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Transition metal complexes of diazenes XLI[1]: cobalt catalyzed addition of internal alkynes to 1,2-diaryldiazenes: formation of 2,3-dihydrocinnolines, mono- and distilbenylazobenzenes

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Abstract

The $CoH_3(PPh_3)_3$ catalyzed addition reaction between azobenzenes and internal alkynes produces 2-stilbenylazobenzenes and isomeric 2,3-dihydrocinnolines which are intermediates in the rhodium catalyzed formation of *N*-anilinoindoles from the same substrates. The structures of six adducts were resolved by single crystal X-ray structural analyses. In both reactions the insertion of the alkyne into a M–H bond and *ortho*-metalation of the 1,2-diazene are key steps of the catalytic cycle. When only one phenyl ring of the diazene is substituted like in 3,5-dichloro- and 3,5-difluoroazobenzene, selectively this ring is *ortho*-metalated in the case of cobalt while only the unsubstituted or both rings are attacked in rhodium catalysis. This difference enables a two-step regioselective cobalt catalyzed synthesis of the corresponding *N*-anilinoindole via isolation of 2-stilbenyl-3,5-difluoroazobenzene and subsequent acid catalyzed rearrangement to the indole derivative. Results obtained with 4-methoxytolan reveal that insertion into the Co–H bond produces regioisomers the ratio of which is determined by the sign of the triple bond polarization. It is postulated that insertion initially affords a *cis*-alkenyl ligand which undergoes an efficient *cis–trans* isomerization except when decafluorotolan is the alkyne; in this case also the *cis*-alkenyl product was isolated. Catalytic amounts of HOAc lead to a tenfold increase of reaction rate. No reaction is observed when sterically demanding substitutents like mesityl and adamantyl are introduced to the triple bond.

Keywords: Cobalt catalysis; Hydride complexes; 1,2-Diaryldiazenes; Alkyne insertion; Stilbenylazobenzene; 2,3-Dihydrocinnoline; *Ortho*-metalation

1. Introduction

During our studies on the activation of 1,2-diazenes we found that the reaction between aromatic azo compounds and internal alkynes catalyzed by Wilkinson's catalyst $RhCl(PPh_3)_3$ in boiling 1-PrOH/HOAc solutions afforded 1:1 adducts which have the structures of hitherto unknown *N*-anilinoindole derivatives [1]. When this reaction was performed in a melt of the substrates and the rhodium complex was replaced by $CoH_3(PPh_3)_3$, new 2:1 adducts were isolated in the form of distilbenylazobenzenes **4** which may undergo ring closure to the isomeric 2,3-dihydrocinnolines **2** (Scheme 1) [2]. The former were obtained exclusively since no isomerization occurred when the azobenzene derivative was substituted in the *m*eta-positions by CH_3 or Cl. It is noted that in all cases the stilbenyl group had a *trans*-configuration except when decafluortolan was used, in this case also the *cis*-stilbenyl isomer of the corresponding 2,3-dihydrocinnoline could be isolated ([2]b). Upon conducting the reaction in Et_2O or THF solution at room temperature (r.t.), it was possible to isolate 1:1 adducts which have a structure of the 2-stilbenylazobenzene type **3** [3]. The formation of these

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products was rationalized by a catalytic cycle [3] out of which some key intermediates are illustrated in Scheme 2.

It is assumed that after loss of dihydrogen the reaction of **A** with tolan affords the *cis*-stilbenyl complex **B**. Subsequent coordination and *ortho*-metalation of azobenzene leads to the intermediate *trans*-**C**, wherein the stilbenyl ligand and the *ortho*-metalated ring are in *trans*-position. Isomerization to *cis*-**C** has to proceed before reductive elimination to the 1:1 adducts **1** and **3** can occur. Alternatively, a second insertion of the alkyne, *ortho*-metalation of the stilbenylphenyl ring and reductive elimination from intermediary **D** may produce the 2:1 adducts **2** and **4**. However, no information is available on the factors which control the regioselectivity of alkyne insertion when an unsymmetrical tolan derivative is used.

In rhodium catalysis, 3,3′,5,5′-tetramethylazobenzene does not react to the corresponding *N*-anilinoindole derivative due to steric hindrance in the *ortho*-metalation step, while 3,5-difluoroazobenzene afforded a mixture of two isomeric indoles and 3,5-dichloroazobenzene exclusively yielded that indole derivative where the unsubstituted phenyl ring has been *ortho*-metalated. Opposite to that, in the cobalt catalyzed reaction 3,3′,5,5′-tetramethylazobenzene and tolan afforded the expected 2-stilbenylazobenzene of type **3** [3]. Since the latter could be converted to the *N*-anilinoindole through a HOAc catalyzed rearrangement [3], this route seemed to open a path to hitherto not accessible indole derivatives. In the following we therefore report on experiments with 3,5-substituted azobenzenes and on the influence of varying steric and electronic properties of the alkyne on the regioselectivity of the reaction.

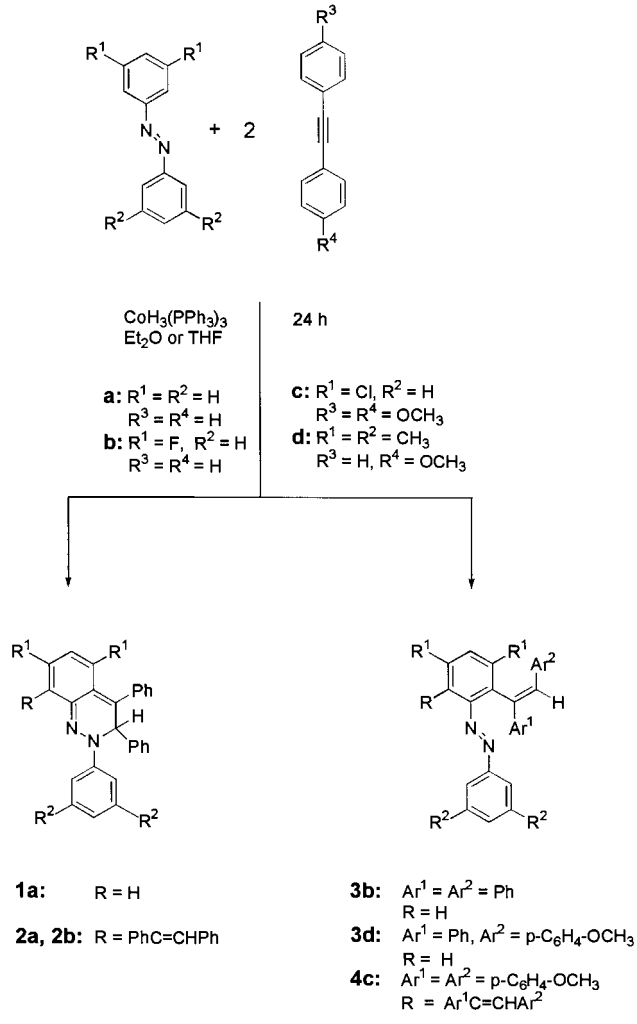
2. Results and discussion

The addition of solid $CoH_3(PPh_3)_3$ to a solution of an 1,2-diazene and an alkyne derivative in the molar ratio of 1:2 in diethyl ether or THF at r.t. [3] afforded the already known **2b** [2], the new 2:1 adducts **4c** and **2a**, and the new 1:1 adducts **3b** and **3d** which could only be purified by preparative HPLC (Scheme 1). In general, the 2,3-dihydrocinnolines **2** are dark red powders while the isomeric distilbenylazobenzenes **4** form orange powders; the 2,3-dihydrocinnolines **1** and isomeric monostilbenylazobenzenes **3** were obtained as red oils or orange powders, respectively. The 2,3-dihydrocinnoline structure is suggested by the photochromic behavior [2,3]. Irradiating a diluted red solution of **1** or **2** for about 1 min leads to a color change to yellow and a decreased absorbance at about 500 nm due to a ring opening to the stilbenylazobenzenes of type **3** or **4**, respectively. Upon standing in the dark for about 10 (**2**) or 80 (**1**) min, the absorbance recovers to its original value.

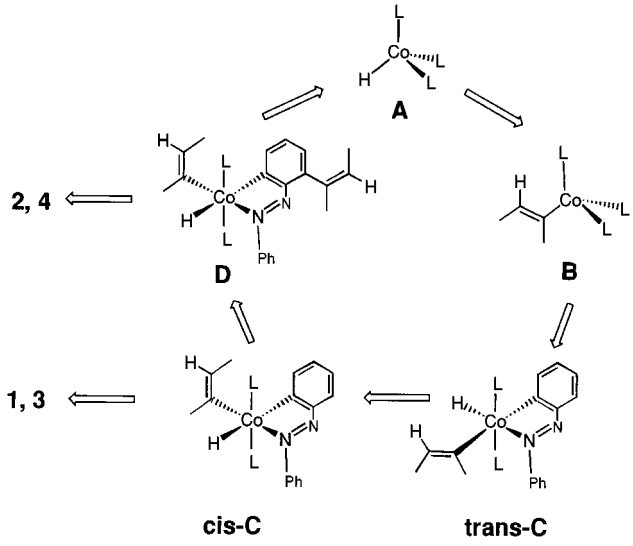
2.1. Reactions with tolan and 4-methoxytolan

As also observed in the melt reaction [2], the reaction between azobenzene and tolan in solution afforded the 2:1 adduct **2a** for which a single crystal X-ray analysis could be performed [4]. In agreement with previous results, according to which in the absence of *meta*-substituents in the azobenzene component the ring closure of the intermediate distilbenylazobenzene to the 2,3-dihydrocinnoline derivative occurs, **2a** has a *trans*-stilbenyl-2,3-dihydrocinnoline structure (Table 1, Fig. 1).

The presence of an *ortho*-quinoid system is evidenced by the two exocyclic double bonds C11–N1 (134.6 pm) and C16–C3 (137.5 pm), and by the alternating bond lengths between C11–C12 (145.1), C12–C13 (135.2), C13–C14 (142.4), C14–C15 (134.2) and C15–C16 (144.9 pm). These data excellently agree with those of



Scheme 1. Products isolated from the reaction of 1,2-diaryldiazenes with mono- and disubstituted alkyne derivatives.



Scheme 2.

the previously characterized **2b** [5]. The two exocyclic double bonds are twisted by 18° as indicated by interplanar angles of 6 and 12°, formed by the plane of C11–C16 with the planes of C11–C16–C3 and C16–C11–N1, respectively. The N–N distance of 135.1 pm is much shorter than expected for a simple single bond (147 pm) suggesting an extension of the conjugated system across N2. This is supported by the planarity of N2 as indicated by the angles N1–N2–C4 (120.2°), C4–N2–C21 (123.8°) and N1–N2–C21 (115.7°). The plane generated by N2, N1, C21 and C4 forms with the *ortho*-quinoid system and with the phenyl ring C21–C26 interplanar angles of 38 and 30°, respectively. Extended conjugation is further evidenced by the N2–C21 bond length of 142.8 pm which is about 4 pm shorter than expected. The short C3–C31 distance of 147.5 pm suggests that also the phenyl ring C31–C36 participates in electron delocalization; the dihedral angle with the quinoid fragment is 49°. sp3-Hybridization of C4 follows from the bond angles N2–C4–C3 (104.5), C3–C4–C41 (113.7) and C41–C4–N2 (116.6°) and the bond lengths of N2–C4 (148.1), C4–C3 (152.3) and C4–C41 (151.3 pm). The bond length C5–C12 of 152.5 pm indicates that the *trans*-stilbenyl group exhibits only minor interactions with the *ortho*-quinoid system. Correspondingly, the latter and the plane generated by C61, C6, C5, C51 form an interplanar angle of 112°.

The reactions between tolan or the monosubstituted 4-methoxytolan and 3,5-difluoroazobenzene or 3,3′,5,5′-tetramethylazobenzene, afforded the 1:1 adducts **3b** and **3d**, respectively, the structures of which were resolved by single crystal X-ray analyses (Table 1, Fig. 2). Both compounds are 2-(*trans*-stilbenyl)azobenzenes and in **3d** the C2-carbon atom of the alkyne became attached to the dimethylphenyl ring; the C1-bound regioisomer **3d′** was formed in only 50% of the amount of **3d**. Of the two expected transition states **E** (Scheme 3) seems to be favored over **F** as also observed in the rhodium catalyzed indole synthesis [1].

The N1–N2 distances amount to 124.7(2) (**3b**) and 124.4(4) pm (**3d**) and exhibit only small deviations from the values obtained for unsubstituted azobenzene (124.3 pm) [6]; the two phenyl rings of the azobenzene fragment C11–C16 and C21–C26 are slightly twisted by 12 (**3b**) and 4° (**3d**), respectively. The C3–C4 distances (133.3(3) (**3b**), 132.9(6) (**3d**) pm) are similar to the double bond length in unsubstituted *trans*-stilbene (131.8 pm) [7] and the interplanar angle between the double bond plane C16–C3–C4 and the azobenzene phenyl ring C11–C16 amount to 63 (**3b**) and 71° (**3d**) indicating that the *ortho*-fluoro substituent in **3b** (van der Waals radius = 135 pm) [8] has less steric influence than the *ortho*-methyl group (200 pm) in **3d**. The two phenyl rings of the stilbenyl fragment C31–C36 and C41–C46 form with the double bond plane C16–C3–C4 interplanar angles of 32 and 43° (**3b**), 35 and 42° (**3d**) and are twisted by 75 and 77°, respectively. As in the case of **2a** the rather long C16–C3 distances (150.3(3) (**3b**) and 150.8(5) (**3d**) pm) and the relatively large interplanar angles mentioned above suggest a rather weak interaction between the azobenzene and stilbene fragments.

No product formation could be observed in the reaction between azobenzene and 4-nitrotolan, while 4-methyltolan afforded the expected adducts but separation of the regioisomers was not achievable by HPLC. The same experimental problem arose when in the latter reaction azobenzene was replaced by 3,5-dichloroazobenzene.

2.2. Reactions with disubstituted tolan derivatives

When 3,5-dichloroazobenzene and the disubstituted 4,4′-dimethoxytolan were employed, the 2:1 adduct **4c** was obtained (Fig. 3). Due to the presence of two sterically demanding stilbenyl substituents the almost coplanar arrangement of the two azobenzene phenyl rings C11–C16 and C21–C26, as observed in the monostilbenyl compounds **3b** and **3d**, is prevented and the interplanar angle increased to 76°. 4,4′-Dimethyltolan in the same reaction afforded very labile 1:1 and 2:1 adducts which could not be isolated as analytically pure materials.

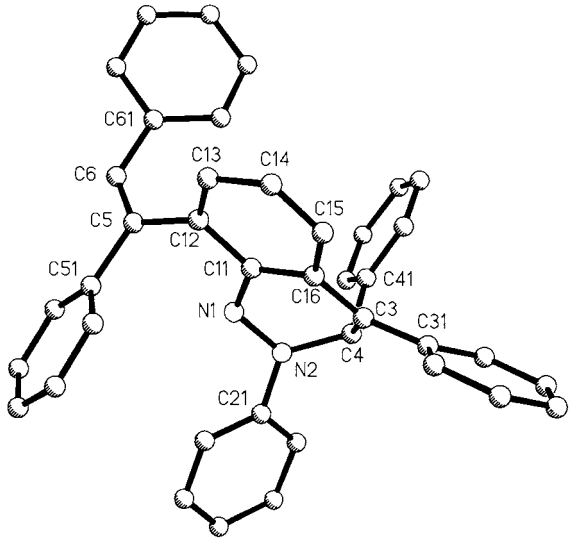
Introduction of sterically demanding substituents at the triple bond resulted in a complete inhibition as indicated by the absence of any addition products in the reactions attempted between azobenzene or 4,4′-dimethylazobenzene with bis(adamantyl)- or bis(mesityl)acetylene. When one aromatic group of the alkyne is replaced by a methyl group as in the reaction of 1-phenylpropyne with azobenzene, no corresponding

Table 1
Selected bond distances (pm)

	2a [4]	**3b**	**4c**	**3d**	*cis*-**3f**	**4f**
N(1)–N(2)	135.1(7)	124.7(2)	120.9(5)	124.4(4)	124.5(3)	125.1(4)
N(1)–C(11)	134.6(8)	142.3(2)	145.6(5)	142.3(5)	143.1(3)	143.6(5)
N(2)–C(21)	142.8(8)	142.9(3)	144.8(5)	143.3(5)	142.7(3)	141.8(5)
C(3)–C(4)	152.3(9)	133.3(3)	133.3(6)	132.9(6)	133.4(4)	132.3(6)
C(16)–C(3)	137.5(9)	150.3(3)	148.8(5)	150.8(5)	148.8(4)	149.6(5)
C(5)–C(6)	126.9(11)		132.5(5)		132.7(5)	
C(12)–C(5)	152.5(10)		149.2(5)		149.2(5)	

adducts but a mixture of oligomerization products were obtained; according to MS analysis they contained one molecule of the diazene and up to seven alkyne molecules.

To investigate the influence of electron withdrawing substituents on the course of the reaction, decafluorotolan was employed. This was the only alkyne which in the melt reaction with 4,4′-dimethylazobenzene at 90°C afforded the corresponding 2,3-dihydrocinnoline with a *cis*-stilbenyl substituent; no reaction occurred when all *meta*-positions are substituted like in 3,3′,5,5′-tetramethylazobenzene [9]. When the reaction was performed in THF solution, different to the preceding reactions with other alkynes, an almost complete conversion of the alkyne to the 2:1 adduct **2e** took place when 4,4′-dichloroazobenzene was employed. FD-MS analysis indicated the absence of any 1:1 adducts. However, these were obtained when 3,5-dichloroazobenzene was used (Scheme 4). The structures of *cis*-**3f** and **4f** were resolved by X-ray analysis (Fig. 4, Table 1), the structure of *trans*-**3f** follows from comparison of UV–vis, HPLC and MS data with the *cis*-isomer. According to HPLC the ratio of *cis*-**3f**:*trans*-**3f** was 7:5.



2a

Fig. 1. Molecular structure of **2a**; hydrogen atoms are omitted for clarity.

The molecular structure of *cis*-**3f** reveals no special features except the presence of a *cis*-decafluorostilbenyl group and a less twisted arrangement of the two stilbenyl phenyl rings (a twist angle of 174° as compared to an average of 76° observed for **3b** and **3d**). Surprisingly, **4f** exhibits *trans*-configuration at both decafluorostilbenyl substituents.

When 2,2′,4,4’,6-pentamethylazobenzene and decafluorotolan were employed, no conversion of the substrates could be observed. Apparently, the decafluorostilbenyl ligand in **B** (Scheme 2) decreases the electron density at the cobalt center to such an extent that in the following step nucleophilic attack at the 2,4-dimethylphenyl ring of the azobenzene ligand cannot occur anymore.

The unique formation of the *cis*-stilbenyl adduct mentioned above indicates that the electron-withdrawing properties of the pentafluorophenyl groups either prevent the complete isomerization of an initially formed *cis*-alkenyl ligand or promote a *cis*-insertion of the alkyne. Although there is no general rule for the stereochemistry of alkyne insertion into M–H or M–C bonds, in most cases a *cis*-insertion is the primary step which often is followed by *cis*/*trans*-isomerization. For the latter various mechanisms have been proposed, including protonation at the alkenyl ligand [10] or metal center [11], and pathways through radical [12] and coordinatively unsaturated intermediates [13]. Bergman et al. postulated that in the reaction between Ni(acac)(PPh_3)Ph with PhCCR (acac, acetylacetonato, R = Ph or CH_3) the *cis*/*trans* isomerization of the σ-alkenyl ligand occurs via rearrangement to a carbenium–carben intermediate [14] as depicted for the present case in Scheme 5. Although isomerization may occur also in the first intermediate **B**, stabilization of the negatively polarized cobalt center should be more efficient in **C** and we propose that it proceeds through the transition state **G**. Destabilization of the positive charge by the pentafluorophenyl group should decrease the stability of **G** and therefore disfavor isomerization which has to compete with reductive elimination to the 1:1 adducts **1** and **3**.

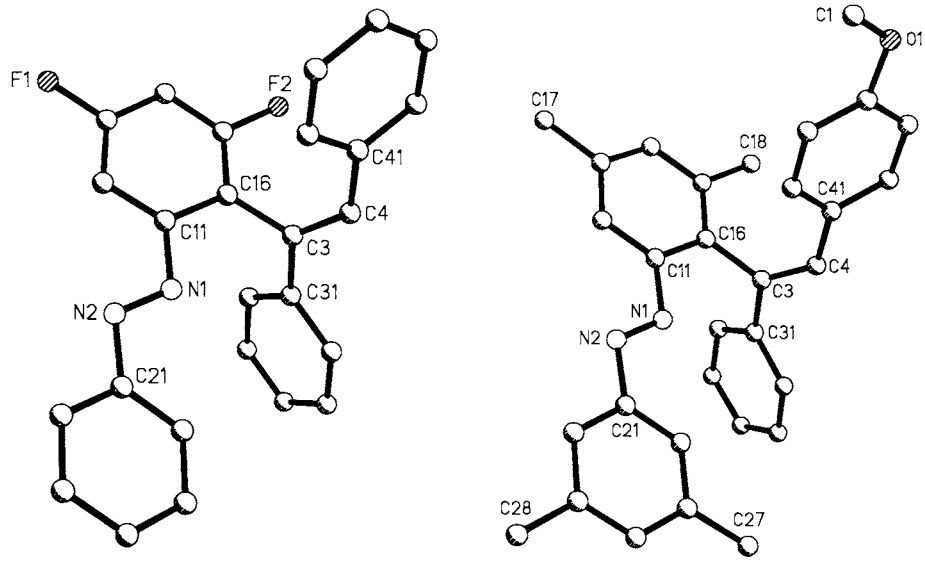
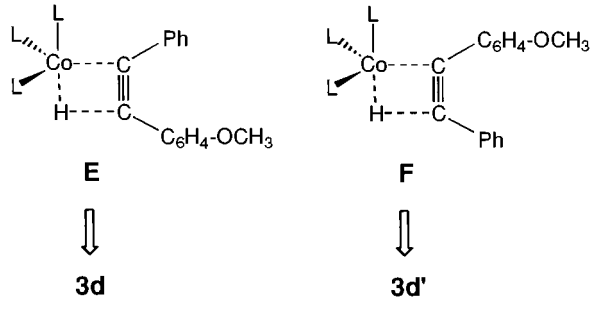


Fig. 2. Molecular structure of **3b** and **3d**; hydrogen atoms are omitted for clarity.

2.3. Rearrangement of *3b* to the corresponding *N*-anilinoindole

In the $RhCl(PPh_3)_3$ catalyzed reaction between 3,5-difluoroazobenzene and tolan, a mixture of two isomeric *N*-anilinoindoles was obtained [15] in the ratio of **5b**:**5b**′ = 5:16, with **5b**′ being the indole in which the unsubstituted phenyl ring has been *ortho*-metalated. Correspondingly, two 2-stilbenylazobenzene derivatives of type **3** should be involved as intermediates. Since in all cobalt catalyzed reactions of unsymmetrically substituted azobenzenes only those products were obtained which arrived from *ortho*-metalation of the substituted phenyl ring, exclusively the expected **3b** and no other regioisomer could be detected (Scheme 6). Refluxing of **3b** in 1-BuOH/HOAc at 115°C, which are the standard conditions for the rhodium catalyzed indole formation [1], afforded the isomeric *N*-anilinoindole **5b** in 95% yield. Although this preparation of **5b** involves two steps it offers a convenient access to a single isomer.



Scheme 3.

2.4. Influence of acids

Since catalytic amounts of HOAc increased yields and turnover numbers of the rhodium catalyzed indole synthesis [1], the effect of various acids was also investigated on the cobalt catalyzed reaction between azobenzene and tolan. In the absence of an acid stirring of the solution was necessary for 24 h to obtain 80% conver-

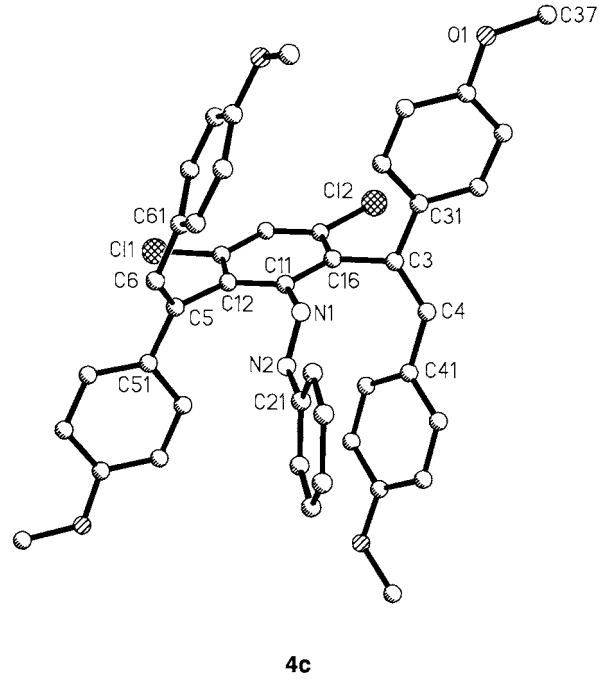
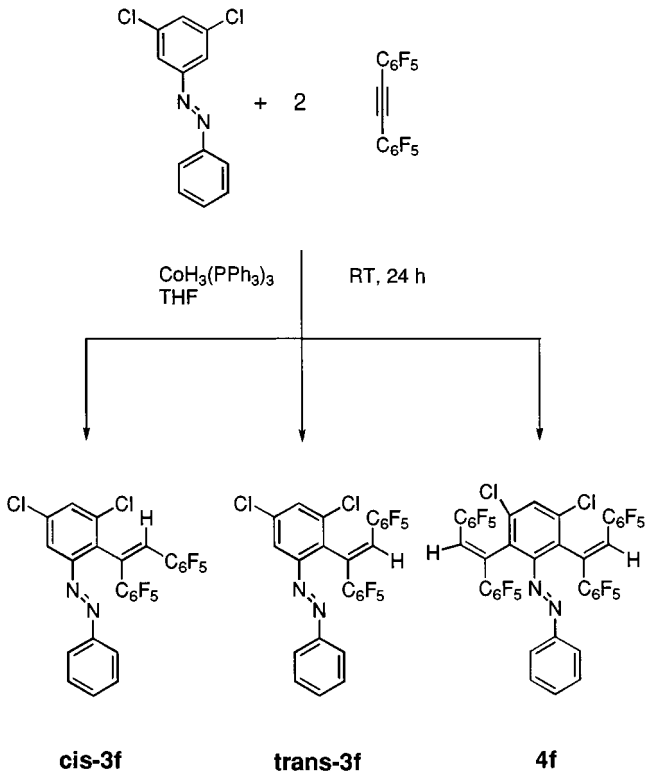


Fig. 3. Molecular structure of **4c**; hydrogen atoms are omitted for clarity.



Scheme 4. Products isolated from the reaction of 3,5-dichloroazobenzene with decafluorotolan.

sion. Contrary to that, the presence of acetic acid induced a complete conversion of the substrates to the 2:1 adduct **2a** as the unique product within 2 h. No intermediate 1:1 adduct **1a** or the corresponding *N*-anilinoindole could be detected by HPLC and MS analyses. Stronger organic acids like trifluoro acetic acid or *para*-toluene sulfonic acid did not improve the reaction. Best results were obtained when the molar ratio of azobenzene: tolan: catalyst: HOAc was 1.0:2.0:0.35:0.15. When the amount of HOAc was increased up to equimolar with azobenzene, the reaction was completely inhibited.

The positive effect of HOAc is further demonstrated by the reaction of 4-methyltolan with azobenzene which afforded the expected 2,3-dihydrocinnolines in form of the 1:1 and 2:1 adducts **1g** and **2g**, respectively. Upon addition of HOAc the yields of **1g** and **2g** increased from 11 and 10% to 12 and 38%, respectively.

3. 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 ratio 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: precolumn (30 mm × 8 mm) attached to main column (250 mm × 8 mm) and both filled with Spherisorb ODS2, 5 μm (RP C18), eluting with CH_3CN:H_2O ratio 5:1 (v/v) at a flow rate of 5.0 ml min^{-1}.

Sample preparation: 100 μl of the reaction solution was withdrawn, evaporated to dryness, and redissolved in 0.5 μl of CH_3CN; 20 μl of this solution was then injected.Preparative isolations: 1 ml of the acetonitrile solution was injected; identical elution agent and filling material were used while the size of precolumn 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 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.

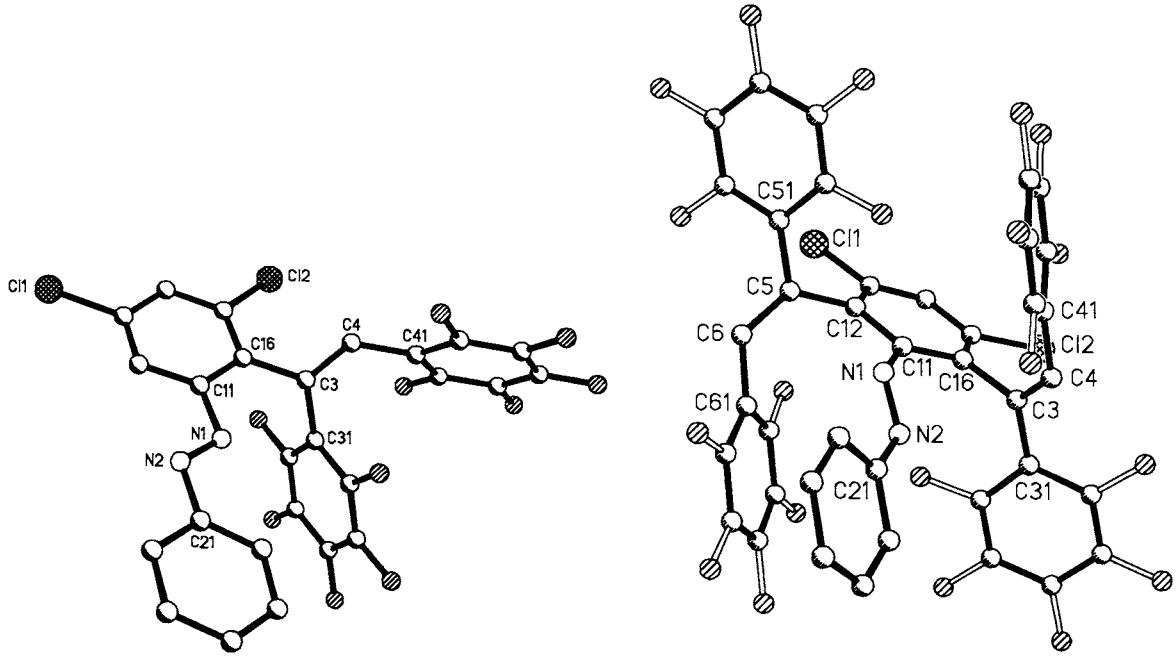
$CoH_3(PPh_3)_3$ was prepared according to literature [16]. Azobenzene (Merck) and tolan (Fluka) were commercially available. 3,3′,5,5′-Tetramethylazobenzene and 4,4′-dichloroazobenzene were synthesized from the corresponding aniline derivatives [17], 3,5-dichloroazobenzene and 3,5-difluoroazobenzene from the corresponding 3,5-dihalogenoanilines and nitrosobenzene [18]. Decafluorotolan was synthesized according to literature [19] from tetrabromoethylene which was obtained via dehydrohalogenation of pentabromoethylene [20].

*3.1. Synthesis of the 2,3-dihydrocinnolines **1** and **2**, the 2-trans-stilbenylazobenzenes **3** and the 2,6-di(trans-stilbenyl)azobenzenes **4***

3.1.1. General procedure

All reactions have been performed in diethyl ether or THF solution. Unless otherwise noted, the general procedure for the synthesis of the mixtures of **1** and **2** or **3** and **4** is described in the following.

The structures of the new 1:1 adducts **3b** and **3d** and the new indole **5b** 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 *trans*-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 7) [21].



cis-3f **4f**

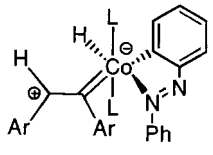
Fig. 4. Molecular structure of *cis*-**3f** and **4f**; hydrogen atoms are omitted for clarity.

*3.1.2. 2,3,4-Triphenyl-8-(trans-stilbenyl)-2,3-dihydrocinnoline (**2a**)*

Azobenzene (728 mg, 4.0 mmol) and tolan (1426 mg, 8.0 mmol) were dissolved 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 color of the solution changed within 5 min from orange over black–green and dark-brown to red. After stirring for another 24 h at r.t., 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 solution 20:1 (v/v). The first orange–red fraction yielded 425 mg (1.18 mmol, 30%) of an orange oil of **1a** and some by-products, the following red fraction afforded 130 mg of a red powder of **2a** [3] (0.24 mmol, 6%), turn-over number (TON): (mmol **1** + **2**)/mmol catalyst: 1.7. The orange–red oil was purified by prep. HPLC yielding 100 mg (0.28 mmol) of **1a** [3]. Single crystals of **2a** were obtained from CH_2Cl_2:MeOH ratio 1:2 (v/v) at r.t.

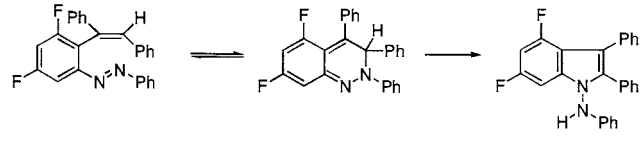
*3.1.3. 2-(trans-Stilbenyl)-3,5-difluoroazobenzene (**3b**) and 2,3,4-triphenyl-5,7-difluoro-8-(trans-stilbenyl)-2,3-dihydrocinnoline (**2b**)*

3,5-Difluoroazobenzene (872 mg, 4.0 mmol), tolan (1426 mg, 8.0 mmol) and $CoH_3(PPh_3)_3$ (745 mg, 0.88 mmol) in 3 ml of diethyl ether were used. The color of solution changed within 2 min from orange over black to dark red. Yields after column chromatography were: 985 mg of an orange oil of **3b** (2.48 mmol, 62%) and by-products, 223 mg (0.39 mmol, 10%) of a red powder of **2b** (TON 3.3). Yield after purification by prep. HPLC: 575 mg of an orange powder of **3b**. **3b**: MS: FD m/z 396 $[M]^+$. Calc. for $C_{26}H_{18}F_2N_2$ (396.4): C, 78.77; H, 4.58; N, 7.07%. Found: C, 79.19; H, 4.72; N, 6.78%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59–6.90 [m, 18H, 4-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): 99.4 (dd, ^2J(F,C) = 23 Hz, ^4J(F,C) = 4 Hz, C-6), 105.9 (t, ^2J(F,C) = 26 Hz, C-4), 123.2 (C-8 and C-12),



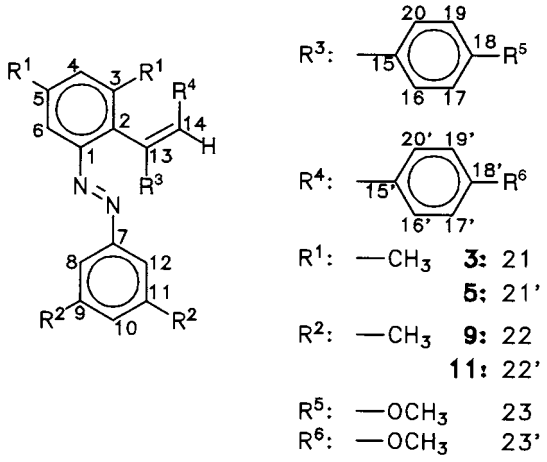
G

Scheme 5.



3b **1b** **5b**

Scheme 6.



Scheme 7.

124.3 (dd, ^2J(F,C) = 19 Hz, ^4J(F,C) = 4 Hz, C-2), 126.5 (C-16 and C-20), 127.2 (C-18′), 127.5 (C-18), 128.1 (C-17′ and C-19′), 128.4 (C-16′ and C-20′), 128.5 (C-17 and C-19), 128.9 (C-9 and C-11), 131.6 (C-12), 132.1 (C-15′), 132.6 (C-14), 137.2 (C-15), 142.6 (C-13), 152.4 (C-7), 152.5 (C-1), 160.6 (dd, ^1J(C,F) = 245 Hz, ^3J(C,F) = 12 Hz, C-5), 162.6 (dd, ^1J(C,F) = 246 Hz, ^3J(C,F) = 12 Hz, C-3). UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 302 (24300). HPLC (CH_3CN:H_2O ratio 5:1 (v/v), 5 ml min^{-1}) retention time [min] (integrated area): 7.3 (5.2×10^6) **3b**, 10.1 (8.5×10^4) [H(PhC=CPh)$_2$H]. Single crystals of **3b** were obtained from CH_2Cl_2:MeOH ratio 1:2 (v/v) at −20°C. **2b**: MS: FD *m*/*z* 574 $[M]^+$. For further characterization see ref. [2].

3.1.4. 2-(trans-4,4′-Dimethoxystilbenyl)-3,5-dichloroazobenzene (3c) and 2,6-di(trans-4,4′-dimethoxystilbenyl)-3,5-dichloroazobenze ne (4c)

A sample of 753 mg (3.0 mmol) of 3,5-dichloroazobenzene, 1430 mg (6.0 mmol) of 4,4′-dimethoxytolan and 735 mg (0.86 mmol) of $CoH_3(PPh_3)_3$ in 13 ml of THF were used. The color of the solution changed after addition of the catalyst only from orange to green–black and not to red since distilbenylazobenzenes **4** absorb at about 500 nm much weaker than the dihydrocinnolines **2**. Yields after column chromatography were: 553 mg of an orange oil of **3c** (1.13 mmol, 38%) and by-products, 382 mg (0.53 mmol, 17%) of an orange powder of **4c** (TON 1.9). Purification of **3c** by prep. HPLC was not performed, since decomposition of **3c** occurred. **4c**: MS: FD *m*/*z* 726 $[M]^+$. Calc. for $C_{44}H_{38}Cl_2N_2O_4$ (728.2): C, 72.63; H, 4.99; N, 3.85%. Found: C, 72.77; H, 5.22; N, 3.84%. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 510 (1000), 302 (59000). Single crystals of **4c** were obtained from CH_2Cl_2:MeOH ratio 1:2 (v/v) at r.t.

3.1.5. 2-(trans-4-Methoxystilbenyl)-3,3′,5,5′-tetramethylazobenzene (3d/3d′) and 2,6-di(trans-4-methoxystilbenyl)-3,3′,5,5′-tetramethylazobenzene (4d/4d′)

A sample of 715 mg (3.0 mmol) of 3,3′,5,5′-tetramethylazobenzene, 1250 mg (6.0 mmol) of 4-methoxytolan and 585 mg (0.69 mmol) of $CoH_3(PPh_3)_3$ in 7 ml of THF were used. The color of the solution changed after addition of the catalyst from orange to green–black. Yields after column chromatography were: 451 mg of an orange oil of **3d/3d′** (1.01 mmol, 34%) and by-products, 150 mg (0.24 mmol, 9%) of an orange powder of **4d**/**4d′** (TON 1.8). Yield after purification by prep. HPLC: first fraction: 160 mg of **3d/3d′**; second fraction: 215 mg of an orange oil of **3d/3d′**. **3d**: MS: FD *m*/*z* 446 $[M]^+$. ^{1}H-NMR (270 MHz, $CDCl_3$) δ (ppm): 7.40 (s, 1H, 10-H), 7.37–7.15 (m, 8H, 8-H, 12-H, 14-H, 16-H to 20-H), 7.12 (s, 1H, 6-H), 6.95 (s, 1H, 4-H), 6.91 (d, 2H, 17′-H and 19′-H), 6.62 (d, 2H, 16′-H and 20′-H), 3.65 (s, 3H, 23′-O–CH_3), 2.41 (s, 3H, 21′-CH_3), 2.27 (s, 6H, 22-CH_3, 22′-CH_3), 2.12 (s, 3H, 21-CH_3). ^{13}C-NMR (67.7 MHz, $CDCl_3$) δ (ppm): 20.1 (C-21), 21.8 (C-22 and C-22′), 22.0 (C-21′), 55.7 (C-23′), 114.2 (C-17′ and C-19′), 114.3 (C-6), 121.5 (C-8 and C-12), 127.1 (C-16 and C-20), 127.4 (C-18), 128.9 (C-17 and C-19), 129.8 (C-14), 130.5 (C-16′ and C-20′), 131.2 (C-15′), 132.8 (C-10), 134.4 (C-4), 137.0 (C-3), 137.8 (C-5), 138.4 (C-15), 138.6 (C-2), 139.0 (C-9 and C-11), 144.3 (C-13), 151.7 (C-1), 153.9 (C-7), 159.1 (C-18′). The corresponding ^{13}C signals of **3d′** are the same as for **3d** within 0.2 ppm. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 459 (700), 309 (18000). HPLC (CH_3CN:H_2O ratio 5:1 (v/v), 5ml min^{-1}) retention time [min] (integrated area): after column chromatography: 14.7 (2.2×10^6) **3d′**, 15.4 (4.5×10^6) **3d** (ratio **3d**:**3d′** was 2:1). After prep. HPLC: first fraction: 14.7 (2.2×10^6) **3d′**, 15.4 (1.4×10^6) **3d** (ratio **3d/3d′** = 2/3); second fraction: 14.7 (7.4×10^5) **3d′**, 15.4 (4.4×10^6) **3d** (ratio **3d/3d′** = 6/1). Single crystals of **3d** were obtained from CH_2Cl_2:MeOH ratio 1:2 (v/v) at −20°C. **4d/4d′**: MS: FD *m*/*z* 655 $[M]^+$. Calc. for $C_{46}H_{42}N_2O2$ (656.3): C, 84.11; H, 6.75; N, 4.26%. Found: C, 84.06; H, 6.64; N, 4.26%. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 461 (2300), 302 (59000).

3.1.6. 2-(4-Chlorophenyl)-3,4-bis(pentafluorophenyl)-8-(decafluorostilbenyl)-2,3-dihydrocinnoline (2e)

A total of 502 mg (2.0 mmol) of 4,4′-dichloroazobenzene, 1432 mg (4.0 mmol) of decafluorotolan and 580 mg (0.68 mmol) of $CoH_3(PPh_3)_3$ in 13 ml of THF were used. The color of the solution changed after addition of the catalyst within 5 min from orange over black to dark red. The formation of an 1:1 adduct could not be detected, neither by thin layer chromatography nor by

FD-MS. Yield after column chromatography (light petroleum ether:diethyl ether ratio 10:1 (v/v)) was: 1242 mg (1.28 mmol, 64%) of a dark red powder of **2e** (TON 1.9). **2e**: MS: FD m/z 966 $[M]^+$. Calc. for $C_{40}H_8Cl_2F_{20}N_2$ (966.0): C, 49.69; H, 0.83; N, 2.90%. Found: C, 50.28; H, 0.76; N, 2.38%. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 523 (8700), 240 (38000).

3.1.7. 2-(cis-Decafluorostilbenyl)-3,5-dichloroazobenzene (cis-3f), 2-(trans-decafluorostilbenyl)-3,5-dichloroazobenzene (trans-3f) and 2,6-di(trans-decafluorostilbenyl)-3,5-dichloroazobenzene (4f)

A total of 502 mg (2.0 mmol) of 3,5-dichloroazobenzene, 1432 mg (4.0 mmol) of decafluorotolan and 955 mg (1.13 mmol) of $CoH_3(PPh_3)_3$ in 12 ml of THF were used. The color of the solution changed after addition of the catalyst immediately from orange to black. Yield after column chromatography [light petroleum ether:THF ratio 20:1 (v/v) up to methylene chloride:diethyl ether ratio 1:1 (v/v)] was: 1267 mg of a mixture of three different products. HPLC (CH_3CN:H_2O ratio 5:1 (v/v), 5 ml min^{-1}) retention time [min] (integrated area): 22.6 (1.3×106) *cis*-**3f**, 26.2 (1.0×106) *trans*-**3f**, 41.4 (1.2×107) **4f**. After purification with prep. HPLC: first fraction: 50 mg (0.08 mmol, 4%); second fraction: 72 mg (0.12 mmol, 6%); third fraction: 778 mg (0.81 mmol, 40%) **4f**, all three fractions were obtained as orange powders (TON 0.9). HPLC (CH_3CN:H_2O ratio 5:1 (v/v), 5 ml min^{-1}) retention time [min] (integrated area): first fraction: 22.6 (1.0×10^6) *cis*-**3f**, 26.2 (3.9×10^4) *trans*-**3f** (ratio *cis*-**3f**/*trans*-**3f** = 25/1); second fraction: 22.6 (1.3×10^5) *cis*-**3f**, 26.2 (9.0×10^5) *trans*-**3f** (ratio *cis*-**3f**/*trans*-**3f** = 1/7); third fraction: 41.4 (7.2×106) **4f**. *cis*-**3f**: MS: FD m/z 608 $[M]^+$; UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 457 (900), 328 (26000); *trans*-**3f**: MS: FD m/z 608 $[M]^+$. UV/Vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 459 (600), 327 (28000). **4f**: MS: FD m/z 966 $[M]^+$. Calc. for $C_{40}H_8Cl_2F_{20}N_2$ (966.0): C, 49.69; H, 0.83; N, 2.90%. Found: C, 49.82; H, 0.61; N, 2.86%. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 476 (1000), 272 (48000). Single crystals of *cis*-**3f** and **4f** were obtained from CH_2Cl_2:MeOH ratio 1:2 (v/v) at -20°C and r.t., respectively.

3.1.8. 2,3/4-Diphenyl-4/3-p-tolyl-2,3-dihydrocinnoline (1g/1g′) and 2,3/4-diphenyl-4/3-p-tolyl-8-(trans-stilbenyl)-2,3-dihydrocinnoline (2g/2g′)

A total of 546 mg (3.0 mmol) of azobenzene, 1152 mg (6.0 mmol) of 4-methyltolan and 355 mg (0.42 mmol) of $CoH_3(PPh_3)_3$ in 4 ml of diethyl ether were used. Before adding the catalyst, 11.5 μl (0.20 mmol) of HOAc were added. The color of the solution changed after addition of the catalyst within 5 min from orange over black to dark red. Upon adding HOAc as co-catalyst, the conversion of reactants increased to about 90% and the reaction time decreased to about 2 h while the yield reached values normally obtained only in reaction with unsubstituted tolan. Yields after column chromatography were: 136 mg of a red oil of **1g**/**1g′** (0.36 mmol, 12%) and by-products, 647 mg (1.14 mmol, 38%) of a dark red powder of **2g**/**2g′** (TON 3.6). Purification of **1g**/**1g′** by prep. HPLC was not performed. **2g**/**2g′**: MS: FD m/z 566 $[M]^+$. Calc. for $C_{42}H_{34}N_2$ (566.8): C, 89.01; H, 6.05; N, 4.94%. Found: C, 88.25; H, 6.34; N, 4.22%. UV–vis (CH_2Cl_2) l_{max} [nm] (e [M^{-1} cm^{-1}]): 512 (10000), 288 (43000).

3.1.9. 2-(trans-4-Methylstilbenyl)-3,5-dichloroazobenzene (4h/4h′) and 2,6-di(trans-4-methylstilbenyl)-3,5-dichloroazobenzene (3h/3h′)

A total of 502 mg (2.0 mmol) of 3,5-dichloroazobenzene, 768 mg (4.0 mmol) of 4-methyltolan and 175 mg (0.21 mmol) of $CoH_3(PPh_3)_3$ in 20 ml of THF were used. The color of the solution changed after addition of the catalyst from orange to green–black. Yields after column chromatography were: 261 mg of an orange oil of **3h**/**3h′** (0.59 mmol, 30%) and by-products, 230 mg (0.36 mmol, 18%) of an orange powder of **4h**/**4h′** (TON 4.5). Purification of **3h**/**3h′** by prep. HPLC was not attempted. **4h**/**4h′**: MS: FD m/z 635 $[M]^+$. Calc. for $C_{42}H_{34}Cl_2N_2$ (634.2): C, 79.36; H, 5.07; N, 4.41%. Found: C, 79.23; H, 5.06; N, 4.05%. UV–vis (CH_2Cl_2) λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 501 (1000), 292 (51000).

3.2. Isomerization of 2-(trans-stilbenyl)-3,5-difluoroazobenzene (3b) to N-anilino-2,3-diphenyl-4,6-difluoroindole (5b) catalyzed by HOAc

A 23.6 mg (5.96 mmol) sample of the orange powder of **3b**, dissolved in 5 ml of 1-BuOH and 3.40 μl of HOAc ([**3b**] = [HOAc] = 1.19×10^{-2} mol l^{-1}), were heated to 115°C. The color 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 and a pale yellow residue (**5b**) was obtained after solvent removal. HPLC analysis: **5b** (4.3 min, initial value: area = 7.8×10^4, final value: area = 9.3×10^5), **3b** (7.3 min, initial value: area = 6.2×10^5, final value: area = 5.6×10^4). **5b**: MS: EI m/z (%): 396 (95) $[M]^+$, 319 (50), $[M-Ph]^+$, 358 (10) $[M-2F]^+$, 304 (100) $[M-NH-Ph]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) (for atom numbering see ref. [2]): 7.35–7.14 [m, 12H, 11-H, 13-H, Ph–H (10 H)], 6.89 (t, 1H, ^3J(H,H) = 7 Hz, 12-H), 6.85 (dd, 1H, ^3J(F,H) = 9 Hz, ^4J(H,H) = 2 Hz, 7-H), 6.66 (dt, 1H, ^3J(F,H) = 9 Hz, ^4J(H,H) = 2 Hz, 5-H), 6.53 (s, 1 H, 8-H), 6.48 (dd, 2 H, ^3J(H,H) = 8 Hz, ^4J(H,H) = 1 Hz,

Table 2
Crystal data and summary of data collection and structure refinement of **3b**, **3d**, **4c**, *cis*-**3f** and **4f**

Compound	**3b**	**3d**·CH_2Cl_2	**4c**	*cis*-**3f**	**4f**
Molecular formula	$C_{26}H_{18}F_2N_2$	$C_{32}H_{32}Cl_2N_2O$	$C_{44}H_{38}Cl_2N_2O_4$	$C_{26}H_8Cl_2F_{10}N_2$	$C_{40}H_8Cl_2F_{20}N_2$
Molecular weight	396.42	530.19	728.22	609.24	967.38
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (pm)	789.7(10)	907.0(2)	992.6(4)	1571.8(3)	1010.8(2)
b (pm)	1124.2(10)	2727.0(3)	1325.3(4)	1074.0(2)	1096.3(2)
c (pm)	1236.9(10)	1170.0(1)	1462.0(8)	1586.2(3)	1628.6(3)
α (°)	69.96(1)	90.0	92.48(4)	90.0	90.02(1)
β (°)	82.03(1)	103.9(1)	100.59(3)	118.50(1)	97.67(1)
γ (°)	79.26(1)	90.0	103.95(2)	90.0	97.19(1)
V (nm^3)	1.010(2)	2.808(7)	1.827(1)	2.353(1)	1.774(1)
Z	2	4	2	4	2
μ (mm−1)	0.090	0.259	0.225	0.376	0.326
$D_{calc.}$ (g cm^{-3})	1.303	1.257	1.323	1.720	1.811
Crystal size (mm)	0.70 × 0.30 × 0.15	0.60 × 0.40 × 0.40	0.60 × 0.40 × 0.40	0.80 × 0.60 × 0.40	0.40 × 0.40 × 0.15
Color	Orange	Orange	Orange	Orange	Orange
2θ range	4.3–54.0	4.6–52.0	4–50	4.7–54.1	4.3–54.0
Scan rate (deg min−1)	3–30	3–30	3–30	6–60	3–30
No. measured reflections	5301	6422	9837	6331	9048
Independent reflections	4332	5489	6420	5150	7714
Observed reflections [$F_o = 4\sigma(F)$]	1616	1899	4448	3297	3964
Extinction coefficient k	0.070(4)	0.008(1)	0.003(3)	0.0061(9)	0.0061(7)
No. parameters refined	344	455	614	394	610
R_1 [$F_o = 4\sigma(F)$]	0.0478	0.0655	0.084	0.0503	0.0605
wR_2 (all data)	0.1177	0.1767	0.237	0.1313	0.1416

10-H, 14-H). ^{13}C-NMR (100.4 MHz, $CDCl_3$) δ (ppm): 92.8 (dd, ^2J(F,C) = 26 Hz, ^4J(F,C) = 4 Hz, C-7), 97.0 (t, ^2J(F,C) = 24 Hz, C-5), 110.5 (dd, ^2J(F,C) = 19 Hz, ^4J(F,C) = 2 Hz, C-3a), 112.7 (C-10 and C-14), 113.1 (C-3), 121.4 (C-12), 126.5 (C-18′), 127.8 (C-16′ and C-20′), 128.2 (C-16 and C-20), 128.3 (C-18), 129.5 (C-11 and C-13), 129.6 (C-15), 130.78 (C-17′ and C-19′), 130.81 (C-17 and C-19), 133.9 (C-15′), 138.3 (C-2), 137.8 (t, ^2J(F,C) = 12 Hz, C-7a), 146.7 (C-9), 156.5 (dd, ^1J(F,C) = 252 Hz, ^3J(F,C) = 14 Hz, C-4), 159.7 (dd, ^1J(F,C) = 240 Hz, ^3J(F,C) = 12 Hz, C-6). ^{19}F-NMR (376.0 MHz, $CDCl_3$, $CFCl_3$ as reference) δ (ppm): −111.3 (C-4-F), −113.7 (C-6-F).

3.3. Influence of various acids

The standard amounts of the substrates were 182 mg (1.0 mmol) of azobenzene and 356 mg (2.0 mmol) of tolan dissolved in 3 ml of diethyl ether. Then 8.59 μl (0.15 mmol) of HOAc and 300 mg (0.35 mmol) of $CoH_3(PPh_3)_3$ were added ([HOAc] = 5.0×10^{-2} mol l^{-1}). The color of the solution changed within 2 min from orange over black to dark red. After stirring for 2 h, a thin layer chromatogram (TLC) [Al_2O_3, petroleum ether:THF ratio 20:1 (v/v)] indicated complete conversion of the substrates to **2a**. The solvent was removed and the residue chromatographed at Al_2O_3 [petroleum ether:THF ratio 10:1 (v/v)] yielding a dark red oil. MS: FD m/z: 537 $[M]^+$.

When 5.72 μl (0.10 mmol) of HOAc and 540 mg (0.64 mmol) of $CoH_3(PPh_3)_3$ were added ([HOAc] = 3.3×10^{-2} mol l^{-1}), a TLC showed after 2 h a yellow (azobenzene), an orange (**1a**) and a red fraction (**2a**); the reaction was qualitatively faster as compared to adding 11.45 μl (0.20 mmol) of HOAc and 360 mg (0.42 mmol) of $CoH_3(PPh_3)_3$ ([HOAc] = 6.7×10^{-2} mol l^{-1}), a simultaneously performed experiment.

When 57.2 μl (1.0 mmol) of HOAc and 260 mg (0.31 mmol) of $CoH_3(PPh_3)_3$ were added ([HOAc] = 0.33 mol l^{-1}), the catalyst was deactivated and no conversion of the substrates could be observed.

Upon adding 11.48 μl (0.15 mmol) of trifluoro acetic acid and 300 mg (0.35 mmol) of $CoH_3(PPh_3)_3$ ([CF_3COOH] = 5.0×10^{-2} mol l^{-1}), a mixture of azobenzene, **1a** and **2a** was observed as indicated by TLC after 2 h. Additionally, a green residue of deactivated catalyst precipitated.

A reaction with 28.5 mg (0.15 mmol) of *p*-toluene sulfonic acid as additive and 525 mg (0.62 mmol) of $CoH_3(PPh_3)_3$ ([*p*-$CH_3C_6H_4SO_3H$] = 5.0×10^{-2} mol l^{-1}) afforded a mixture of azobenzene, **1a** and **2a** as indicated by TLC after 2 h, no precipitation of a green powder of deactivated catalyst was observed.

3.4. Photochromic behavior

Irradiating a diluted solution of the 2,3-dihydrocinnoine **2a** ($[\mathbf{2a}] < 10^{-3}$ mol l^{-1}) with a laboratory halogen lamp (12 V/20 W) for 1 min ($\lambda > 375$ nm) leads to a color change from red to yellow and to a decreasing absorbance at about 500 nm due to the ring opening to the corresponding 2,6-distilbenylazobenzene **4a**. Upon standing in the dark for 10 min, the absorbance recovered to its original value. The corresponding ring closure reaction of **3a** produced by irradiation of **1a** needed a reaction time of 80 min.

3.5. Crystal structure determinations

Suitable single crystals of **3b**, **3d**.CH_2Cl_2, **4c**, *cis*-**3f** and **4f** were sealed under N_2 in glass capillaries. Intensity data were collected at 200 K on a Siemens P4 diffractometer using Mo–K_α radiation ($\lambda = 71.073$ pm, graphite monochromator). Data were corrected for Lorentz and polarization effects while an absorption correction has not been applied. All structures were solved by direct methods [22] and refined using full-matrix least-squares procedures on F^2 values (SHELXL-93 [23]). All non-H atoms were refined with anisotropic displacement parameters. The positions of all H atoms could be localized in a difference fourier synthesis. With the exception of the hydrogen atoms of the CH_2Cl_2 solvate molecule in **3d**·CH_2Cl_2 where both the positional and a thermal parameter were kept fixed during the refinement, all other H atoms were refined isotropically. For all compounds an empirical extinction correction has been applied using the function (see Table 2). Selected crystallographic data and further details of the data collection and refinement of **3b**, **3d**·CH_2Cl_2, **4c**, *cis*-**3f** and **4f** are summarized in Table 2 [24].

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References

[1] (a) P. Reisser, Y. Wakatsuki, H. Kisch, Monatsh. Chemie 126 (1995) 1. (b) U.R. Aulwurm, J.U. Melchinger, H. Kisch, Organometallics 14 (1995) 3385.
[2] (a) G. Halbritter, F. Knoch, A. Wolski, H. Kisch, Angew. Chem. Int. Ed. Engl. 106 (1994) 1676; Angew. Chem. Int. Ed. Engl. 33 (1994) 1603. (b) G. Halbritter, F. Knoch, H. Kisch, J. Organomet. Chem. 492 (1995) 87.
[3] U. Dürr, F.W. Heinemann, H. Kisch, J. Organomet. Chem. 541 (1997) 307.
[4] U. Dürr, F. Knoch, H. Kisch, Z. Kristallogr. 212 (1997) 173. Atom numbering has been changed for the sake of comparison with the mono- and distilbenylazobenzenes.
[5] H. Kisch, F. Knoch, D. Fenske, G. Halbritter, Z. Kristallogr. 210 (1995) 222.
[6] C.J. Brown, Acta Crystallogr. 21 (1966) 146.
[7] C.J. Finder, M.G. Newton, N.L. Allinger, Acta Crystallogr. B 30 (1974) 411.
[8] A. Streitwieser, C.H. Heathcock, in: Organische Chemie, 2nd reprint of 1st ed., Verlag Chemie, Weinheim, 1990, p. 118.
[9] G. Halbritter, Personal Communication.
[10] H. Boon, M. Rausch, J. Chem. Soc. Chem. Comm. (1977) 397.
[11] H. Werner, J. Wolf, U. Schubert, K. Ackermann, J. Organomet. Chem. 317 (1986) 327.
[12] H. Clark, C. Wong, J. Am. Chem. Soc. 99 (1977) 7073.
[13] D. Hart, J. Schwartz, J. Organomet. Chem. 87 (1975) 11.
[14] (a) J.M. Huggins, R.G. Bergman, J. Am. Chem. Soc. 103 (1981) 3002. (b) J.M. Huggins, R.G. Bergman, J. Am. Chem. Soc. 101 (1979) 4410.
[15] U.R. Aulwurm, Ph.D. Thesis, University Erlangen-Nürnberg, Erlangen, Germany, 1996.
[16] A. Sacco, M. Rossi, Inorg. Synth. XII (1970) 12.
[17] K.H. Schündehütte, in: E. Muller (Ed.), Houben-Weyl: Methoden der Organischen Chemie, vol. 10/3, Thieme Verlag, Stuttgart, 1965, p. 373.
[18] K.H. Schündehütte, in: E. Muller (Ed.), Houben-Weyl: Methoden der Organischen Chemie, vol. 10/3, Thieme Verlag, Stuttgart, 1965, p. 332.
[19] R.G. Gastinger, E.F. Tokas, M.D. Rausch, J. Org. Chem. 43 (1978) 159.
[20] W. Taylor, A.M. Ward, J. Chem. Soc. 34 (1934) 2006.
[21] M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der organischen Chemie, 3rd revised ed, Thieme Verlag, Stuttgart, 1987, p. 152.
[22] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467.
[23] G.M. Sheldrick, SHELXL-93. Program for crystal structure refinement, University of Göttingen, Germany, 1993.
[24] Further details of the single crystal X-ray analyses can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen by citing the depository numbers CSD-402565 (**2a**), CSD-407241 (**3b**), CSD-407242 (**3d**·CH_2Cl_2), CSD-407243 (*cis*-**3f**), CSD-407244 (**4c**) and CSD 407245 (**4f**), the names of the authors and the references.