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Selective Hydrogenation of Alkynes Catalyzed by Trinuclear Rhodium Hydride Complexes of the Type $[\{(Rh[PP^*]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$

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Styrene and its derivatives are widely applied in the chemical industry for polymerisation,[1] organic synthesis, metathesis,[2] hydroformylation[3] and hydroamination.[4] Although styrene itself is produced on an industrial scale by oxidation–dehydration or catalytic dehydrogenation of ethylbenzene,[5] alternative syntheses for substituted styrenes are also of general interest. In this respect, especially for more functionalised substrates, the selective hydrogenation of alkynes (semihydrogenation) to the corresponding styrenes is an interesting option.[6] Typically, such selective hydrogenations are performed by using the heterogeneous Lindlar catalyst.[7] Since the introduction of the rhodium-based Wilkinson catalyst, homogeneous systems have also been explored for the selective hydrogenation of alkynes.[8] Here, different catalysts for the semihydrogenation of terminal[9] and more challenging internal[10] alkynes have been developed that give good to excellent selectivity. Nevertheless, the reduction of 1,2-diarylalkynes in particular proves difficult. For example, these substrates form easily binuclear vinyl–rhodium–hydride complexes, however the hydride does not insert into the Rh–C bond and, therefore, no hydrogenation is accomplished.[11] Nevertheless, Williams, Muetterties et al. report that binuclear rhodium(I)–hydride complexes can catalyze the *trans* selective hydrogenation under high pressures of up to 102 bar (1 bar = 100 kPa).[12] In 2010, the group of Plietker also applied mononuclear ruthenium hydride complexes to reduce diarene alkynes in very good yields.[13] For example, diphenylacetylene is reduced at 1 bar hydrogen pressure and ambient temperature by using 2.5 mol% catalyst loading for 12 h to give *cis*-stilbene in an excellent yield of 97%.

Moreover, beside the direct hydrogenation of alkynes, transfer hydrogenations also offer an attractive alternative, especially on laboratory scale as no pressure equipment is necessary.[14]

In the last two years, some of us reported the synthesis and characterisation of novel trinuclear rhodium(III)-hydride complexes containing seven hydrides with the diphosphine ligands TangPhos ((1S,1′S,2R,2′R)-1,1′-di-tert-butyl-(2,2′)-diphospholane), *t*Bu-BisP* (1,2-bis-(*R*,*R*)-[*tert*-butyl(methyl)phosphino]ethane) and Me-BPE (1,2-bis(2*R*,5*R*)-2,5-dimethylphospholan-1-yl)-ethane).[15] Owing to their interesting structural properties, we examined the catalytic potential of these novel rhodium complexes in hydrogenations. Based on this work, we present here for the first time the use of specific trinuclear rhodium complexes as efficient and highly selective catalysts for the selective hydrogenation of internal alkynes.

Initial experiments revealed the general reactivity of the trinuclear rhodium hydride complexes of the type $[\{(Rh[PP^*]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$ for the hydrogenation of diphenylacetylene at atmospheric hydrogen pressure and 30 °C in methanol. Notably, the substrate is hydrogenated without any induction period.[16] As shown in Figure 1, the hydrogen consumption is dependent largely on the respective phosphine ligand in the trinuclear rhodium complex. Complexes with the diphosphine ligands TangPhos and *t*Bu-BisP* exhibit significantly higher activity compared to the cluster with Me-BPE. With the first two complexes at a substrate to catalyst molar ratio of 100, full conversion is achieved after only 30 min reaction time. A high selectivity towards the *E* isomer is also achieved (see Table 1). Notably, only stilbene is obtained and no further hydrogenation to the alkane is observed.

For the following reactions, complex $[\{(Rh[TangPhos]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$ was used owing to its better selectivity und reproducibility (Figure S2). Firstly, different solvents were tested in the hydrogenation of the model substrate diphenylacetylene, demonstrating coordinating solvents to be superior to the non-coordinating one (see Table S1). Typically, at lower substrate concentration the hydrogen consumption of the reaction showed a first order reaction kinetic (see Figure 1, ——). The determined pseudo rate constant was 194 min^{-1}. On in-

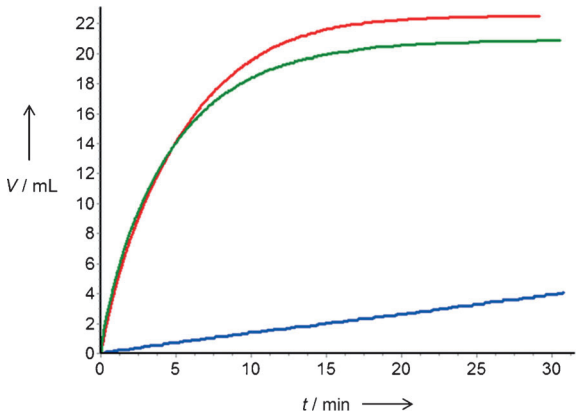

Figure 1. Hydrogen consumption in the semihydrogenation of diphenylacetylene in MeOH (substrate/catalyst molar ratio 100) at 1.01 bar total pressure and 30.0 °C with catalyst $[\{(Rh[TangPhos]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$ (0.009 mmol, ——), $[\{(Rh[t\text{Bu-BisP*}]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$ (0.0084 mmol, ——) and $[\{(Rh[\text{Me-BPE}]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$ (0.009 mmol, ——).

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Table 1. Conversion and selectivity for the semihydrogenation of diphenylacetylene with a substrate to catalyst [{(Rh[PP*]H)$_3$(μ_2-H)$_3$(μ_3-H)}(BF$_4$)$_2$] molar ratio of 100 in MeOH at 30.0 °C under 1.01 bar total pressure.

PP*	Conversion [%]	Selectivity (*Z*/*E*/alkane)
TangPhos	100	96:4:0
*t*Bu-BisP*	100	90:10:0
Me-BPE	17	–

creasing the concentration of the substrate, a Michaelis–Menten-type kinetic behaviour was observed. The hydrogenation curve can no longer be described completely as a first order reaction and the initial reaction rate increases with substrate concentration (Table 2, Figure 2).[17]

Further mechanistic investigations (e.g., by NMR spectroscopy) in the relevant range of the saturation kinetics could not be measured, even at a substrate/catalyst molar ratio of 10000. Another increase in the concentration of the substrate was limited by its solubility and, therefore, the determination of the saturation kinetics was not possible.

NMR spectroscopic investigations revealed that the trinuclear complex [{(Rh[TangPhos]H)$_3$(μ_2-H)$_3$(μ_3-H)}(BF$_4$)$_2$] was still present in solution after the hydrogenation. It has been reported that hydridic trinuclear complexes can be formed reversibly from their corresponding solvate complexes.[15a,c] To examine if

Table 2. Hydrogenation of diphenylacetylene at different substrate to catalyst molar ratios and 100% conversion.

Substrate to catalyst ratio	Selectivity (*Z*/*E*/alkane) [%]
100	96:4:0
1000	98:2:0
2500	98:2:0
5000	98:2:0
10000	n.d.[a]

[a] Owing to solubility.

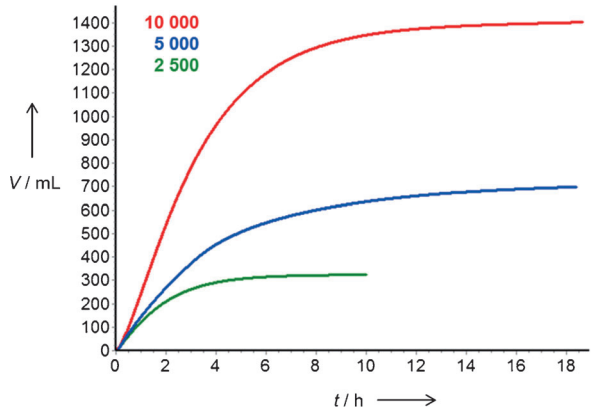
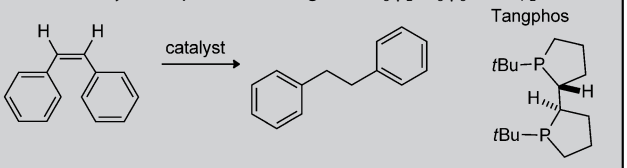


Figure 2. Hydrogen consumption in the semihydrogenation of diphenylacetylene in MeOH at 1.01 bar total pressure and 30.0 °C with 0.0054 mmol [{(Rh[TangPhos]H)$_3$(μ_2-H)$_3$(μ_3-H)}(BF$_4$)$_2$] at different substrate/catalyst molar ratios: 2500 (—), 5000 (—) and 10000 (—).

the initial complex or the solvent complex represents the active catalyst, we tested the monomeric solvate complex under the same reaction conditions (2 h, 30.0 °C and 1.01 bar total pressure). The selectivity of the solvate complex [{Rh(TangPhos)(MeOH)$_2$}BF$_4$] was lower, especially at higher levels of conversion and, in contrast to the trinuclear hydride complex, reduction to the alkane was also observed (24% alkane after 2 h, Table S2). Additionally, we tested the hydrogenation of *cis*-stilbene for both complexes at 2 bar hydrogen, 40 °C and 3 h reaction time. Again, major differences were revealed for the trinuclear and the monomeric catalyst. Only for the mononuclear complex, reduction to the alkane was detected (Table 3). Therefore, we conclude that the trinuclear hydride complex also represents an active species in the reduction of the alkyne. Certainly, the coordination of the substrate to the trinuclear hydride complex remains unclear.

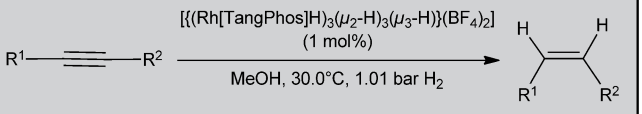
Table 3. Hydrogenation of *cis*-stilbene at 40 °C, under 2 bar H_2 for 3 h with the monomeric solvate complex [{Rh(TangPhos)(MeOH)$_2$}BF$_4$] and the trinuclear hydride species [{Rh(TangPhos)H}$_3$(μ_2-H)$_3$(μ_3-H)(BF$_4$)$_2$].



Entry	Catalyst	Solvent	Conv. [%]
1	[{Rh(TangPhos)(MeOH)$_2$}BF$_4$]	MeOH	85
2	[{Rh(TangPhos)(THF)$_2$}BF$_4$]	THF	68
3	[{Rh(TangPhos)H}$_3$(μ_2-H)$_3$(μ_3-H)(BF$_4$)$_2$]	MeOH	0
4	[{Rh(TangPhos)H}$_3$(μ_2-H)$_3$(μ_3-H)(BF$_4$)$_2$]	THF	0

Next, we tested the reactivity of different substituted 1,2-diarylacetylenes (Table 4). In general, all substrates were highly selectively reduced, although the reactivity decreased. For example, a chloride substituent in the *para*-position of the aryl group lowered the reactivity and a time of 7 h was required to obtain full conversion (Table 4, entry 2). On the other hand, an acetyl group in the aromatic ring did not significantly influence the reactivity of the system (Table 4, entry 3). The corresponding hydrogen consumption curves are shown in Figure S4. In

Table 4. Hydrogenation of different internal alkynes catalyzed by the TangPhos-trinuclear hydride complex at 1.01 bar total pressure in MeOH at 30.0 °C.



Entry	R^1	R^2	*t*	Selectivity (*Z*/*E*/alkane)[a]	Isolated yield [%]
1	Ph	Ph	30 min	96:4:0	96
2	Ph	*p*-Cl-Ph	7 h	96:4:0	89
3	Ph	*p*-COMe-Ph	35 min	92:8:0	90
4	$COOCH_3$	$COOCH_3$	110 min	95:2:3	92
5[b]	Ph	CH_3	4 h	98:0:2	–

[a] Determined by GC analysis. [b] Conditions: T = 50 °C, THF solvent, P = 2 bar H_2.

addition, the electron-poor bis(dimethoxycarbonyl)acetylene and phenylpropyne also allowed for high selectivity towards the corresponding *cis*-alkene. However, in contrast to the diaryl derivatives, hydrogenation to the corresponding alkane was observed (Table 4, entries 4–5).

Interestingly, the hydrogenation of the more complex substrate 1,4-diphenylbutadiyne led to reduction and subsequent dimerisation. For unambiguous structural determination, an X-ray characterisation could be performed. The molecular structure is shown in Figure 3.

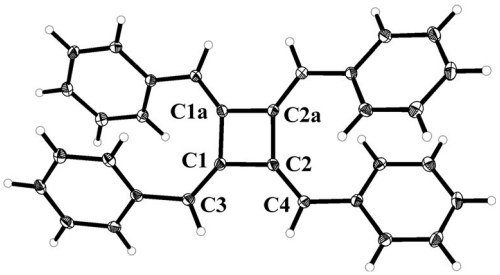


Figure 3. Molecular structure of 1,2,3,4-tetrabenzylidenecyclobutane (ORTEP, 30% probability ellipsoids). Selected distances [Å]: C1–C1A 1.499(2), C1–C2 1.501(2), C1–C3 1.347(2), C2–C4 1.340(2) and angles [°]: C1A–C1–C2 89,67(2), C2A–C2–C1 89,78(5).

Conjugated double bonds often show similar behaviour compared to triple bonds; therefore, we also tested the hydrogenation of *trans*,*trans*-1,4-diphenyl-1,3-butadiene in the presence of $[\{(Rh[TangPhos]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$. After 6 h full conversion was obtained, with 1,4-diphenyl-2-butene as the main product and an *E*-1/*E*-2-ene/alkane molar ratio of 92:4:4.

In summary, trinuclear rhodium hydride complexes $[\{(Rh[PP^*]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$ in combination with the diphosphine ligands TangPhos and *t*Bu-BisP* are well-suited catalysts for the selective hydrogenation of alkynes and dienes. In case of 1,2-diarylacetylenes, the corresponding *cis*-alkenes are obtained in high yield under mild reaction conditions (1 bar H_2, 30 °C). For the reduction of diphenylacetylene with the complex $[\{(Rh[TangPhos]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$, TONs of up to 10000 were achieved. In contrast to the mononuclear rhodium solvent complex $[\{Rh(PP^*)(MeOH)_2\}BF_4]$, no formation of alkanes is observed. The product formation rate can be described as Michaelis–Menten-kinetic.

Experimental Section

General

All hydrogenations were carried out under oxygen- and moisture-free conditions using standard Schlenk techniques (argon). The hydrogenation devise is described in Ref. [18].

THF was distilled from sodium benzophenone ketyl immediately prior to use. MeOH was freshly distilled over magnesia turnings prior to use, CD_3OD over $LiAlH_4$ and CD_2Cl_2 over CaH_2. Subsequent removal of traces of oxygen for both deuterated solvents was performed in six freeze–thaw cycles. Diphenylacetylene, 1-chloro-(4-phenylethynyl)benzene and 4′-(phenylethynyl)acetophenone were ordered from Sigma Aldrich and recrystallised in MeOH under argon.

The catalyst $[\{(Rh[PP^*]H)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)\}(BF_4)_2]$ (0.01 mmol) was sealed as a *solid* in a glass ampoule under an argon atmosphere. The preparation of the catalyst is described in detail in Ref. [15c]. The ampoule was placed in a double walled reactor, followed by 1 mmol of the alkyne (normally 100 fold excess), which was then dissolved in 15 mL MeOH. The solution was stirred carefully so as not to break the ampoule. After three freeze–thaw cycles under hydrogen and once the reactor had been thermostatted to 30 °C, the ampoule was broken by means of stirring. The hydrogen consumption was recorded under isobaric conditions with an apparatus which has been designed for precise volumetric measurements.

NMR spectroscopy: $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{13}C distortionless enhancement by polarization transfer and ^1H NMR spectra were obtained on a Bruker ARX-300 or ARX- 400 spectrometer at 297–298 K and were referenced internally to the deuterated solvent (^{13}C, CD_2Cl_2: $\delta_{reference} = 54$ ppm, CD_3OD: $\delta_{reference} = 49.2$ ppm) or to protic impurities in the deuterated solvent (^1H, $CDHCl_2$: $\delta_{reference} = 5.31$ ppm, CD_3OD: $\delta_{reference} = 3.32$ ppm). For chemical shifts in $^{31}P\{^1H\}$ NMR spectra, 85% H_3PO_4 was used as an external standard.

IR spectroscopy: Nicolet 6700 FT-IR spectrometer from Bruker Optik GmbH with a Smart Endurance attenuated total reflection spectrometer (Platinum ATR, diamond/ZnSe) was used.

MS: Mass spectrometric measurements were performed on a time-of-flight LC/MS 6210 spectrometer (Agilent Technologies).

X-ray structure determination: Diffraction data were collected at low temperature on a Bruker Kappa APEX II Duo diffractometer by using MoK_α radiation. The structure was solved by using direct methods (SHELXS-97)[19] and refined by full matrix least square techniques against F^2 (SHELXL-97). An XP system (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed into theoretical positions and were refined by using the riding model.

Crystal data for 1,2,3,4-tetrabenzylidenecyclobutane: $C_{26}H_{41}BF_4NO_3P_2Rh{\cdot}C_4H_{10}O$; crystal size $0.39\times0.34\times0.32$ mm; orthorhombic space group *Fdd2*, $a = 25.8940(6)$, $b = 11.8397(3)$, $c = 14.2610(3)$ Å, $V = 4372.10(18)$ Å^3, $T = 150(2)$ K, $Z = 8$, ρcalcd $= 1.241$ g cm^{-3}, $\mu(MoK_\alpha) = 0.070$ mm^{-1}; 11879 total reflections ($\Theta_{max} = 27.10$); 2374 reflections ($R = 0.0297$) measured; 2418 unique reflections with $I > 2\sigma(I)$; 145 refined parameters; final $wR(F^2) = 0.0802$ ($I > 2\sigma(I)$); final $R_1 = 0.0305$ and final $wR(F^2) = 0.0814$ (all data); fit on F^2: 1.023.
CCDC 933005 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Characterisation data

Stilbene: HR-MS (EI): theoretical for $C_{14}H_{12}$: 180.0933; found: 180.0928 $[M]^+$. IR: $\tilde{\nu} = 3055$, 3020, 1597, 1493, 1449, 1070, 1027, 961, 924, 762, 690, 524 cm^{-1}.

cis-Stilbene: ^1H NMR (CD_3OD): $\delta = 6.4$ (2H, CH), 6.9–7.1 ppm (CH, phenyl). ^{13}C NMR (CD_3OD): $\delta = 138.5$ (C), 131.2 (CH), 129.9 (CH), 129.2 (CH), 128.1 ppm (CH). GC–MS (EI, 70 eV): m/z (%) = 180 (100) $[M]^+$, 165 (43), 152 (11), 89 (12), 76 (9).

trans-Stilbene: ^{1}H NMR ($CDHCl_2$): $\delta = 7.55–7.51$ (4H, CH), 7.39 −7.33 (4H, CH), 7.29–7.25 (2H, CH), 7.14 ppm (2H, CH). ^{13}C NMR (CD_2Cl_2): $\delta = 137.65$ (C), 129.01 (CH), 128.88 (CH), 127.97 (CH), 126.79 ppm.

cis-1-(4-Styrylphenyl)ethanone: ^{1}H NMR ($CDHCl_2$): $\delta = 7.82–7.79$ (CH, phenyl), 7.35–7.33 (2H, CH, phenyl), 7.26 (5H, CH), 2.25 ppm (3H, CH_3). ^{13}C NMR (CD_2Cl_2): $\delta = 197.5$ (C), 142.5 (C), 137.0 (C), 135.9 (C), 132.5 (CH), 129.4 (CH), 129.2 (CH), 129.1 (CH), 128.6 (CH), 128.4 (CH), 127.7 (CH), 26.6 ppm (CH_3). GC–MS (EI, 70 eV): *m/z* (%) = 222 (65) $[M]^+$, 207 (100), 178 (70), 152 (15), 89 (9), 76 (6), 43 (8). R_f = 0.42 (ethyl acetate/*n*-hexane 10:90). HR-MS (EI): theoretical for $C_{14}H_{12}$: 222.1039; found: 222.1040 $[M]^+$.

4-Chlorostilbene: The separation of both isomers occurred by a bulb-to-bulb Kugelrohr distillation. Firstly, the *cis*-4-chlorostilbene was observed as a colourless oil, then *trans*-4-chlorostilbene as a white solid (vacuum, 75 °C). HR-MS (EI): theoretical for $C_{14}H_{12}$: 214.0538; found: 214.0543 $[M]^+$. IR: $\tilde{\nu} = 3020$, 2924, 1488, 1448, 1405, 1087, 1073, 966, 816 (υ_{C-Cl}), 751, 689, 527 cm^{-1}. $R_f = 0.77$ (ethyl acetate/*n*-hexane 20:80).

cis-4-Chlorostilbene: ^{1}H NMR (CD_3OD): $\delta = 7.0–7.18$ (9H, CH, phenyl), 6.4–6.6 ppm (2H, CH, double bond). ^{13}C NMR (CD_3OD): $\delta =$ 138.3 (C), 137.3 (C), 133.8 (C), 132.2 (CH), 131.5 (CH), 130.0 (CH), 129.9 (CH), 129.4 (CH), 129.3 (CH), 128.4 ppm (CH). GC–MS (EI, 70 eV): *m/z* (%) = 214 (68) $[M]^+$, 199 (8), 178 (100), 151 (12), 89 (15), 76 (15), 51 (6).

trans-4-Chlorostilbene: ^{1}H NMR ($CDHCl_2$): $\delta = 7.55–7.44$ (5H, CH, phenyl), 7.40–7.24 (4H, CH, phenyl), 7.1 ppm (2H, CH, double bond). ^{13}C NMR (CD_2Cl_2): $\delta = 137.4$ (C), 136.4 (C), 133.4 (C), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.3 (CH), 128.1 (CH), 127.6 (CH), 126.9 ppm (CH). GC–MS (EI, 70 eV): *m/z* (%) = 214 (69) $[M]^+$, 179 (100), 178 (87), 177 (22), 176 (17), 152 (14), 89 (19), 88 (12), 76 (17), 75 (12), 63 (10).

Diethyl maleate: ^{1}H NMR ($CDCl_3$): $\delta = 6.18$ (2H, double bond), 4.20 (4H, CH_2), 1.25 (6H, CH_3). ^{13}C NMR ($CDCl_3$): 165.2 (C), 129.7 (CH), 61.1 (CH_2), 13.9 ppm (CH_3). GC–MS (EI, 70 eV): *m/z* (%) = 172 (0.02) $[M]^+$, 127 (25), 99 (100), 54 (11), 29 (21).

cis-Prop-1-enylbenzene: ^{1}H NMR ([D_8]THF): $\delta = 7.22$ (5H, CH, phenyl), 6.41 (1H, CH), 5.73 (1H, CH, double bond), 1.86 ppm (3H, CH_3). ^{13}C NMR ([D_8]THF): $\delta = 138.7$ (C), 131.4 (CH), 129.8 (CH), 129.0 (CH), 127.4 (CH), 127.2 (CH), 15.0 ppm (CH_3). GC–MS (EI, 70 eV): *m/z* (%) = 118 (72) $[M]^+$, 117 (100), 115 (44), 103 (10), 91 (32), 89 (8), 77 (9), 63 (11), 51 (13), 39 (13).

(*E*)-But-1-ene-1,4-diyldibenzene: GC–MS (EI, 70 eV): *m/z* (%) = 208 (14) $[M]^+$, 117 (100), 91 (33), 77 (4), 65 (15), 51 (5), 39 (6).

(*E*)-1,4-Diphenylbut-2-ene: GC–MS (EI, 70 eV): *m/z* (%) = 208 (7) $[M]^+$, 130 (42), 117 (100), 104 (20), 91 (43), 77 (11), 65 (15), 51 (11), 39 (10).

1,2,3,4-Tetrabenzylidenecyclobutane: GC–MS (EI, 70 eV): *m/z* (%) = 408 (100) $[M]^+$, 317 (92), 252 (16), 204 (24), 165 (8), 91 (7).

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Keywords: alkynes · homogeneous catalysis · hydride complexes · rhodium · selective hydrogenation

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