Supporting Information for

Synthesis of 1,4-Dichloro-1,3-butadienes by Rhodium-Complex-Catalyzed Reaction of Terminal Alkynes with Trichloroacetyl Chloride

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I. General Procedures

All manipulations involving air and moisture-sensitive compounds were carried out under atmosphere of dry argon or nitrogen, by using standard Schlenk tube techniques. All solvents were distilled over appropriate drying agents prior to use. ^1H NMR (300 MHz), $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz), $^{29}\text{Si}\{^1\text{H}\}$ NMR (60 MHz) and $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectra were recorded at ambient temperature, using CDCl_3 as solvent unless otherwise noted. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts were reported in ppm relative to internal Me_4Si . $^{29}\text{Si}\{^1\text{H}\}$ NMR chemical shift was reported in ppm relative to internal Me_4Si . $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts were reported in ppm relative to external aq 85% H_3PO_4 . GC was run using a column (SUS column 2.0 mm ϕ $\times$ 2.0 m) packed with silicone OV17 5% on Chromosorb W (60/80 mesh). GCMS was run at an ionization potential of 70 eV. High resolution mass spectra were obtained at an ionization potential of 70 eV.

1-Octyne, 1-decyne, *tert*-butylacetylene, 5-chloro-1-pentyne, 5-hexynonitrile, methyl 5-hexynoate, trimethylsilylacetylene, 3-phenyl-1-propyne, phenylacetylene, *p*-methoxyphenylacetylene, *p*-tolylacetylene, *p*-fluorophenylacetylene, 1-ethynylcyclohexene, ethynylferrocene, 4-octyn, methyl propiolate, trichloroacetyl chloride) and triphenylarsine were obtained from commercial source and distilled/recrystallized prior to use. Ethynylthiophene,¹ 4-(*tert*-butyldimethylsiloxy)-1-butyne,² $[\text{RhCl}(\text{CO})_2]_2$,³ $[\text{Rh}(\text{acac})(\text{CO})]_2$,⁴ tribromoacetyl bromide,⁵ tris[(3,5-dimesityl)phenyl]phosphine⁶ and authentic samples of *fac,cis*- $\text{RhCl}_3(\text{CO})(\text{PMe}_3)_2$ and *mer,trans*- $\text{RhCl}_3(\text{CO})(\text{PMe}_3)_2$ ⁷ were prepared according to the literature.

To estimate the ^1H NMR yield of **3a**, intensity of the olefinic proton signal was quantified with reference to that of the proton signal arising from 1,1,2,2-tetrachloroethane used as internal standard. The program for ^1H NMR measurement was set as follows: pulse = 30°, acquisition time = 2.65 sec, pulse delay = 3.65 sec.

II. Characterization of products

Products **3b**, **3i**, **3k** and **4**, documented in the literature,⁸ were identified by comparison of the spectroscopic data with those reported and products **3c**, **3j** and **3l** were fully characterized with satisfactory elemental analysis. The other products **3a**, **3d**, **3e**, **3f**, **3g**, **3h** and **3m** displayed satisfactory spectroscopic data, including HRMS, but without satisfactory elemental analysis. For ^1H and ^{13}C NMR spectra of **3a**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **3j**, **3l** and **3m**, see Appendixes 1-20. ^1H and ^{13}C NMR spectra of **3b**, **3i** and **3k** are also included in Supporting Information as Appendixes 21-26. Structures of several byproducts were characterized by GC and GCMS, the latter of which are also listed below.

An isomer of (Z,Z)-1,4,7,10-tetrachlorodeca-4,6-diene (**3c**)

GCMS analysis of the reaction of 5-chloro-1-pentyne suggested that a trace (< 1% yield) of an isomer of (Z,Z)-1,4,7,10-tetrachlorodeca-4,6-diene (**3c**) appeared to have been formed. GCMS (EI, 70 eV) *m/z* (% relative intensity) 276 (M^+ , 87), 239 (24), 211 (32), 175 (20), 167 (35), 139 (100), 113 (19), 103 (30).

X-Ray analysis of (Z,Z)-1,6-diphenyl-2,5-dichloro-2,4-hexadiene (**3f**)

Single crystals were obtained by recrystallization from a CH_2Cl_2 /hexane (99/1) solution. A yellow crystal (= 0.25 $\times$ 0.30 $\times$ 0.50 mm) was used for X-ray diffraction data collection on a diffractometer with $\text{MoK}\alpha$ radiation (= 0.7107 Å). $\text{C}_9\text{H}_8\text{Cl}_2$, *M* = 156.65, triclinic, *Pnma*(#62), *a* =

5.684(4) Å, $b = 8.214(5)$ Å, $c = 8.368(5)$ Å, $\alpha = 71.04(2)^\circ$, $\beta = 82.51(2)^\circ$, $\gamma = 82.59(2)^\circ$, $V = 364.8(4)$ Å³, $Z = 2$, D (calc.) = 1.426 g/cm³. Total reflection collected = 2476, GOF = 0.984, R ($I > 2.00\sigma(I)$) = 0.035, R_w ($I > 2.00\sigma(I)$, all reflections) = 0.053. Selected bond distances and angles are summarized in Tables S1-1 and S1-2.

Figure S1. Molecular structure of **3f**. The hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at the 30% probability level.

Reaction of methyl propiolate

The reaction run as in the representative reaction procedure did not form the desired product, but only oligomers appeared to be formed on the basis of the following GCMS analysis.

Dimer of methyl propiolate: GCMS (EI) m/z (% relative intensity) 168 (M^+ , 3), 155 (13), 154 (100), 152 (7).

Trimer of methyl propiolate, isomer A: GCMS (EI) m/z (% relative intensity) 252 (M^+ , 7), 222 (12), 221 (100), 194 (2), 191 (2).

Trimer of methyl propiolate, isomer B: GCMS (EI) m/z (% relative intensity) 252 (M^+ , 34), 222 (14), 221 (100), 193 (7).

Reaction of tribromoacetyl bromide with 1-decyne

The reaction was run and analyzed similarly to the representative reaction procedure to reveal the formation of (*Z,Z*)-9,12-dibromoicosa-9,11-diene **4** in 41% NMR yield. GC and GCMS analyses appeared to suggest that large quantities of isomeric 1,2-dibromo-1-decenes were also formed as byproducts, but no effort was made to quantify them.

1,2-Dibromo-1-decene

Isomer 1: GCMS (EI, 70 eV) m/z (% relative intensity) 298 (M^+ , 6), 199 (10), 137 (32), 119 (10), 95 (77), 81 (100), 69 (41).

Isomer 2: GCMS (EI, 70 eV) m/z (% relative intensity) 298 (M^+ , 8), 199 (4), 137 (25), 119 (10), 95 (84), 81 (100), 69 (26).

III. Formation and reaction of rhodium complexes relevant to the mechanism

General procedure for the reaction of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ with trichloroacetyl chloride in CDCl_3

The procedure is exemplified by the experiment run at 0 °C, which was as follows. To a

yellow solution of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ (10.0 mg, 0.0314 mmol) in CDCl_3 (0.45 mL) kept at 0 °C was added trichloroacetyl chloride (3.5 μL , 0.0314 mmol). The color changed near instantaneously to red. After 15 min at the temperature, the mixture was analyzed ^{31}P NMR spectroscopy to display a major doublet at -1.27 ppm ($^1J_{\text{Rh-P}} = 72.8$ Hz) assignable to *fac,cis*- $\text{RhCl}_3(\text{CO})(\text{PMe}_3)_2$ (***fac,cis-5***) and a minor doublet at -0.91 ppm ($^1J_{\text{Rh-P}} = 76.3$ Hz), together with two more even minor doublets at -2.32 and -3.78 ppm..

Catalytic reaction using a material obtained by treating RhCl_3 with two equivalents of $\text{P}(o\text{-Tol})_3$.

RhCl_3 (4.3 mg, 0.021 mmol), $\text{P}(o\text{-Tol})_3$ (12.2 mg, 0.0400 mmol) and ethanol (1.0 mL) were mixed in a 20 mL Schlenk tube to develop a pink slurry in 3 min, which was heated for 30 min to give a yellow solution. Evaporation of ethanol left yellow solid. ^{31}P NMR measurement in CDCl_3 indicated that the material contained paramagnetic species at least partially and displayed broad signals at 50.8, -22.1 ppm in addition to another signal at 40.0 ppm, which could be assigned to $\text{O}=\text{P}(o\text{-Tol})_3$.⁹ No signal was found -27.9 ppm due to free $\text{P}(o\text{-Tol})_3$.¹⁰ Although we do understand that the material was not pure, we used it as such in a catalytic reaction under the standard conditions (130 °C, 12 h, in ethylbenzene), since the color of our material was totally different from $\text{RhCl}_2[\text{P}(o\text{-Tol})_3]_2$, reported by Bennett.¹¹ Analysis of the resulting mixture showed 100% conversion of 1-octyne (GC) and 28% yield of **3a** (^1H NMR).

IV. Tables for bond lengths and bond angles of 3f and 6

Table S1-1. Bond lengths (Å) of (Z,Z)-1,6-diphenyl-2,5-dichloro-2,4-hexadiene (**3f**)

atom	atom	distance	atom	atom	distance
Cl(1)	C(2)	1.7480(17)	C(1)	C(1)*	1.449(2)
C(1)	C(2)	1.338(2)	C(2)	C(3)	1.497(2)
C(3)	C(4)	1.522(2)	C(4)	C(5)	1.390(2)
C(4)	C(9)	1.385(2)	C(5)	C(6)	1.393(2)
C(6)	C(7)	1.378(3)	C(7)	C(8)	1.390(2)
C(8)	C(9)	1.386(2)			

Table S1-2. Bond angles (°) of (Z,Z)-1,6-diphenyl-2,5-dichloro-2,4-hexadiene (**3f**)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)*	C(1)	C(2)	126.33(15)	Cl(1)	C(2)	C(1)	120.93(13)
Cl(1)	C(2)	C(3)	114.22(11)	C(1)	C(2)	C(3)	124.85(15)
C(2)	C(3)	C(4)	114.96(15)	C(3)	C(4)	C(5)	119.12(17)
C(3)	C(4)	C(9)	122.07(14)	C(5)	C(4)	C(9)	118.75(17)
C(4)	C(5)	C(6)	120.44(19)	C(5)	C(6)	C(7)	120.25(16)
C(6)	C(7)	C(8)	119.69(18)	C(7)	C(8)	C(9)	119.85(19)
C(4)	C(9)	C(8)	121.00(15)				

Tables S2-1. Bond lengths (Å) of $[\text{Rh}(\mu\text{-Cl})\text{Cl}_2(\text{PMe}_3)_2]_2$ (**6**)

atom	atom	distance	atom	atom	distance
Rh1	Cl1	2.350(2)	Rh1	Cl1 [*]	2.350(2)
Rh1	Cl2	2.371(2)	Rh1	Cl2 [*]	2.371(2)
Rh1	P1	2.331(4)	Rh1	P2	2.351(4)
Rh2	Cl2	2.493(2)	Rh2	Cl2 [*]	2.493(2)
Rh2	Cl3	2.328(4)	Rh2	Cl4	2.336(4)
Rh2	P3	2.256(3)	Rh2	P3 [*]	2.256(3)
P1	C1	1.804(13)	P1	C1 [*]	1.804(13)
P1	C2	1.793(15)	P2	C3	1.777(15)
P2	C4	1.804(13)	P2	C4 [*]	1.804(13)
P3	C5	1.771(13)	P3	C6	1.93(2)
P3	C7	1.91(2)	P3	C8	1.78(2)
P3	C9	1.73(2)	C6	C9	0.89(4)
C7	C8	0.96(4)			

Tables S2-2. Bond angles (°) of $[\text{Rh}(\mu\text{-Cl})\text{Cl}_2(\text{PMe}_3)_2]_2$ (**6**)

atom	atom	atom	angle	atom	atom	atom	angle
Cl1	Rh1	Cl1 [*]	94.21(9)	Cl1	Rh1	Cl2	90.88(9)
Cl1	Rh1	Cl2 [*]	174.89(9)	Cl1	Rh1	P1	87.06(10)
Cl1	Rh1	P2	87.42(10)	Cl1 [*]	Rh1	Cl2	174.89(9)
Cl1 [*]	Rh1	Cl2 [*]	90.88(9)	Cl1 [*]	Rh1	P1	87.06(10)
Cl1 [*]	Rh1	P2	87.42(10)	Cl2	Rh1	Cl2 [*]	84.02(9)
Cl2	Rh1	P1	92.89(11)	Cl2	Rh1	P2	93.14(11)
Cl2 [*]	Rh1	P1	92.89(11)	Cl2 [*]	Rh1	P2	93.14(11)
P1	Rh1	P2	171.89(15)	Cl2	Rh2	Cl2 [*]	79.07(9)
Cl2	Rh2	Cl3	90.12(11)	Cl2	Rh2	Cl4	90.84(11)
Cl2	Rh2	P3	93.12(9)	Cl2	Rh2	P3 [*]	172.19(10)
Cl2 [*]	Rh2	Cl3	90.12(11)	Cl2 [*]	Rh2	Cl4	90.84(11)
Cl2 [*]	Rh2	P3	172.19(10)	Cl2 [*]	Rh2	P3 [*]	93.12(9)
Cl3	Rh2	Cl4	178.76(16)	Cl3	Rh2	P3	89.65(11)
Cl3	Rh2	P3 [*]	89.65(11)	Cl4	Rh2	P3	89.52(10)
Cl4	Rh2	P3 [*]	89.52(10)	P3	Rh2	P3 [*]	94.68(11)
Rh1	Cl2	Rh2	98.44(8)	Rh1	P1	C1	116.0(4)
Rh1	P1	C1 [*]	116.0(4)	Rh1	P1	C2	111.7(6)
C1	P1	C1 [*]	106.2(6)	C1	P1	C2	102.6(5)
C1 [*]	P1	C2	102.6(5)	Rh1	P2	C3	110.4(5)
Rh1	P2	C4	116.8(4)	Rh1	P2	C4 [*]	116.8(4)
C3	P2	C4	103.0(5)	C3	P2	C4 [*]	103.0(5)
C4	P2	C4 [*]	105.2(5)	Rh2	P3	C5	111.4(5)
Rh2	P3	C6	111.3(10)	Rh2	P3	C7	117.7(10)
Rh2	P3	C8	117.8(8)	Rh2	P3	C9	122.0(11)
C5	P3	C6	94.3(11)	C5	P3	C7	88.5(10)
C5	P3	C8	113.7(9)	C5	P3	C9	109.7(12)
C6	P3	C7	125.9(14)	C6	P3	C8	105.7(12)
C6	P3	C9	27.5(13)	C7	P3	C8	29.9(12)

C7	P3	C9	102.3(14)	C8	P3	C9	78.6(13)
P3	C6	C9	64(2)	P3	C7	C8	68(2)
P3	C8	C7	83(2)	P3	C9	C6	89(2)

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Appendix 1: ^1H NMR spectrum of (Z,Z)-7,10-dichlorohexadeca-7,9-diene (**3a**)

Appendix 2: ^{13}C NMR spectrum of (Z,Z)-7,10-dichlorohexadeca-7,9-diene (**3a**)

Appendix 3: ^1H NMR spectrum of (Z,Z)-1,4,7,10-tetrachloro-4,6-decadiene (**3c**)

Appendix 4: ^{13}C NMR spectrum of (Z,Z)-1,4,7,10-tetrachloro-4,6-decadiene (**3c**)

Appendix 5: ^1H NMR spectrum of (Z,Z)-5,8-dichlorododeca-5,7-dienodinitrile (**3d**)

Appendix 6: ^{13}C NMR spectrum of (Z,Z)-5,8-dichlorododeca-5,7-dienodinitrile (**3d**)

Appendix 7: ^1H NMR spectrum of dimethyl (Z,Z)-5,8-dichlorododeca-5,7-dienedioate (**3e**)

Appendix 8: ^{13}C NMR spectrum of dimethyl (Z,Z)-5,8-dichlorododeca-5,7-dienedioate (**3e**)

Appendix 9: ^1H NMR spectrum of (Z,Z)-1,6-diphenyl-2,5-dichloro-2,4-hexadiene (**3f**)

Appendix 10: ^{13}C NMR spectrum of (Z,Z)-1,6-diphenyl-2,5-dichloro-2,4-hexadiene (**3f**)

Appendix 11: ^1H NMR spectrum of (Z,Z)-1,4-dichloro-1,4-bis(trimethylsilyl)butadiene (**3g**)

Appendix 12: ^{13}C NMR spectrum of (Z,Z)-1,4-dichloro-1,4-bis(trimethylsilyl)butadiene (**3g**)

Appendix 13: ^1H NMR spectrum of (Z,Z)-1,4-dichloro-1,4-bis(1-cyclohexenyl)butadiene (**3h**)

Appendix 14: ^{13}C NMR spectrum of (Z,Z)-1,4-dichloro-1,4-bis(1-cyclohexenyl)butadiene (**3h**)

Appendix 15: ^1H NMR spectrum of (Z,Z)-1,4-dichloro-1,4-di(4-methoxyphenyl)-1,3-butadiene (**3j**)

Appendix 16: ^{13}C NMR spectrum of (Z,Z)-1,4-dichloro-1,4-di(4-methoxyphenyl)-1,3-butadiene (**3j**)

Appendix 17: ^1H NMR spectrum of (Z,Z)-1,4-dichloro-1,4-di(4-fluorophenyl)-1,3-butadiene (**3I**)

Appendix 18: ^{13}C NMR spectrum of (Z,Z)-1,4-dichloro-1,4-di(4-fluorophenyl)-1,3-butadiene (**31**)

Appendix 19: ^1H NMR spectrum of (Z,Z)-1,4-dichloro-1,4-di(2-thienyl)-1,3-butadiene (**3m**)

Appendix 20: ^{13}C NMR spectrum of (Z,Z)-1,4-dichloro-1,4-di(2-thienyl)-1,3-butadiene (**3m**)

Appendix 21: ^1H NMR spectrum of (Z,Z)-3,6-dichloro-2,2,7,7-tetramethyl-3,5-octadiene (**3b**)

Appendix 22: ^{13}C NMR spectrum of (Z,Z)-3,6-dichloro-2,2,7,7-tetramethyl-3,5-octadiene (**3b**)

Appendix 23: ^1H NMR spectrum of (Z,Z)-1,4-dichloro-1,4-diphenyl-1,3-butadiene (**3i**)

Appendix 24: ^{13}C NMR spectrum of (Z,Z)-1,4-dichloro-1,4-diphenyl-1,3-butadiene (**3i**)

Appendix 25: ^1H NMR spectrum of (Z,Z)-1,4-dichloro-1,4-di(*p*-tolyl)-1,3-butadiene (**3k**)

Appendix 26: ^{13}C NMR spectrum of (Z,Z)-1,4-dichloro-1,4-di(*p*-tolyl)-1,3-butadiene (**3k**)