 (C-7). UV–vis (CH$_2$Cl$_2$) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 306 (11 300). HPLC (CH$_3$CN–H$_2$O = 5/1 (v/v), 5 ml min^{-1}) retention time [min] (integrated area): 10.7 (1.4 × 10^5) unknown, 21.9 (2.8 × 10^6) **4d**.

4.1.9. Isomerization of 2-(trans-stilbenyl)-3,3′,5,5′-tetramethylazobenzene **4d** to N-3,5-dimethylanilino-2,3-diphenyl-4,6-dimethylindole **6d** catalysed by HOAc

63.6 mg (0.15 mmol) of the orange oil of **4d**, dissolved in 4 ml of 1-BuOH and 8.74 μl of HOAc ([**4d**] = [HOAc] = 3.82 × 10^{-2} mol l^{-1}), were heated to 110 °C. The colour of the solution changed within 30 min from orange to pale yellow and a blue fluorescence (λ_{exc} = 366 nm) was observed. The reaction was stopped after 2 h, and a pale yellow residue was obtained after solvent removal. HPLC-analysis: **4d** (22.2 min, initial value: area = 2.4 × 10^6, final value: area = 8.7 × 10^4); **6d** (8.2 min, initial value: area = 8.7 × 10^4, final value: area = 3.5 × 10^6).

6d. MS: FD m/z 416 [M]$^+$. ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm) (for atom numbering see Ref. [3]): 7.35–7.11 (m, 11H, 8-H, Ph–H (10 H)), 6.95 (s, 1H, 7-H), 6.75 (s, 1H, 5-H), 6.53 (s, 1H, 12-H), 6.35 (d, 2H, 10-H, 14-H), 2.37 (s, 3H, 6-CH$_3$), 2.20 (s, 6H, 11-CH$_3$ and 13-CH$_3$), 2.14 (s, 3H, 4-CH$_3$). ^{13}C NMR (67.7 MHz, CDCl$_3$) δ (ppm): 21.1 (C-23), 22.2 (C-22 and C-22′), 22.3 (C-23′), 108.3 (C-7), 111.1 (C-10 and C-14), 116.3 (C-3), 123.0 (C-12), 123.2 (C-5), 124.4 (C-3a), 125.2 (C-18′), 127.2 (C-18), 128.0 (C-6), 128.2 (C-16′ and C-20′), 128.4 (C-4, C-16 and C-20), 131.2 (C-17′ and C-19′), 131.7 (C-17 and C-19), 132.6 (C-15), 133.3 (C-15′), 137.3 (C-11 and C-13), 137.8 (C-7a), 139.8 (C-2), 148.3 (C-9). UV–vis (CH$_2$Cl$_2$) λ_{max} [nm]: 304.

4.1.10. 2,6-Di(trans-stilbenyl)-3,5-dichloroazobenzene **2e** and 2-(trans-stilbenyl)-3,5-dichloroazobenzene **4e**

1004 mg (4.0 mmol) of 3,5-dichlorazobenzene and 1426 mg (8.0 mmol) of diphenylacetylene and 520 mg (0.61 mmol) of CoH$_3$(PPh$_3$)$_3$ in 20 ml of THF were used. The changes in the colour of solution were analogous to **2d** and **4d**. Yields after column chromatography were: 200 mg of an orange powder of **4e** (0.47 mmol, 12%) and by-products, 838 mg (1.38 mmol, 36%) of an orange powder of **2e**. Because of the insolubility of **4e** in CH$_3$CN a second column chromatography was performed instead of prep. HPLC. Yield: 105 mg of an orange powder of **4e**.

2e. MS: FD m/z 607 [M]$^+$. Calcd for C$_{40}$H$_{28}$Cl$_2$N$_2$ (607.6): C, 79.07; H, 4.65; N, 4.61. Found: C, 79.69; H, 4.80; N, 5.09. UV–vis (CH$_2$Cl$_2$) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 505 (700), 291 (55 900). **4e**. MS: FD m/z 429 [M]$^+$. Calcd for C$_{26}$H$_{18}$Cl$_2$N$_2$ (429.4): C, 72.73; H, 4.23; N, 6.52. Found: C, 72.92; H, 4.32; N, 6.06. ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm): 7.53–6.74 (m, 18H, 4-H, 6-H, 8-H, 9-H 10-H, 11-H, 12-H, PhC=CHPh (11H)). ^{13}C NMR (67.7 MHz, CDCl$_3$) δ (ppm): 115.1 (C-6), 123.3 (C-8 and C-12), 126.5 (C-16 and C-20), 127.2 (C-18), 127.5 (C-18′), 128.2 (C-17 and C-19), 128.3 (C-16′ and C-20′), 128.4 (C-17′ and C-19′), 128.9 (C-9 and C-11), 131.1 (C-10), 131.7 (C-14), 132.0 (C-4), 134.8 (C-5), 135.3 (C-3), 135.9 (C-2), 136.9 (C-15), 137.3 (C-15′), 141.7 (C-13), 152.3 (C-7), 152.4 (C-1). UV–vis (CH$_2$Cl$_2$) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 455 (400), 302 (39 700). HPLC (CH$_3$CN–H$_2$O = 5/1 (v/v), 5 ml min^{-1}) retention time [min] (integrated area): 6.2 (2.3 × 10^4) unknown, 12.0 (1.8 × 10^6) **4e**. Single crystals were obtained by recrystallization from CH$_2$Cl$_2$–MeOH = 1/2 (v/v) at room temperature.

4.1.11. Isomerization of 2-(trans-stilbenyl)-3,5-dichloroazobenzene **4e** to N-anilino-2,3-diphenyl-4,6-dichloroindole **6e** catalysed by HOAc

103.5 mg (0.24 mmol) of the orange powder of **4e**, dissolved in 3 ml of 1-BuOH and 13.80 μl of HOAc ([**4e**] = [HOAc] = 8.03 × 10^{-2} mol l^{-1}), were heated to 110 °C. The colour of the solution changed within 30 min from orange to pale yellow and a blue fluorescence (λ_{exc} = 366 nm) was observed. The reaction was stopped after 2.5 h, the solvent removed and a pale yellow residue was obtained. HPLC-analysis: **4e** (13.9 min, initial value: area = 1.2 × 10^6, final value: area = 1.4 × 10^5); **6e** (7.5 min, initial value: area = 2.6 × 10^4, final value: area = 1.5 × 10^6).

6e. MS: FD m/z 428 [M]$^+$. ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm) (for atom numbering see Ref. [3]): 7.34–7.10 (m, 14H, 8-H, 11-H, 13-H, Ph–H (10 H)), 6.90 (t, 1H, 12-H), 6.84 (s, 1H, 5-H), 6.58 (s, 1H, 7-H), 6.48 (d, 2H, 10-H, 14-H). ^{13}C NMR (67.7 MHz, CDCl$_3$) δ (ppm): 109.4 (C-7), 113.3 (C-10 and C-14), 115.9 (C-3), 122.1 (C-12), 123.3 (C-5), 127.5 (C-18′), 127.9 (C-3a), 128.0 (C-16′ and C-20′), 128.7 (C-16 and C-20), 128.9 (C-18), 129.2 (C-4), 129.5 (C-6), 130.2 (C-11 and C-13), 131.2 (C-17′ and C-19′), 131.6 (C-15), 132.8 (C-17 and C-19), 134.4 (C-15′), 138.5 (C-7a), 140.4 (C-2), 147.3 (C-9). UV–vis (CH$_2$Cl$_2$) λ_{max} [nm]: 307.

4.2. Mechanistic investigations

4.2.1. Evidence for H$_2$ formation

426 mg (2.34 mmol) of azobenzene and 834 mg (4.68 mmol) of diphenylacetylene were dissolved in 25 ml of diethyl ether and added at room temperature

dropwise within 2 min under stirring to 1.985 g (2.34 mmol) of dry $CoH_3(PPh_3)_3$. The colour of the solution changed from orange to black. 20 min after mixing the reaction was stopped and the gas phase was characterized by EI-MS in the range of 0.6 to 4.0 mass units with a mass spectrometer preheated for 4 days to exclude any memory effects. MS: EI (70 eV) m/z (%): blank: 2.0 (5) $[H_2]^+$, 1.0 (2) $[H]^+$; sample: 2.0 (50) $[H_2]^+$, 1.0 (14) $[H]^+$.

4.2.2. Reaction of $CoH_3(PPh_3)_3$ with tolan in absence of azobenzene

372 mg (2.08 mmol) of diphenylacetylene were dissolved in 20 ml of THF and added at room temperature dropwise within 2 min under stirring to 885 mg (1.04 mmol) of dry $CoH_3(PPh_3)_3$. The colour of the solution changed to black. 30 min after mixing the reaction was stopped. The formation of the linear tetramer of tolan (octaphenyloctatetraene) with $m/e = 714$, the linear trimer (hexaphenylhexatriene) with $m/e = 536$, the cyclic (tetraphenylcyclobutadiene) and linear (tetraphenylbutadiene) dimer with $m/e = 356$ and 358 respectively, and stilbene with $m/e = 180$ could be observed. Since diphenylacetylene with $m/e = 178$ could be detected only in minor traces, the two-fold excess of diphenylacetylene compared with the catalyst had been converted almost quantitatively within 30 min after mixing the reactants. MS: EI (70 eV) m/z (%): 714 (3) $[H(PhC=CPh)_4H]^+$, 536 (6) $[H(PhC=CPh)_3H]^+$, 358 (13) $[H(PhC=CPh)_2H]^+$, 356 (12) $[cyclo-(PhC=CPh)_2]^+$, 278 (22) $[O=PPh_3]^+$, 262 (100) $[PPh_3]^+$, 180 (10) $[PhHC=CHPh]^+$, 178 (1) $[PhCCPh]^+$.

4.2.3. Reaction of $CoH_3(PPh_3)_3$ with azobenzene in absence of tolan

223 mg (1.23 mmol) of azobenzene were dissolved in 20 ml of THF and added dropwise at room temperature within 2 min under stirring to 1040 mg (1.23 mmol) of dry $CoH_3(PPh_3)_3$. The colour of the solution changed to black. 1 h after mixing the reaction was stopped. MS: EI (70 eV) m/z (%): 353 (18) $[Ph_3P=NPh]^+$, 278 (4) $[O=PPh_3]^+$, 262 (100) $[PPh_3]^+$, 184 (2) $[PhHN=NHPh]^+$, 182 (1) $[PhN=NPh]^+$.

4.2.4. Reaction of $CoH_3(PPh_3)_3$ with (1) 4-methoxytolan and (2) 3,3′,5,5′-tetramethylazobenzene 1d

400 mg (1.92 mmol) of 4-methoxytolan were dissolved in 10 ml of diethyl ether and added at room temperature dropwise within 2 min under stirring to 815 mg (0.96 mmol) of dry $CoH_3(PPh_3)_3$. The green colour of the suspended catalyst changed to reddish brown within 2 min after mixing the reactants. After 40 min the reaction was stopped and the solution analysed by FD-MS. MS: FD m/z (%): 626 (10) $[H(PhC=CC_6H_4OCH_3)_3H]^+$, 418 (18)

$[H(PhC=CC_6H_4OCH_3)_2H]^+$, 416 (12) $[cyclo-(PhC=CC_6H_4OCH_3)_2]^+$, 278 (23) $[O=PPh_3]^+$, 262 (100) $[PPh_3]^+$, 210 (70) $[PhHC=CHC_6H_4OCH_3]^+$, 208 (1) $[PhCCC_6H_4OCH_3]^+$. Immediately after MS characterization 229 mg (0.96 mmol) of solid 1d were added under stirring. 30 min later, another FD-MS analysis was performed. In addition to the peaks described above, the mass spectra contained the peak of 1d at $m/e = 238$, formation of the 1:1 or 2:1 adduct 4d′ or 2d′ could not be detected.

4.2.5. Reaction of $CoH_3(PPh_3)_3$ with (1) 3,3′,5,5′-tetramethylazobenzene 1d and (2) 4-methoxytolan

150 mg (0.63 mmol) of 1d were dissolved in 10 ml of diethyl ether and added at room temperature dropwise within 2 min under stirring to 535 mg (0.63 mmol) of dry $CoH_3(PPh_3)_3$. The catalyst was suspended with green colour and the orange solution changed its colour to black 15 min after mixing the reactants. After 40 min the reaction was stopped and the solution was analysed by FD-MS. MS: FD m/z (%): 381 (18) $[Ph_3P=NC_6H_3(CH_3)_2]^+$, 278 (22) $[O=PPh_3]^+$, 262 (100) $[PPh_3]^+$, 238 (95) $[1d]^+$. Immediately after MS characterization 262 mg (1.26 mmol) of solid 4-methoxytolan were added under stirring. 30 min later, another FD-MS characterization was performed. MS: FD m/z (%): 654 (5) $[2d′]^+$, 626 (3) $[H(PhC=CC_6H_4OCH_3)_3H]^+$, 446 (2) $[4d′]^+$, 418 (4) $[H(PhC=CC_6H_4OCH_3)_2H]^+$, 416 (2) $[cyclo-(PhC=CC_6H_4OCH_3)_2]^+$, 278 (6) $[O=PPh_3]^+$, 262 (60) $[PPh_3]^+$, 238 (32) $[1d]^+$, 210 (8) $[PhHC=CHC_6H_4OCH_3]^+$, 208 (100) $[PhCCC_6H_4OCH_3]^+$.

4.2.6. Isomerization of 2-(2,4,6-trimethylphenyl)-3,4-diphenyl-6,8-dimethyl-2,3-dihydrocinnoline 5g to 2,3-diphenyl-5,7-dimethylindole 7g

220 mg (0.51 mmol) of 5g were dissolved in 20 ml of 1-BuOH and thereafter 29 µl (0.51 mmol) of HOAc were added. Upon heating the red solution under stirring to 100 °C, the colour changed to black within 5 min. Stirring was continued for another hour and then the solvent was removed. The black residue was purified by prep. HPLC yielding 30 mg (0.10 mmol, 20%) of 2,3-diphenyl-5,7-dimethylindole 7g and 10 mg of a mixture of two compounds which could not be completely characterized by NMR-techniques, but the FD-mass spectrum, showing a peak at $m/z = 431$ $[M]^+$, and the different retention times (10.4 min vs. 28.2 min for 5g) indicate the formation of the N-anilinoindole 6g.

7g. MS: EI (70 eV) m/z (%): 298 (100) $[M]^+$, 220 (10) $[M - Ph]^+$, 178 (18) $[Ph-C=C-Ph]^+$; FD m/z 297 $[M]^+$. For atom numbering see Ref. [3]. ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm): 8.01 (s, br, 1H, N–H), 7.46–7.24 (m, 11H, Ph–H and 4-H), 6.90 (s, 1H, 6-H), 2.51 (s, 3H, 7-CH$_3$), 2.42 (s, 3H, 5-CH$_3$). ^{13}C NMR

(67.7 MHz, $CDCl_3$) δ (ppm): 17.3 (C-21), 22.2 (C-22), 115.9 (C-3), 117.6 (C-7), 120.5 (C-4), 125.7(C-6), 126.8 (C-18'), 128.2 (C-18), 128.9 (C-16' and C-20'), 129.2 (C-16 and C-20), 129.3 (C-3a), 129.4 (C-17' and C-19'), 130.7 (C-5), 130.9 (C-17 and C-19), 133.7 (C-15'), 134.4 (C-15), 134.7 (C-7a), 136.1 (C-2). Calcd for $C_{26}H_{19}N$ (297.4): C, 88.85; H, 6.44; N, 4.71. Found: C, 87.76; H, 6.43; N, 4.48.

4.3. Kinetic measurements

4.3.1. In general

For the measurement of the initial rate as a function of substrate concentration the following standard procedure was applied. To 9.5 ml of a solution of HOAc in 1-BuOH heated in a thermostated oil bath to $80.0 \pm 0.1\,°C$ there were added in one shot 2.5 mg (6.94 × 10^{-6} mol) of 5a dissolved in 500 μl of 1-BuOH. Samples of 500 μl were withdrawn after 15, 30, 45, 60, 90 and 120 min, evaporated to dryness, redissolved in 500 μl of acetonitrile, and the concentration of N-anilino-2,3-diphenylindole (given in the following as dimensionless numbers in the unit of 10^{-4} mol l^{-1}) was determined as described above. Reproducibility was within ± 10%.

4.3.2. Initial rates as a function of HOAc concentration

[HOAc] = 1.73 × 10^{-4} mol l^{-1} (molar ratio of HOAc/5a = 0.25): 0.50; 0.60; 0.87; 1.10; 1.40 and 1.75; $d[P]/dt = 1.90 × 10^{-8}$ mol l^{-1} s. [HOAc] = 3.47 × 10^{-4} mol l^{-1} (0.50): 0.55; 0.82; 1.13; 1.40; 1.90 and 2.30; $d[P]/dt = 2.88 × 10^{-8}$ mol l^{-1} s. [HOAc] = 6.94 × 10^{-4} mol l^{-1} (1.0): 0.80; 1.12; 1.45; 1.95; 2.70 and 3.40; $d[P]/dt = 4.25 × 10^{-8}$ mol l^{-1} s. [HOAc] = 1.04 × 10^{-3} mol l^{-1} (1.5): 0.90; 1.45; 2.10; 2.55; 3.40 and 4.05; $d[P]/dt = 5.83 × 10^{-8}$ mol l^{-1} s. [HOAc] = 1.39 × 10^{-3} mol l^{-1} (2.0): 1.10; 1.70; 2.45; 2.85; 4.00 and 5.10; $d[P]/dt = 6.47 × 10^{-8}$ mol l^{-1} s. [HOAc] = 5.00 × 10^{-3} mol l^{-1} (7.20): 2.30; 3.60; 4.95; 5.56; 6.73; reaction complete; $d[P]/dt = 1.50 × 10^{-7}$ mol l^{-1} s. [HOAc] = 1.00 × 10^{-2} mol l^{-1} (14.40): 5.18; 5.29; 6.11; 6.73; reaction complete; $d[P]/dt = 2.38 × 10^{-7}$ mol l^{-1} s. [HOAc] = 5.00 × 10^{-2} mol l^{-1} (72.05): 5.02; 6.38; 7.25; reaction complete; $d[P]/dt = 6.45 × 10^{-7}$ mol l^{-1} s.

4.3.3. Initial rates as a function of concentration of 5a

[HOAc] = 6.94 × 10^{-4} mol l^{-1} for all five measurements; 5a = 3.47 × 10^{-4} mol l^{-1} (molar ratio 5a/HOAc = 0.50): 0.51; 0.82; 1.14; 1.43; 1.92 and 2.43; $d[P]/dt = 3.54 × 10^{-8}$ mol l^{-1} s. 5a = 4.86 × 10^{-4} mol l^{-1} (0.70): 0.65; 1.09; 1.44; 1.89; 2.53 and 3.27; $d[P]/dt = 4.52 × 10^{-8}$ mol l^{-1} s. 5a = 6.94 × 10^{-4} mol l^{-1} (1.00): 0.85; 1.25; 1.95; 2.50; 3.20 and 4.35; $d[P]/dt = 6.12 × 10^{-8}$ mol l^{-1} s. 5a = 1.04 × 10^{-3} mol l^{-1} (1.50): 1.32; 2.21; 3.12; 3.85; 5.22 and

6.52; $d[P]/dt = 9.52 × 10^{-8}$ mol l^{-1} s. 5a = 1.39 × 10^{-3} mol l^{-1} (2.00): 1.40; 2.65; 3.65; 4.87; 5.75 and 8.20; $d[P]/dt = 1.28 × 10^{-7}$ mol l^{-1} s.

4.3.4. Temperature dependence in the presence of HOAc

[5a] = [HOAc] = 6.94 × 10^{-4} mol l^{-1} for all five measurements; 343 K: 0.50; 1.02; 1.30; 1.60; 2.25 and 2.80; $d[P]/dt = 3.33 × 10^{-8}$ mol l^{-1} s; from Eq. (1) and the concentrations given above, the rate constant is calculated as $k = 3.8 × 10^{-3}$ (mol $l^{-1})^{-0.6}$ s^{-1}. 348 K: 0.65; 1.60; 1.75; 2.25; 2.85 and 3.67; $d[P]/dt = 4.56 × 10^{-8}$ mol l^{-1} s; $k = 5.2 × 10^{-3}$ (mol $l^{-1})^{-0.6}$ s^{-1}. 353 K: 0.71; 1.40; 1.98; 2.52; 3.50 and 4.22; $d[P]/dt = 6.02 × 10^{-8}$ mol l^{-1} s; $k = 7.0 × 10^{-3}$ (mol $l^{-1})^{-0.6}$ s^{-1}. 358 K: 1.05; 1.97; 2.65; 3.40; 4.55 and 5.50; $d[P]/dt = 7.92 × 10^{-8}$ mol l^{-1} s; $k = 9.0 × 10^{-3}$ (mol $l^{-1})^{-0.6}$ s^{-1}. 363 K: 1.20; 2.22; 3.12; 3.90; 5.60 and 6.30; $d[P]/dt = 9.78 × 10^{-8}$ mol l^{-1} s; $k = 1.1 × 10^{-2}$ (mol $l^{-1})^{-0.6}$ s^{-1}.

4.3.5. Temperature dependence in the absence of HOAc

[5a] = 6.94 × 10^{-4} mol l^{-1} for all five measurements; 343 K: 0.37; 0.33; 0.46; 0.56; 0.68 and 0.83; $d[P]/dt = 7.93 × 10^{-9}$ mol l^{-1} s; $k = 1.1 × 10^{-5}$ s^{-1}. 348 K: 0.41; 0.50; 0.53; 0.67; 0.92 and 1.12; $d[P]/dt = 1.17 × 10^{-8}$ mol l^{-1} s; $k = 1.7 × 10^{-5}$ s^{-1}. 353 K: 0.86; 0.97; 1.09; 1.21; 1.56 and 1.60; $d[P]/dt = 1.36 × 10^{-8}$ mol l^{-1} s; $k = 2.0 × 10^{-5}$ s^{-1}. 358 K: 0.77; 0.96; 0.98; 1.46; 1.68 and 2.18; $d[P]/dt = 1.97 × 10^{-8}$ mol l^{-1} s; $k = 2.8 × 10^{-5}$ s^{-1}. 363 K: 0.42; 0.71; 0.87; 1.02; 1.40 and 1.91; $d[P]/dt = 2.22 × 10^{-8}$ mol l^{-1} s; $k = 3.2 × 10^{-5}$ s^{-1}.

4.3.6. Initial rates as a function of various additives

[HOAc] = [NaOAc] = 6.94 × 10^{-4} mol l^{-1} (molar ratio additive/5a = 1.0): 1.46; 1.94; 2.26; 2.69; 3.67 and 4.42; $d[P]/dt = 4.77 × 10^{-8}$ mol l^{-1} s. [2,2,6,6-Tetramethylpiperidine] = 6.94 × 10^{-2} mol l^{-1} (100.0): 0.34; 0.74; 0.88; 1.12; 1.35 and 1.50; $d[P]/dt = 1.74 × 10^{-8}$ mol l^{-1} s.

Acknowledgements

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