Transition Metal Complexes of Diazenes, XLIII[◇]

# Rhodium-Catalyzed Synthesis of Naphthalene Derivatives Through Cyclodimerization of Arylalkynes[☆]

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Received May 14, 1998

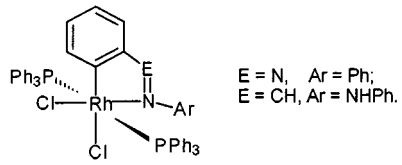
**Keywords:** Rhodium catalysis / C–C coupling / C–H activation / Alkynes / Trisubstituted naphthalenes

$RhCl(PPh_3)_3$ in the presence of excess hydrochloric acid and azobenzene in refluxing 1-pentanol catalyzes the cyclodimerization of arylalkynes to 1,2,3-substituted naphthalene derivatives. This enables an easy access to 1,2,3-triphenylnaphthalene (**1**), 7-methoxy-1,2,3-tris(*p*-methoxyphenyl)naphthalene (**2**), 7-methyl-1,2,3-tris(*p*-methylphenyl)naphthalene (**3**), and 7-nitro-3-(*p*-nitrophenyl)-1,2-diphenylnaphthalene (**4**). A co-cyclodimerization of tolan with 4-octyne affords 3-phenyl-1,2-dipropylnaphthalene (**5**). The structure of **4** was resolved by single-crystal X-ray structural analysis. The rate of formation of **1** is first-order with respect to tolan and $RhCl(PPh_3)_3$ and exhibits activation parameters of $\Delta H^{\ddagger}$ = 94.7 ± 10 kJ mol$^{-1}$ and $\Delta S^{\ddagger}$ = 36 ± 6 J K$^{-1}$ mol$^{-1}$. Replacing HCl by HBr and HI decreases the rate by 28 and 55%, respectively. Although naphthalene formation occurs also in the absence of azobenzene, its presence stabilizes the catalyst, accelerates the reaction, and inhibits formation of 1-chlorostilbene, which is the major by-product. When $RhCl(PCy_3)_2$ is used as the catalyst, naphthalene formation even in the absence of azobenzene is highly selective, but proceeds much slower. No reaction is observed in non-protic solvents.

## Introduction

Transition-metal-assisted or -catalyzed oligomerizations of alkynes afford a variety of linear-chain or annulated compounds by direct C−C coupling. In general, annulation does not involve a C−H activation step.[2−5] Except photochemical reactions, direct syntheses of naphthalene derivatives through cyclodimerization of aryl alkynes were scarcely reported. For example metallic lithium suspensions assist formation of 1,2,3-triphenylnaphthalene from tolan.[6] Phenylacetylene was stoichiometrically dimerized to 1-phenylnaphthalene by "active" palladium ($PdCl_2$ and $NaBH_4$) while tolan and other diarylalkynes were inert.[7] Cyclodimerization of the latter alkynes occurred as a side-reaction in the $RhCl_3 \cdot 3\ H_2O$ and Aliquat-336® catalyzed cyclotrimerization; an oxidative C−H addition involving an intermediate $Rh^V$ complex was proposed to rationalize the naphthalene formation.[8] Wilkinson et al. reported a similar synthesis of 1,2-diphenylbenzylideneindene.[9] During our investigations on the rhodium-catalyzed indole synthesis from tolan and azobenzene[10] we observed that in refluxing 1-pentanol solution 1,2,3-triphenylnaphthalene is produced through cyclodimerization of tolan when $RhCl_2(C,N\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2$ and 2-chloroazobenzene or $RhCl_2(C,N\text{-}C_6H_4CH{=}NNHC_6H_5)(PPh_3)_2$ were present, but the reaction was slow and of poor chemoselectivity (Figure 1).[11][12]

Figure 1. $RhCl_2(C,N\text{-}C_6H_4E{=}NC_6H_5)(PPh_3)_2$




Different to the indole synthesis, where catalytic amounts of acetic acid improved both rate and selectivity, no beneficial effect was observed for naphthalene formation. However, this was the case when mineral acids were employed. In the following we describe a novel catalytic system which allows the easy synthesis of 1,2,3-triphenylnaphthalene (**1**), 7-methoxy-1,2,3-tris(*p*-methoxyphenyl)naphthalene (**2**), 7-methyl-1,2,3-tris(*p*-methylphenyl)naphthalene (**3**), 7-nitro-3-(*p*-nitrophenyl)-1,2-diphenylnaphthalene (**4**), and 3-phenyl-1,2-dipropylnaphthalene (**5**).

## Results and Discussion

### Cyclodimerization of Tolan by Various Catalysts

During investigations of the synthesis of **1** in the presence of *ortho*-metalated azobenzene and hydrazone com-

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[◇] Part XLII: Ref.[1].

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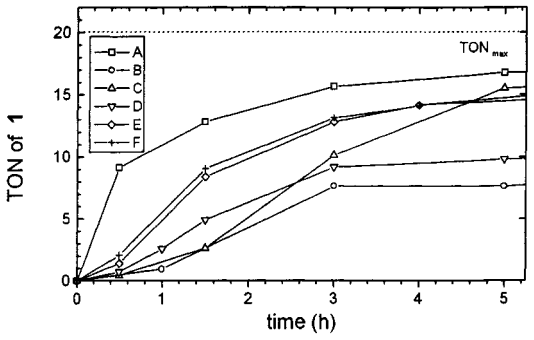
Figure 2. Time dependence of the turnover number of **1** in the presence of various catalytic systems; 0.05 mmol of rhodium complex and 2.0 mmol of tolan in the presence of 0.15 mL of HCl (aq. 37%)in 25 mL of refluxing 1-pentanol solution: $RhCl(PPh_3)_3$ and PhN=NPh (0.25 mmol) (A); $RhCl(PPh_3)_3$ (B); $RhCl_2(C,N\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2$ (C); $RhCl_2(C,N\text{-}C_6H_4CH{=}NNHC_6H_5)(PPh_3)_2$ (D); $RhHCl(C,N\text{-}CH_3C_6H_3N{=}NC_6H_4CH_3)(PCy_3)_2$ (E); $RhCl(PCy_3)_2$ (F)




plexes,[13] we found that $RhCl(PPh_3)_3$ and $RhCl(PCy_3)_2$ are also catalytically active but require the presence of HCl. In Figure 2 the catalytic activity of various systems is summarized.

Highest TON (turn over number) values were obtained with $RhCl(PPh_3)_3$ and azobenzene (catalyst **I**, Figure 2, curve A), followed by $RhCl_2(C,N\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2$ (curve C), $RhHCl(C,N\text{-}CH_3C_6H_3N{=}NC_6H_5)(PCy_3)_2$ (curve E) and $RhCl(PCy_3)_2$ (curve F). The hydrazone complex $RhCl_2(C,N\text{-}C_6H_4CH{=}NNHC_6H_5)(PPh_3)_2$ (curve D), and Wilkinson's complex (curve B) were less active.

When azobenzene in the catalytic system **I** was replaced by hydrazobenzene, benzylidenephenylimine, aniline, triethylamine, and various other monodentate nitrogen ligands, formation of **1** still occurred, however at a much lower rate. This clearly indicates that an anticipated *ortho*-metalation of azobenzene is not involved in its positive action. Addition of bidentate nitrogen ligands like phenanthroline and 2,2′-bipyridyl instead of azobenzene inhibited the reaction completely. When $RhCl(PPh_3)_3$ was employed without azobenzene the initial rate did not change significantly but the catalyst was easily deactivated and the reaction stopped after 3 h (Figure 2, curve B); furthermore, the addition product of HCl to tolan, 1-chlorostilbene, was produced in an amount of 20% relative to **1**. This value increased to 30% when HCl and $RhH(PPh_3)_4$ were preheated for 20 min. From these results it can be concluded that azobenzene efficiently prevents addition of HCl to the alkyne mediated by rhodium complexes. In the absence of HCl, the reaction of tolan with $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, or $RhH(CO)(PPh_3)_3$ alone in refluxing pentanol did not afford **1**.

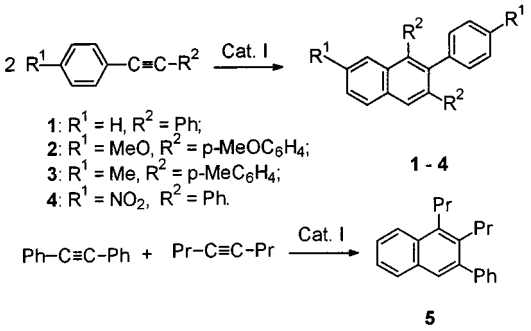
When Wilkinson's catalyst was replaced by $RhCl(PCy_3)_2$, even in the absence of azobenzene a highly selective production of **1** occurred without the concomitant formation of any by-products. However, the reaction proceeded with only moderate rate, comparable to that of the two orthometalated complexes (Figure 2, curve F).

**Cyclodimerization of Arylalkynes**

It was found that only diarylalkynes can be cyclodimerized to naphthalene derivatives (Scheme 1). Introduction of electron-donating substituents accelerated the reaction while electron-withdrawing ones had the opposite effect. According to HPLC analysis, unsymmetrically substituted diarylalkynes like *p*-nitrophenylacetylene afforded four regioisomers with a slight preference of the product formed by *ortho*-metalation of the *p*-nitrophenyl group. Isolated yields of **1**−**3** and **4**−**5** were in the range of 60−85% and 37%, respectively. Mixed alkyl/aryl-substituted alkynes were difficult to cyclodimerize, especially when electron-withdrawing substituents were present. Accordingly, $PhC_2CO_2Et$ and $PhC_2COMe$ could not be converted to the corresponding naphthalene. Contrary to that, the latter alkyne can be cyclodimerized by $RhCl_3$ and Aliquat-336® in a mixed tetrachloroethane/water solvent.[8]

In an attempt to accomplish a co-cyclodimerization, tolan and 4-octyne were employed as the substrates. Although **5** was produced in moderate yield, it could not be obtained analytically pure (Scheme 1).

Scheme 1




The structures of the naphthalene derivatives were confirmed by multidimensional H-H COSY, NOEs, NOESY, C-H HETCOR, COLOC NMR techniques.[14] A single-crystal X-ray analysis of **4** confirmed the proposed structure (Figure 3, Table 1). The C−C bonds of the naphthalene ring agree with the values reported for perchloro-1,2,3-triphenylnaphthalene.[15] The three phenyl rings at C1, C2, and C3 are twisted out of the naphthalene plane by 76.3°, 69.0°, and 126.4°, respectively, and both nitro groups are aligned with the corresponding ring planes.

Figure 3. ORTEP drawing (drawn at 50% probability level) of **4**

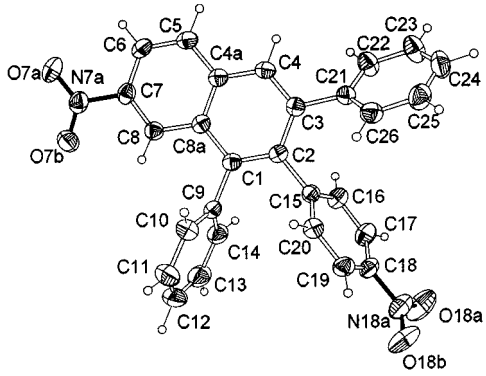


Table 1. Selected bond lengths [Å] and bond angles [°] for **4**

| | | | |
|---|---|---|---|
| C(7)−C(8) | 1.366(2) | C(6)−C(7)−C(8) | 123.3(1) |
| C(6)−C(7) | 1.396(2) | C(8)−C(7)−N(7a) | 117.7(1) |
| C(5)−C(6) | 1.358(2) | C(6)−C(7)−N(7a) | 119.0(1) |
| C(5)−C(4a) | 1.425(2) | C(5)−C(6)−C(7) | 118.7(1) |
| C(4)−C(4a) | 1.410(2) | C(6)−C(5)−C(4a) | 120.9(1) |
| C(4a)−C(8a) | 1.421(2) | C(4)−C(4a)−C(8a) | 118.9(1) |
| C(3)−C(4) | 1.374(2) | C(4)−C(3)−C(21) | 117.8(1) |
| C(2)−C(3) | 1.432(2) | C(2)−C(3)−C(21) | 122.5(1) |
| C(3)-C(21) | 1.496(2) | C(1)−C(2)−C(15) | 119.0(1) |
| C(1)−C(2) | 1.388(2) | C(3)−C(2)−C(15) | 120.7(1) |
| C(2)−C(15) | 1.500(2) | C(2)−C(1)−C(9) | 121.9(1) |
| C(1)−C(8a) | 1.433(2) | C(8a)−C(1)−C(9) | 118.4(1) |
| C(1)−C(9) | 1.498(2) | C(8)−C(8a)−C(4a) | 118.6(1) |
| C(8a)−C(8) | 1.414(2) | C(4a)−C(8a)−C(1) | 119.6(1) |

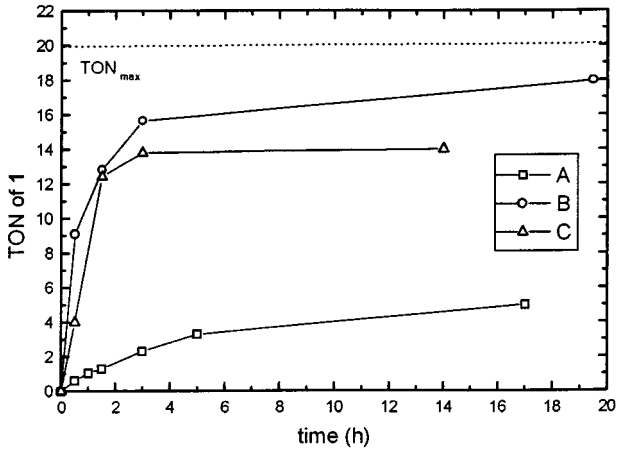
### Mechanistic Investigations

The reaction is strongly solvent-dependent and does not occur in non-protic solvents like THF, acetonitrile, triethylamine, toluene, chlorobenzene, DMF, tetrachloroethane, nitrobenzene, aniline, and DMSO. In methanol, even upon refluxing for 3 days, no naphthalene could be detected, whereas this was possible when the boiling point of the alcohol was above 100°C. All of the following experiments were performed with catalyst **I** in refluxing 1-pentanol solution.

### Influence of the Acid

Changing the molar ratio [HCl]/[Rh] from 34:1 to 1:1 decreased the initial turnover rate (TOR) of **1** from 18 to 0.7 $h^{-1}$ indicating that stoichiometric amounts of HCl cannot sustain a high catalytic activity (Figure 4). Varying the same ratio to 68:1, reduced the TOR down to 8 $h^{-1}$. When $HCl_{conc}$ was substituted by $HBr_{conc}$ and $HI_{conc}$, the TOR decreased from 18 to 13 and 6, respectively.

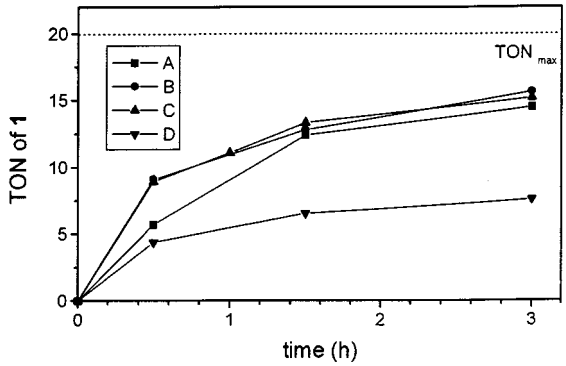
Figure 4. Influence of HX on catalytic activity of catalyst **I**: [HCl]/[Rh] = 1:1 (A), 34:1(B), 68:1 (C)




### Influence of Azobenzene

Upon variation of the ratio [Rh]/[$PhN_2Ph$] at a fixed [Rh]/[$PhC_2Ph$] value from 1:1 to 1:5, 1:10, and 1:40, it turned out that the highest TORs were observed at the values of 1:5 and 1:10 (Figure 5).

Figure 5. Influence of azobenzene concentrations on catalytic activity catalyst **I**: [Rh]/[azobenzene] = 1:1 (A), 1:5 (B), 1:10 (C), 1:40 (D)




### Kinetic Measurements

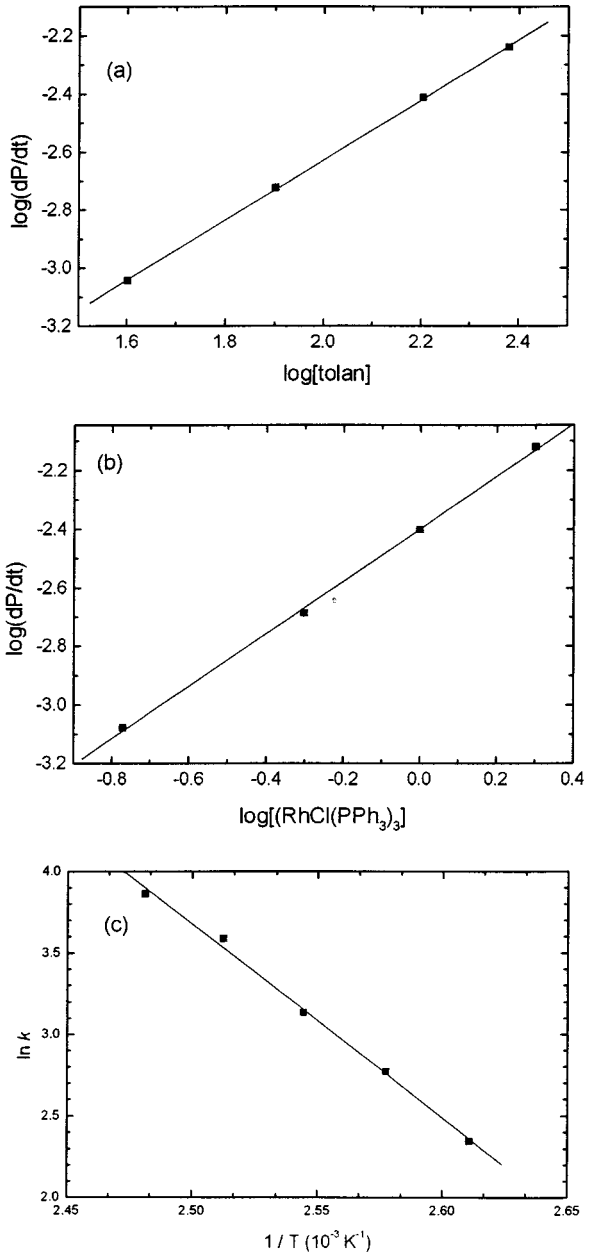
The initial reaction rate as function of different substrate concentrations was measured by monitoring the formation of **1** by HPLC (d*P*/d*t*, Figures 6a, 6b). From the slopes of 1.03 and 0.9 as obtained from a plot of logarithm of initial rate vs. logarithm for tolan and $RhCl(PPh_3)_3$, respectively, a reaction order of unity is assumed for both components. When the catalyst concentration was increased above 0.5 mol/L, the reaction became slower while a higher concentration of tolan favored cyclotrimerization to hexaphenylbenzene. These results suggest that the transition state of the rate-determining step contains one molecule of tolan coordinated to a mononuclear rhodium complex. Activation parameters of $\Delta H^{+} = 94.7 \pm 10$ kJ $mol^{-1}$ and $\Delta S^{+} = 36 \pm 6$ J $K^{-1}$ $mol^{-1}$ were calculated from the temperature dependence of the rate constant in the range of 105−130°C (Figure 6c).

### Postulated Catalytic Cycle

From the results presented above a plausible mechanism for the cyclodimerization in the presence of catalyst **I** is schematically depicted in Scheme 2.

It is recalled that in the absence of HX tolan and azobenzene undergo a $RhCl(PPh_3)_3$-catalyzed co-cyclodimerization affording *N*-anilino-2,3-diphenylindole.[10] This reaction is inhibited by the presence of the mineral acid in favor of the alkyne cyclodimerization to 1,2,3-triphenylnaphthalene. According to the reaction conditions it is assumed that the first step is loss of a $PPh_3$ ligand followed by oxidative addition of HX to **A** affording the rhodium(III) intermediate **B** (Scheme 2). Since it is known from the literature that HX reacts with $RhCl(PR_3)_3$ (R = Ph, Cy) already at room temperature,[16][17] it seems unlikely that the slower naphthalene formation in the presence of HBr and HI is due to slowing down of this reaction step. Subsequent insertion of the alkyne into the Rh−H bond should be a fast process

Figure 6. Plot of log(d*P*/d*t*) vs. logarithm of the concentration of tolan (a) and $RhCl(PPh_3)_3$ (b); Arrhenius plot (c)




as known for the corresponding reaction of acetylene with $RhHCl_2(PPh_3)_2$.[17][18] Successive *cis*/*trans* isomerization of the vinyl ligand leads to **C**. Although this is a rhodium(III) complex, it is postulated to undergo *ortho*-metalation as reported for comparable cases.[18][19] In view of the presence of weak intramolecular CH···$XRh^{III}$ interactions in related hexacoordinated rhodium(III) complexes,[1] a multicenter transition state as depicted in Figure 7 is proposed. This would rationalize the slower rate found in the presence of HBr and HI since the interaction is weaker when the electronegativity of X decreases.[20] In agreement with the observed rate law, this step should be rate-determining. As a competitive reaction, reductive $C(sp^2)-Cl$ elimination from **C** leads to 1-chlorostilbene, the major by-product in the absence of azobenzene, but only formed in traces in its presence. As a weak base, azobenzene may facilitate elimination of HX and therefore favor *ortho*-metalation of tolan over reductive elimination of 1-chlorostilbene. As indicated in Scheme 2, azobenzene or a derivative thereof may be coordinated to the rhodium center throughout the whole catalytic cycle. Insertion of the second alkyne into an Rh−C bond of **D** and reductive $C(sp^2)-C(sp^2)$ elimination leads to **1** and the starting complex **A**.

Scheme 2. Postulated catalytic cycle for catalyst **I** ($RhCl(PPh_3)_3$, PhN=NPh, and HCl in 1-pentanol)

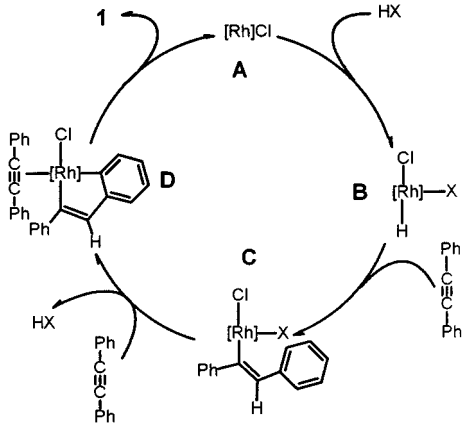
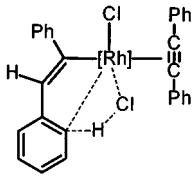



Figure 7. Transition state postulated for the *ortho*-metalation step; see also Scheme 2

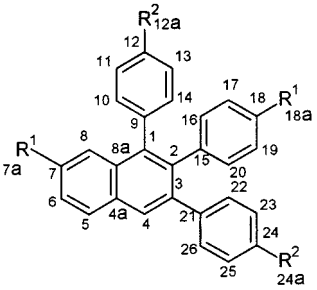


This work was supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *Degussa AG*. We thank Dr. *M. Moll* for the NMR measurements. L. H. is indebted to the *Hanns-Seidel-Stiftung* and the *Chinese Government* for a fellowship.

## Experimental Section

*General:* Unless otherwise mentioned, all operations were performed under dry and oxygen-free nitrogen using standard Schlenk techniques. All solvents were degassed and saturated with nitrogen before use. Rhodium trichloride hydrate was obtained from Degussa AG. Commercial triphenylphosphane, and *trans*-azobenzene (Aldrich, Merck) were used after recrystallization from ethanol. Commercial tolan, 4-octyne, 1-phenyl-1-propyne, ethyl 3-phenylpropiolate, 4-phenyl-3-butyn-2-one, dimethyl acetylenedicarboxylate, 3-pentyn-1-ol were directly used without any purification. $RhCl(PPh_3)_3$,[21] $RhCl(PCy_3)_2$,[22] $RhCl_2(C,N\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2$[23], $RhCl_2(C,N\text{-}C_6H_4CH{=}NNHPh)(PPh_3)_2$,[11] $RhHCl(C,N\text{-}CH_3C_6H_3N{=}NC_6H_4CH_3)(PCy_3)_2$,[24] $Rh(CO)Cl(PPh_3)_2$,[25] $RhH(PPh_3)_4$[26] and $RhH(CO)(PPh_3)_3$[27] were prepared according to literature procedures.

Scheme 3. Atom numbering of compounds **1**−**4** used for NMR signal assignment




$^1$H- and $^{13}$C-NMR spectra were measured in $CDCl_3$ as solvent and TMS as internal standard at 400 (or 270) and 100 (or 67) MHz, respectively, and IR spectra in KBr unless otherwise noted. − 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 (70eV). − Elemental analysis: Carlo Erba 1106 (CHN). − 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 $CH_3CN/H_2O$ = 5:1 (v/v) at a flow rate of 5.0 mL/min. − Preparative isolations: 1 mL of the acetonitrile solution was injected; identical elution agent and filling material was used while the size of precolumn and main column was 30 mm × 32 mm and 250 mm × 32 mm, respectively; the flow rate was 35 mL/min.

*General Procedure for the Synthesis of Trisubstituted Naphthalenes:* A solution of 46.2 mg (0.05 mmol) of $RhCl(PPh_3)_3$ in 5 ml of 1-pentanol and 0.15 ml (1.71 mmol) of HCl (conc., 37%) were stirred upon refluxing in an oil bath at 160°C for 1 min. Thereafter, 48 mg (0.25 mmol) of azobenzene, dissolved in 5 ml of 1-pentanol, was added to the reaction mixture and stirred under reflux for 20 min. Subsequently, 356 mg (2.0 mmol) of tolan or 2.0 mmol of a derivative thereof, dissolved in 20 ml of 1-pentanol were added dropwise within 15 to 20 min. Stirring the reaction mixture under reflux was continued for another 3 h. After removal of the solvent, the resulting orange residue was chromatographed on silica gel ($SiO_2$-60, $d$ = 1.5 cm, $l$ = 10 cm) with toluene as eluting agent. A colorless fraction was collected, the solvent removed and the gray residue recrystallized from $CH_2Cl_2$/MeOH = 1:5 (v/v). 216 mg (1.2 mmol, 60%) of **1** (mp. 151°C) was obtained. − $C_{28}H_{20}$ (356.5): calcd. C 93.94, H 5.60; found C 94.13, H 5.60. − MS (FD, $CH_2Cl_2$); *m/z*: 356 [$M^+$]. − $^1$H NMR ($CDCl_3$, 270 MHz): d = 7.93 (s, 1 H, 4-H), 7.90 (d, 1 H, 5-H), 7.57 (d, 1 H, 8-H), 7.47 (t, 1 H, 6-H), 7.35 (t, 1 H, 7-H), 7.10−7.25 (m, 10 H) and 6.82−6.95 (m, 5 H) for the 15 protons of the three substituent phenyl rings. − $^{13}$C NMR ($CDCl_3$, 100 MHz): d = 124.4 (C-12), 125.6 (C-18), 125.6 (C-24), 126.0 (C-6), 126.1 (C-7), 126.8 (C-17), 126.8 (C-19), 126.8 (C-8), 127.5 (C-11), 127.5 (C-13), 127.5 (C-23), 127.5 (C-25), 127.9 (C-5), 128.7 (C-4), 130.0 (C-10), 130.0 (C-14), 131.2 (C-22), 131.2 (C-26), 131.5 (C-16), 131.5 (C-20), 132.0 (C-8a), 132.6 (C-4a), 138.1 (C-3), 139.1 (C-2), 139.4 (C-9), 139.9 (C-1), 140.0 (C-21), 142.0 (C-15).

*Various Catalytic Systems:* General procedure described above; catalysts and TON of **1** were given as follows: (1) $RhCl(PPh_3)_3$ and azobenzene: 9 (0.5 h), 13 (1.5 h), 16 (3 h), 17 (5 h), 18 (19.5 h); (2) $RhCl(PPh_3)_3$: 1 (1 h), 8 (3 h), 9 (5 h), 12 (17 h); (3) $RhCl_2$(*C,N*-$C_6H_4N{=}NC_6H_5$)$(PPh_3)_2$: 0.4 (0.5 h), 3 (1.5 h), 10 (3 h), 16 (5 h), 16 (7 h); (4). $RhCl_2$(*C,N*-$C_6H_4CH{=}NNHC_6H_5$)$(PPh_3)_2$: 0.7 (0.5 h), 3 (1 h), 5 (1.5 h), 9 (3 h), 9 (5 h), 12 (20 h); (5) RhHCl(*C,N*-$CH_3C_6H_3N{=}NC_6H_4CH_3$)$(PCy_3)_2$: 1.4 (0.5 h), 8 (1.5 h), 13 (3 h), 14 (4 h), [thereafter solid tolan was added, the TON of **1** reached 325 ($TON_{max}$ = 500) upon refluxing for 4 d]; (6) $RhCl(PCy_3)_2$: 2 (0.5 h), 9 (1.5 h), 14 (3 h), 14 (4 h). [thereafter, addition of solid tolan afforded a TON of 174 ($TON_{max}$ = 250) upon refluxing for 4 d]. Unless otherwise noted, the general procedure as described for **1** was applied for the following syntheses. The resulting residue obtained from column chromatography was further purified by preparative HPLC.

*Synthesis of 2−5*

*7-Methoxy-1,2,3-tris(4-methoxyphenyl)naphthalene* (**2**): 476 mg (2.0 mmol) of 4,4′-dimethoxytolan and 46.2 mg (0.05 mmol) of $RhCl(PPh_3)_3$ were refluxed for 5 h. The raw product was recrystallized from hexane, yielding 367 mg (1.54 mmol, 84%) of **2** (mp 177°C). − $C_{32}H_{28}O_4$ (476.6): calcd. C 80.65, H 5.92; found C 80.39, H 6.09. − MS (FD, $CH_2Cl_2$); *m/z*: 476 [$M^+$]. − $^1$H NMR: ($CDCl_3$, 400 MHz): d = 7.79 (s, 1 H, 4-H), 7.75 (d, 1 H, 5-H), 7.14 (dd, 1 H, 6-H), 7.05 (dt, 2 H, 22/26-H), 7.03 (dt, 2 H, 10/14-H), 6.88 (s, 1 H, 8-H), 6.77 (dt, 2 H, 11/13-H), 6.74 (dt, 2 H, 16/20-H), 6.70 (dt, 2 H, 23/25-H), 6.49 (dt, 2 H, 17/19-H), 3.77 (s, 3 H, 24a-OMe), 3.73 (s, 3 H, 12a-OMe), 3.67 (s, 3 H, 7a-OMe), 3.65 (s, 3 H, 18a-OMe). − $^{13}$C NMR ($CDCl_3$, 100 MHz): d = 54.9 (C-18a), 55.0 (C-7a), 55.1 (C-24a), 55.9 (C-12a), 105.5 (C-8), 112.5 (C-17), 112.5 (C-19), 113.0 (C-23), 113.0 (C-25), 113.2 (C-11), 113.2 (C-13), 118.4 (C-6), 128.3 (C-4), 128.7 (C-4a), 129.4 (C-5), 131.1 (C-22), 131.1 (C-26), 132.2 (C-9), 132.2 (C-10), 132.2 (C-14), 132.5 (C-16), 132.5 (C-20), 133.0 (C-15), 133.5 (C-8a), 134.9 (C-21), 137.6 (C-1), 137.9 (C-3), 138.6 (C-2), 157.3 (C-18), 157.7 (C-7), 157.9 (C-12), 157.9 (C-24). − HPLC ($CH_3CN/H_2O$ = 5:1 (v/v), 5 mL/min): retention time [min] = 6.4.

*7-Methyl-1,2,3-tris(4-methylphenyl)naphthalene* (**3**): 412 mg (2.0 mmol) of 4,4′-dimethyltolan and 46.2 mg (0.05 mmol) of $RhCl(PPh_3)_3$ were refluxed for 2 h; 264 mg (1.28 mmol, 64%) of **3** (mp. 148°C). − $C_{32}H_{28}$ (412.6): calcd. C 93.16, H 6.84; found C 92.84 H 6.92. − MS (FD, $CH_2Cl_2$); *m/z*: 412 [$M^+$]. − $^1$H NMR: ($CDCl_3$, 400 MHz): d = 7.83 (s, 1 H, 4-H), 7.78 (d, 1 H, 5-H), 7.31 (ds, 1 H, 8-H), 7.29 (t, 1 H, 6-H), 7.04 (dt, 2 H, 10/14-H), 7.02 (dt, 2 H, 22/26-H), 7.01(dt, 2 H, 23/25-H), 6.95 (dt, 2 H, 11/13-H), 6.73 (dt, 2 H, 16/20-H), 6.73 (dt, 2 H, 17/19-H), 2.37 (s, 3 H, 7a-Me), 2.31 (s, 3 H, 24a-Me), 2.23 (s, 3 H, 12a-Me), 2.14 (s, 3 H, 18a-Mea). − $^{13}$C NMR: ($CDCl_3$, 100 MHz): d = 21.1 (C-18a), (C-24a), 21.3 (C-12a), 22.7 (C-7a), 125.8 (C-8), 127.6 (C-16), 127.6 (C-20), 127.7 (C-4), 128.1 (C-6), 128.2 (C-11), 128.2 (C-13), 128.2 (C-22), 128.2 (C-26), 128.4 (C-5), 129.9 (C-10), 129.9 (C-14), 131.0 (C-8a), 131.1 (C-23), 131.3 (C-17), 131.3 (C-19), 132.3 (C-4a), 131.1 (C-25), 134.7 (C-7), 135.5 (C-12), 135.5 (C-18), 135.5 (C-24), 136.6 (C-21), 137.3 (C-15), 138.2 (C-9), 138.5 (C-3), 139.1 (C-1), 139.5 (C-2). − HPLC [$CH_3CN/H_2O$ = 5/1 (v/v), 5 mL/min]: retention time [min] = 17.65.

*7-Nitro-2-(4-nitrophenyl)-1,3-diphenylnaphthalene* (**4**) *and Regioisomers:* 447 mg (2.0 mmol) of 4-nitrotolan and 46.2 mg (0.05 mmol) of $RhCl(PPh_3)_3$ were refluxed for 15 h. Three different regioisomers were detected by analytical HPLC with retention times of 5.07, 5.47, 5.71 min, the ratio of the integration areas was 5:1:1. After removal of the solvent, the gray residue was washed with 5 mL of methanol. Since one regioisomer was rather insoluble in acetonitrile, 161 mg (0.72 mmol, 36%) of **4** could be isolated as an analytically pure yellow powder. − $C_{28}H_{18}N_2O_4$ (447.1): calcd. C 75.33, H 4.06, N 6.27; found C 75.33 H 4.02, N 6.17. − MS (FD, $CH_2Cl_2$); *m/z* 446 [$M^+$]. − $^1$H NMR: ($CDCl_3$, 270 MHz): d = 8.56

[ds, 1 H, $^4J$(8-H, 6-H) = 2.2 Hz, 8-H], 8.31 [dd, 1 H, $^3J$(5-H, 6-H) = 10 Hz, $^4J$(8-H, 6-H) = 2.2 Hz, 6-H], 8.07 [d, 1 H, $^3J$(5-H, 6-H) = 10 Hz 5-H], 8.06 (s, 1 H, 4-H), 7.84 [dt, 2 H, $^3J$(17-H, 16-H) = 9 Hz, 17/19-H], 7.32 (m, 3 H, 11/12/13-H), 7.23 (m, 3 H, 23/24/25-H), 7.14 (m, 4 H, 10/14/22/26-H), 7.04 (dt, 2 H, 16/20-H). − $^{13}$C NMR ($CDCl_3$, 100 MHz): d = 120.2 (C-8), 112.9 (C-11), 122.4 (C-17), 122.4 (C-19), 123.9 (C-6), 127.5 (C-24), 128.2 (C-25), 128.0 (C-12), 128.2 (C-23), 128.8 (C-17), 128.4 (C-13), 128.4 (C-11), 128.9 (C-4), 137.3 (C-2), 129.7 (C-5), 129.7 (C-14), 129.7 (C-10), 130.1 (C-8a), 130.8 (C-22), 130.8 (C-26), 132.1 (C-16), 132.1 (C-20), 135.5 (C-7), 136.9 (C-4a), 138.0 (C-18), 140.1 (C-9), 141.7 (C-21), 143.1 (C-2), 146.1 (C-3), 146.1 (C-15), 146.5 (C-1). − HPLC [$CH_3CN$/$H_2O$ = 5:1 (v/v), 5 mL/min]: retention time (integrated area) [min] of raw material = 5.07 (5.48 × $10^5$) (**4**); 5.47 (9.27 × $10^4$) (**4′**); 5.71 (1.37 × $10^5$) (**4′′**) (ratio of **4**/**4′**/**4′′** = 5:1:1). − **4′** and **4′′** exhibited identical molecular peaks at *m/z* 446 (FD-MS). Due to the similar HPLC retention times of all three regioisomers, further purification by preparative HPLC was not attempted. − Single crystals for X-ray analysis of **4** were obtained from a $CH_3CN$ solution exposed to air. Intensity data were collected with a Siemens P4 diffractometer at 200 K, using graphite-monochromated Mo-$K_\alpha$ radiation (λ = 0.71073 Å). Cell constants were obtained from the setting angles of 18 reflections in the range of 32.2° < 2θ < 35.0°. The ω-scan technique was applied using variable scan speeds (3.0−30°/min). The structure was solved by direct methods (SHELXS-86).[28] Structure refinement was carried out using full-matrix least-squares methods on $F^2$ (SHELXL-93).[29] All non-hydrogen atoms with anisotropic displacement parameters. All hydrogen atoms could be localized in a difference fourier map and were isotropically refined. The relevant crystal data are listed in Table 2. Further details of crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101516. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk)

Table 2. Crystal data and details of structure refinement parameters for **4**

| | |
|---|---|
| formula | $C_{28}H_{18}N_2O_4$ |
| molecular weight | 446.44 |
| crystal size [mm] | 0.70 × 0.70 × 60 |
| crystal system | monoclinic |
| space group | $P2_1/c$ |
| *a* [Å], α [°] | 8.712(2), 90 |
| *b* [Å], β [°] | 15.747(6), 91.02(2) |
| *c* [Å], γ [°] | 16.113(4), 90 |
| *V* [Å$^3$], *Z* | 2210(1), 4 |
| μ(Mo-$K_\alpha$) [mm$^{-1}$] | 0.091 |
| $D_{calcd.}$ [g/cm$^3$] | 1.342 |
| Temperature [K] | 200 |
| *F*(000) | 928 |
| no. of reflections collected | 8682 |
| no. of unique reflections | 4836 ($R_{int}$ = 0.0557) |
| no. of observed reflections | 2794 |
| obs. criterion | $F_o > 4\sigma(F_o)$ |
| no. of refinement parameter | 379 |
| $R_1$ (observed data) | 0.0359 |
| $wR_2$ (all data) | 0.0831 |
| $\Delta\rho_{max/min}$ [e Å$^{-3}$] | 0.213/−0.189 |
| *S* (all data) | 0.774 |

*Attempted Reactions with Various Alkynes:* Upon applying the general synthesis procedure for **1** to 1-phenylpropyne, 4-phenyl-3-butyn-2-one, and ethyl 3-phenylpropiolate no dimerization products were detected by analytical HPLC after 3 d of refluxing in 1-pentanol.

*3-Phenyl-1,2-dipropylnaphthalene* (**5**): A mixture of 356 mg (2 mmol) of tolan and 220 mg (2 mmol) of 4-octyne in 20 mL of 1-BuOH was added dropwise to a solution of 46.2 mg (0.05 mmol) of $RhCl(PPh_3)_3$ in 5 mL of 1-BuOH. After refluxing for 5 h, **5** and **1** were formed in a molar ratio of **5**/**1** = 5:1. After 14 h of refluxing, both alkynes were completely consumed and the ratio of **5**/**1** changed to 5:3. After removal of the solvent, the residue was chromatographed on $SiO_2$-60 with toluene as eluting agent. The resulting gray residue was further purified by prep. HPLC affording 226 mg (0.78 mmol, 39%) of a white oil of **5**. − $C_{22}H_{24}$ (288.4): calcd. C 91.61, H 8.39; found C 89.54, H 9.04.[30] − MS (FD, $CH_2Cl_2$); *m/z*: 288 [M$^+$]. − $^1$H NMR ($CDCl_3$, 270 MHz): d = 8.03 (d, 1 H, 8-H), 7.75 (d, 1 H, 5-H), 7.52 (s, 1 H, 4-H), 7.40−7.42 (m, 2 H, 6/7-H), 7.33−7.42 {m, 5 H, [7.34 (t, 1 H, 25/27-H), 7.38 (t, 17/19-H), 7.37 (d, 2 H, 16/20-H)]}, 3.09 (td, 2 H, 9/9′-H of C-1-C$H_2$CH$_2$CH$_3$), 2.69(td, 2 H, 12/12′-H of C-2-C$H_2$CH$_2$CH$_3$), 1.75 (td, 2 H, 10/10′-H of C-1-CH$_2$C$H_2$CH$_3$), 1.41(td, 2 H, 13/13′-H of C-2-CH$_2$C$H_2$CH$_3$), 1.14 (td, 3 H, 11/11′-H of C-1-CH$_2$CH$_2$C$H_3$), 0.78 (td, 3 H, 14/14′-H of C2-CH$_2$CH$_2$C$H_3$). − $^{13}$C NMR ($CDCl_3$, 100 MHz): d = 14.9 (C-11), 24.6 (C-10), 31.1 (C-9), 32.5 (C-12), 24.6 (C-13), 124.0 (C-8), 124.9 (C-6), 125.7 (C-7), 127.4 (C-4), 14.6 (C-14), 127.8 (C-16), 128.5 (C-5), 129.4 (C-17), 126.7 (C-18), 129.4 (C-19), 127.8 (C-20), 131.9 (C-8a), 132.5 (C-4a), 136.2 (C-1), 136.4 (C-2), 141.3 (C-3), 143.0 (C-15). − HPLC [$CH_3CN/H_2O$ = 5:1 (v/v), 5 mL/min]: retention time (integrated area) [min] of raw material (4 h refluxing) = 8.5 (1.3 × $10^5$) (**1**); 13.4 (6.9 × $10^5$) (**5**); (ratio of **5**/**1** = 5:1); (14 h refluxing) = 8.5 (4.4 × $10^5$) (**1**); 13.4 (9 × $10^5$) (**5**); (ratio of **5**/**1** = 2:1).

*Kinetic Measurements*

*General:* For the measurement of the initial rate as a function of substrate concentration the general procedure as described for the synthesis of **1** was applied except that the oil bath was thermostated to 130.0 ± 0.1°C. Samples of 200 μL were withdrawn after 30, 60, 90, and 120 min, concentrated to dryness without further separation of the catalyst and redissolved in 4 mL of acetonitrile. The concentrations of **1** (given in the following as dimensionless numbers in the unit of $10^{-3}$ mol L$^{-1}$) were determined via a calibration curve. Reproducibility was within ±10%. Detailed data are available as Supporting Information.

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☆ Dedicated to Professor *Arnd Vogler* on the occasion of his 60th birthday.


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