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

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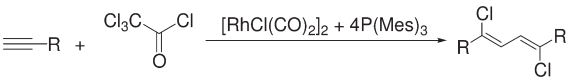

Chlorinative dimerization of terminal alkynes with trichloroacetyl chloride as chlorine donor proceeds in the presence of rhodium catalysts to give (*Z*,*Z*)-1,4-dichloro-1,3-butadienes stereoselectively. Ligand screening has revealed that reactions using sterically bulky and electron-donating ligands like trimesitylphosphine are high yielding. The reaction is compatible with a range of functional groups to give the title compounds nearly quantitatively in most cases. A mechanistic possibility involving coupling of β-chloroalken-1-yl intermediate has been discussed.

Introduction

Since 1,3-dienes are extremely useful intermediates to synthesize, for instance, biologically active heterocyclic compounds, a wide range of 1,3-diene compounds have been documented and numerous synthetic methods have been developed.[1] Among the huge family of 1,3-butadienes, however, the structural variation of 1,4-dihalo-1,3-butadienes is very limited, presumably because synthetic methodologies have not been widely explored although these compounds are also potentially useful in organic synthesis. Indeed, use of these compounds can be seen in the synthesis of conjugated polyenes,[2] benzene derivatives,[3] naphthalenes,[4] cyclopentadiene derivatives,[5] pyridines,[6] furans,[7] thiophenes,[8] pyrrole,[8b] siloles and other group 14 congeners,[9] phospholes,[10] and other pnictogen congeners.[11]

As for the synthesis of 1,4-dihalo-1,3-butadienes, two newer general procedures are known, in addition to a plethora of those for particular structures. One involves cyclization of two molecules of alkynes with early transition metal complexes like Zr/Ti complexes forming metalacyclopentadienes followed by quenching with appropriate halogens.[12] This procedure, although the yield is not always high, has been most frequently used to prepare diiodo compounds in the synthetic application for siloles, phospholes, and other similar compounds,[9−11] due to their high reactivity. The other is halogenative coupling of terminal alkynes with appropriate halogen sources like iodine or up to 4-fold excess of cupric halides in the presence of a catalytic quantity of platinum or palladium halide.[13] However, these methods are not free from drawbacks. The former requires a stoichiometric quantity of Zr or Ti reagent, the metal in which is not retained in the final products, and the latter with palladium catalyst is a heterogeneous reaction, which may hamper utilization in a large scale synthesis.

(1) Luh, T.-Y.; Wong, K.-T. *Synthesis* **1993**, 349.
(2) (a) Kiehl, A.; Eberhardt, A.; Müllen, K. *Liebigs Ann.* **1995**, 223. (b) Yamamoto, T.; Ohya, K.; Kobayashi, K.; Okamoto, K.; Koie, S.; Fukumoto, H.; Koizumi, T.-a.; Yamaguchi, I. *Macromolecules* **2009**, *42*, 3207.
(3) Fukuhara, K.; Takayama, Y.; Sato, F. *J. Am. Chem. Soc.* **2003**, *125*, 6884.
(4) Wang, Z.; Wang, C.; Xi, Z. *Tetrahedron Lett.* **2006**, *47*, 4157.
(5) (a) Chambers, R. D.; Greenhall, M. P. *J. Chem. Soc., Chem. Commun.* **1990**, 1128. (b) Hu, Q.; Wang, C.; Li, D.; Xi, Z. *Org. Biomol. Chem.* **2007**, *5*, 2114.
(6) Wang, C.; Wang, Z.; Liu, L.; Wang, C.; Liu, G.; Xi, Z. *J. Org. Chem.* **2006**, *71*, 8565.
(7) Briscoe, M. W.; Chambers, R. D.; Mullins, S. J.; Nakamura, T.; Vaughan, J. F. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3119.
(8) (a) Geering, E. J. *J. Org. Chem.* **1959**, *24*, 1128. (b) Briscoe, M. W.; Chambers, R. D.; Mullins, S. J.; Nakamura, T.; Drakesmith, F. G. *J. Chem. Soc., Chem. Commun.* **1990**, 1127. (c) Itsuda, H.; Kimura, S. (Seitetsu Kagaku Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 1990048575 A2, **1990**.
(9) (a) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. *J. Organomet. Chem.* **1995**, *499*, C7. (b) Yamaguchi, S.; Jin, R.-Z.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060. (c) Ura, Y.; Li, Y.; Tsai, F.-Y.; Nakajima, K.; Kotara, M.; Takahashi, T. *Heterocycles* **2000**, *52*, 1171. (d) Sanji, T.; Mori, T.; Sakurai, H. *J. Organomet. Chem.* **2006**, *691*, 1169. (e) Wang, C.; Luo, Q.; Sun, H.; Guo, Z.; Xi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 3094.
(10) (a) Turcitu, D.; Nief, F.; Ricard, L. *Chem.—Eur. J.* **2003**, *9*, 4916. (b) Nief, F.; de Borms, B. T.; Ricard, L.; Carmichael, D. *Eur. J. Inorg. Chem.* **2005**, 637.
(11) Ashe, A. J. III; Al-Ahmad, S.; Pilotek, S.; Puranik, D. B.; Elschenbroich, C.; Behrendt, A. *Organometallics* **1995**, *14*, 2689.
(12) (a) Negishi, E.-i.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Yamaguchi, S.; Jin, R.-Z.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060.
(13) (a) Ananikov, V. P.; Mitchenko, S. A.; Beletskaya, I. P. *Russ. J. Org. Chem.* **2002**, *38*, 636. (b) Li, J.-H.; Liang, Y.; Xie, Y.-X. *J. Org. Chem.* **2004**, *69*, 8125. (c) See also: Ananikov, V. P.; Mitchenko, S. A.; Beletskaya, I. P. *J. Organomet. Chem.* **2001**, *636*, 175.

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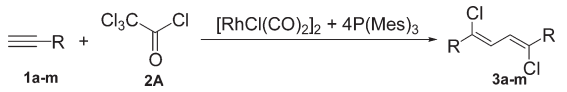
SCHEME 1. Rhodium-Catalyzed Synthesis of 1,4-Dichloro-1, 3-butadienes Starting with Terminal Alkynes with Trichloroacetyl Chloride



During the course of our study on the Rh(acac)(CO)-($AsPh_3$)-catalyzed addition reaction of chloroacetyl chloride with terminal alkynes,[14] we found accidentally that the reaction of 1-octyne **1a**, run with trichloroacetyl chloride **2A** used in place of chloroacetyl chloride (at 110 °C, Rh-(acac)(CO)($AsPh_3$), 5 mol %), proceeded in a different direction, forming (*Z*,*Z*)-7,10-dichlorohexadeca-7,9-diene **3a** as undesired product in 63% yield (Scheme 1, R = *n*-C_6H_{13}). Further study has provided us with an easy and high-yielding access to (*Z*,*Z*)-1,4-dichloro-1,3-butadienes in a homogeneous process (Scheme 1). The details will be disclosed in this paper.

Results and Discussion

Trial Experiments for High-Yielding Conditions. Although the yield of **3a** in the accidental discovery of the reaction was not too low, trial experiments to search for higher-yielding conditions, mainly through ligand and solvent screening, were run in the presence of various rhodium catalyst systems (2 mol % with respect to rhodium atom). The procedure using $[RhCl(CO)_2]_2$ in conjunction with P(2,4,6-trimethylphenyl)$_3$ ($PMes_3$) in a chlorobenzene solution has proved satisfactory, as summarized in Table 1.

Initial ligand screening carried out by using (acetylacetonato)rhodium complexes at 130 °C in a 20 mL Schlenk tube revealed that, as was observed in the addition of chloroacetyl chloride with alkynes, $AsPh_3$ appeared to be better performing than PPh_3 (entries 1 and 2). However, plain Rh(acac)-$(CO)_2$ without any additional ligand (entry 3) was better performing, and Rh(acac)$(CO)_2PMes_3$ was even better, in particular, when 2 equiv of $PMes_3$ was used (entries 4 and 5). Similar trends were also observed with chlororhodium catalyst systems. Thus, RhCl(CO)$(PPh_3)_2$ (entry 6) appears to be less effective than plain $[RhCl(CO)_2]_2$ (entry 7) and the $[RhCl(CO)_2]_2-4AsPh_3$ system (entry 8), although better than $[RhCl(CO)_2]_2-4SbPh_3$ (entry 9). Among chlororhodium catalyst systems, $[RhCl(CO)_2]_2-4PMes_3$ was the best (entry 10). Other ligands, like P(*o*-Tol)$_3$, P(1-Naph)$_3$, and $PMes_2Ph$, which are more sterically demanding than PPh_3 but less bulky than $PMes_3$, displayed intermediate yields (entries 11−13). P[2,4,6-(^{i}Pr)$_3C_6H_2]_3$, an even more bulky ligand, furnished a somewhat low yield as compared with $PMes_3$ (entry 14). BSP, a seemingly bulky ligand of a bowl shape,[15] performed much worse than $PMes_3$ and similar to PPh_3 (entry 15); this is presumably because the steric congestion in the close proximity of the rhodium center is not so serious. Among triarylphosphines (entries 6, 16, and 17), a distinct electronic effect was also observed; the yield decreased in the order of P(*p*-$MeOC_6H_4)_3$ > PPh_3 > P(*p*-$ClC_6H_4)_3$, suggesting that a more donating ligand is better performing, which is consistent with the highest yield obtained with $PMes_3$. The use of RhCl(CO)$(PMe_3)_2$ catalyst ligated by more electron-donating PMe_3 resulted in a very poor yield (entry 18). However, RhCl(CO)$(PCy_3)_2$, ligated by highly electron-donating but sterically more demanding ligand, performed better than RhCl(CO)$(PMe_3)_2$, which agrees with the foregoing steric effect of the ligand (entry 19). Chelating phosphines also gave intermediate yields, more or less similarly to PPh_3 (entries 20−23). Despite the rather clear trends observed in the ligand effect study, the origin of the ligand-dependent variation in the yield is ambiguous at this time. This may be associated with a sterically bulky ligand being able to hamper the formation of dinuclear rhodium species from mononuclear species, which are envisioned to be responsible for the catalysis (vide infra).

Choice of a solvent also plays an important role. Screening was carried out by using the $[RhCl(CO)_2]_2 + 4PMes_3$ catalyst system at a lower temperature (100 °C) to more clearly extract discernible effect. The results shown in Table 1 conclude chlorobenzene is the solvent of choice although

TABLE 1. Rhodium-Catalyzed Reaction of 1-Octyne 1a with Trichloroacetyl Chloride 2A[a]

entry	catalyst system	temp (°C), solvent[b]	conv[c] (%)	yield[d] (%)
1	$Rh(acac)(CO)_2 + 1AsPh_3$	130, E	99	20
2	$Rh(acac)(CO)(PPh_3)$	130, E	98	11
3	$Rh(acac)(CO)_2$	130, E	99	30
4	$Rh(acac)(CO)_2 + 1PMes_3$	130, E	99	52
5	$Rh(acac)(CO)_2 + 2PMes_3$	130, E	99	65
6	$RhCl(CO)(PPh_3)_2$	130, E	98	19
7	$[RhCl(CO)_2]_2$	130, E	98	30
8	$[RhCl(CO)_2]_2 + 4AsPh_3$	130, E	nd	28
9	$[RhCl(CO)_2]_2 + 4SbPh_3$	130, E	98	6
10	$[RhCl(CO)_2]_2 + 4PMes_3$	130, E	98	62
11	$[RhCl(CO)_2]_2 + 4P(o\text{-Tol})_3$	130, E	98	40
12	$[RhCl(CO)_2]_2 + 4P(1\text{-Naph})_3$	130, E	98	39
13	$[RhCl(CO)_2]_2 + 4PMes_2Ph$	130, E	99	50
14	$[RhCl(CO)_2]_2 + 4P[2,4,6\text{-}^iPr)_3C_6H_2]_3$	130, E	100	54
15	$[RhCl(CO)_2]_2 + 4BSP$[e]	130, E	100	16
16	$[RhCl(CO)_2]_2 + 4P(p\text{-}ClC_6H_4)_3$	130, E	>99	5
17	$[RhCl(CO)_2]_2 + 4P(p\text{-}MeOC_6H_4)_3$	130, E	100	36
18	$RhCl(CO)(PMe_3)_2$	130, E	95	8
19	$[RhCl(CO)_2]_2 + 4PCy_3$	130, E	100	29
20	$[RhCl(CO)_2]_2 + 2dppe$	130, E	98	27
21	$[RhCl(CO)_2]_2 + 2dppp$	130, E	98	23
22	RhCl(CO)(dppb)	130, E	43	14
23	$[RhCl(CO)_2]_2 + 2dppf$	130, E	>99	18
24	$[RhCl(CO)_2]_2 + 4PMes_3$	100, P	100	50
25	$[RhCl(CO)_2]_2 + 4PMes_3$	100, D	100	69
26	$[RhCl(CO)_2]_2 + 4PMes_3$	100, T	100	52
27	$[RhCl(CO)_2]_2 + 4PMes_3$	100, C	100	78
28[f]	$[RhCl(CO)_2]_2 + 4PMes_3$	130, E	100	70
29[f]	$[RhCl(CO)_2]_2 + 4PMes_3$	130, C	100	84
30[f,g]	$[RhCl(CO)_2]_2 + 4PMes_3$	130, C	100	91

[a]Reaction conditions: **1a** (1.0 mmol), **2A** (1.0 mmol), rhodium complex (2 mol % Rh), ligand (4 mol %), solvent (1 mL), in a 20 mL Schlenk tube, 12 h. [b]E = ethylbenzene, P = propionitrile, D = 1,4-dioxane, T = toluene, C = chlorobenzene. [c]Determined by GC using *n*-tetradecane as an internal standard. [d]Determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. [e]BSP = tris[(3,5-dimesityl)phenyl]phosphine. [f]Run in a 5 mL Schlenk tube. [g]Reaction time 3 h, 5 mol % Rh and 10 mol % ligand.

(14) Kashiwabara, T.; Fuse, K.; Hua, R.; Tanaka, M. *Org. Lett.* **2008**, *10*, 5469.

(15) Niyomura, O.; Iwasawa, T.; Sawada, N.; Tokunaga, M.; Obora, Y.; Tsuji, Y. *Organometallics* **2005**, *24*, 3468. For design and synthesis of BSP and related heteroatom compounds, see: Ohzu, Y.; Goto, K.; Kawashima, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 5741 and references cited therein.

1,4-dioxane is also better performing than toluene and propionitrile (entries 24−27).

Finally, we turned our attention to the size of the reaction vessel. Most of the trial experiments were run at 130 °C, which is higher than the boiling point of trichloroacetyl chloride (114−116 °C). In a large reaction vessel, the Cl_3CCOCl reagent is probably enriched in the gas phase, thus reducing its concentration in the solution. We assumed that the use of a small-sized Schlenk tube could afford a higher yield. Indeed, when a reaction in ethylbenzene solvent using the $[RhCl(CO)_2]_2 + 4PMes_3$ catalyst system was run in a 5 mL airtight Schlenk tube, the yield increased to 70% (entry 28) as compared with 62% obtained in a 20 mL Schlenk tube reaction (entry 10). This modification, when applied to a reaction in chlorobenzene, offered 84% yield (entry 29). By increasing the catalyst quantity from 2 to 5 mol % (with respect to rhodium atom), the yield was further improved to 91% in a shorter reaction time (3 h) to provide a satisfactory recipe (entry 30).

Since only chlorine among the constituents in Cl_3CCOCl was found in the products, we occasionally scrutinized the resulting mixture by GCMS to identify the fate of carbonyl functionality in Cl_3CCOCl, but all attempts failed. Another approach, somewhat associated with this, is to examine the possible use of other chlorine compounds. Under the optimized conditions (entry 30, Table 1), the reactions with C_2Cl_6, CCl_4 and $(COCl)_2$ afforded **3a** in 41, 4, and 26% yields, respectively, suggesting that the presence of the carbonyl functionality in the starting chlorine sources is not a prerequisite for the catalysis.

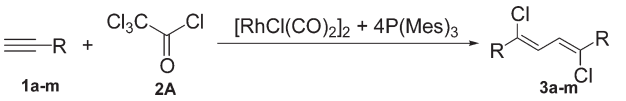
Besides rhodium catalysts, we also attempted to use ruthenium compounds as catalyst. However, $RuCl_3$, alone or in combination with PPh_3 or $AsPh_3$, $[RuCl_2(p\text{-cymene})]_2$, and $RuCl_2(CO)_2(PPh_3)_2$ were all basically inactive (2 mol % catalyst, 130 °C in ethylbenzene).

Synthetic Scope and Limitation. The satisfactory recipe identified in the foregoing section could be applied successfully to a variety of terminal alkynes as summarized in Table 2. Products **3b**, **3i**, **3k**, and **4**, documented in the literature,[13b] were identified by comparison of the spectroscopic data with those reported and the others also displayed satisfactory spectroscopic data. However, to unambiguously confirm the stereochemistry at least in one case, product **3f** was analyzed by X-ray crystallography, which verified (*Z*,*Z*)-configuration as shown in Figure S1 (Supporting Information).

Besides 1-octyne, other aliphatic acetylenes, inclusive of functionalized ones, such as *tert*-butylacetylene (**1b**), 5-chloro-1-pentyne (**1c**), 5-hexynenitrile (**1d**), methyl 5-hexynoate (**1e**), 3-phenyl-1-propyne (**1f**), and trimethylsilylacetylene (**1g**), also conform to the reaction procedure, without deterioration of the functional group. Cyclohexenylacetylene (**1h**), a conjugated enyne, participates in the reaction as well. Aromatic acetylenes (**1i**−**l**) and 2-thienylacetylene (**1m**) are also good substrates affording (near) quantitative yields, irrespective of the nature of the substituents. However, 4-(*tert*-butyldimethylsiloxy)-1-butyne (**1n**) and 3-methoxy-1-propyne (**1o**) appear to have reacted in different directions to end up with a messy mixture of unidentified products. Methyl propiolate (**1p**) and ferrocenylacetylene (**1q**) do not afford the desired products at all. 4-Octyne (**1r**), an internal acetylene, is totally inert.

What is rather amazing through the successful reactions is the formation of the product as a single isomer; no other regio- and stereoisomeric butadiene was observed in these catalytic reactions.

TABLE 2. Rhodium-Catalyzed Chlorinative Dimerization of Terminal Alkynes with Trichloroacetyl Chloride 2A[a]



1a-m 2A 3a-m

entry	alkyne	R =	product	yield (%)
1	**1a**	*n*-hexyl	**3a**	88
2	**1b**	*tert*-Bu	**3b**	75
3	**1c**	3-chloropropyl	**3c**	98[b]
4	**1d**	3-cyanopropyl	**3d**	90
5	**1e**	3-(methoxycarbonyl)propyl	**3e**	96
6	**1f**	benzyl	**3f**	80
7	**1g**	trimethylsilyl	**3g**	70
8	**1h**	1-cyclohexenyl	**3h**	72
9	**1i**	Ph	**3i**	98
10	**1j**	*p*-anisyl	**3j**	94
11	**1k**	*p*-tolyl	**3k**	92
12	**1l**	*p*-fluorophenyl	**3l**	96
13	**1m**	2-thienyl	**3m**	97

[a]Reaction conditions: A mixture of **1** (1.0 mmol), **2A** (1.0 mmol), $[RhCl(CO)_2]_2$ (0.025 mmol), and $PMes_3$ (0.10 mmol) in chlorobenzene (1.0 mL) was stirred for 3 h at 130 °C in a 5 mL Schlenk tube. [b]A trace (< 1%) of another isomer appears to have been formed as analyzed by GCMS.

Extension of the procedure to the reaction of tribromoacetyl bromide (**2B**) with 1-decyne (90 °C, 3 h, in a 5 mL Schlenk tube), although full optimization had not been made, revealed the formation of (*Z*,*Z*)-9,12-dibromoicosa-9,11-diene **4** in 43% NMR yield. GC and GCMS analyses suggested the formation of 1,2-dibromodecene as byproducts. Quite puzzling is that the 1,2-dibromodecene was a mixture of two isomers in an approximately 1:1 ratio (presumably *E*- and *Z*-isomers on the basis of GCMS analysis), although only (*Z*,*Z*)-9,12-dibromoicosa-9,11-diene **4** was formed as the sole dimeric product.[16] The formation of the isomeric 1,2-dibromodecenes might be associated with partial involvement of external attack of bromine generating (*E*)-*β*-bromoalkenyl intermediate. Such an elemental process has been verified by Beletskaya and co-workers in platinum-catalyzed iodinative dimerization of terminal alkynes (vide infra).[13a,c]

Mechanistic Consideration. Li and co-workers have developed a closely related process to synthesize 1,4-dihalobutadiene compounds by using palladium halides as catalyst. The mechanism they proposed comprises halopalladation with an alkyne leading to XCR=CHPdX species (X = Cl, Br), insertion of another alkyne molecule to generate (4-halo-1,3-butadien-1-yl)PdX species, and sp^2-C−X reductive elimination.[13b] We do not have any decisive evidence to exclude the same type mechanism for the present rhodium-catalyzed reaction. The formation of 1,2-dibromodecenes (vide supra) as byproduct in the present study may be rationalized by premature reductive elimination at the stage that follows the similar halometalation process. However, as far as rhodium(III) phosphine complexes are concerned, sp^2-C−X reductive elimination involved in the last step leading to the

(16) A similar observation in the palladium-catalyzed reaction of phenylacetylene with $CuBr_2$ has been reported by Li and co-workers. See ref 13b.

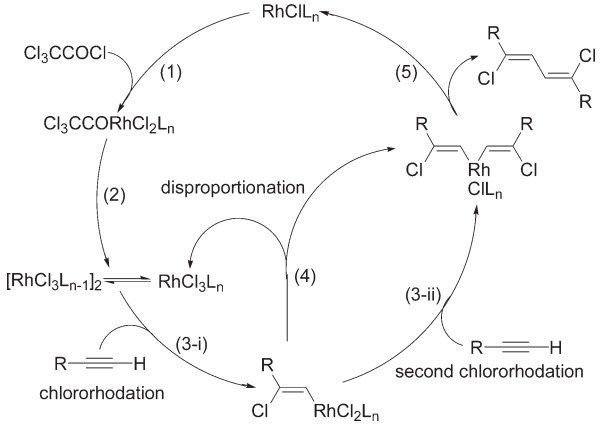
dihalo-1,3-diene formation is envisioned to be a tricky task.[17] What is required with this in mind is to work out another mechanism that does not proceed via successive insertion of two alkyne molecules. An obvious candidate is a radical mechanism. To look into this possibility, we ran two types of experiments in the presence of a radical scavenger or styrene as a probe. A reaction run in the presence of TEMPO (0.5 mmol, 50 mol %) under the same conditions as in entry 30 (Table 1) did not result in an appreciable change in the yield of **3a** (89% vs 91% observed in entry 30), supporting that the formation of **3a** does not involve radical species. However, another reaction run under the same conditions in the presence of styrene (1.0 mmol) resulted in a complete conversion of styrene to polystyrene ($M_n = 880$, $M_w = 1580$) and the yield of **3a** decreased to 13% (vs 91% observed in entry 30), while a control experiment, in which a chlorobenzene solution of styrene and $[RhCl(CO)_2]_2$ + $4PMes_3$ catalyst was heated in the absence of **1a** and **2A** under the same conditions, did not polymerize styrene to an appreciable extent (≤5% conversion). We presume that radical species can be generated under the catalytic conditions but the species does not participate directly in the catalysis forming dichlorobutadienes.

Another aspect worth noting is the high stereoselectivity forming only *Z*,*Z*-isomers in the catalysis, which also appears to exclude a radical mechanism. Configurational instability of alkenyl radicals has been substantiated in quite a few publications[18] and utilized in synthetic application since the work by Stork demonstrated.[19] In view of these precedents, dimerization of free RCCl=CH• radical does not appear to be a realistic route to dichlorobutadiene.

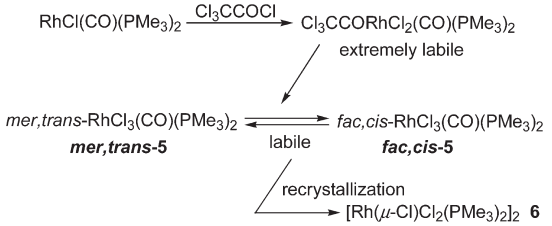
The elimination of possible mechanisms on the basis of the foregoing consideration leaves a third mechanism via direct conversion of two β-chloroalkenyl−metal bonds to the dimer (Scheme 2). Note, however, that the "direct conversion" covers a variety of mechanistic details (vide infra). Scheme 2 illustrates only reductive elimination of bis(β-chloroalkenyl)rhodium species resulting from chlororhodation at two Cl−Rh bonds in one molecule with alkyne (route 3-i followed by 3-ii) or disproportionation of two (β-chloroalkenyl)rhodium species (route 4).

We presume that the catalysis is initiated by oxidative addition of trichloroacetyl chloride with a chlororhodium(I) complex (route 1), which is somehow followed by generation of $RhCl_3L_n$ species such as $RhCl_3(CO)L_2$ (route 2), and insertion of an alkyne takes place (route 3). As for the oxidative addition, we have been unable, despite our best efforts, to generate or isolate neat adducts of $Cl_3CC(O)RhCl_2(CO)L_2$. Even $Cl_3CC(O)RhCl_2(CO)(PMe_3)_2$ ligated by PMe_3, a powerful stabilizing ligand for complexes of this type,[14,20] appears extremely labile (Scheme 3). Thus, an

SCHEME 2. Outline of Possible Mechanism



SCHEME 3. Attempted Oxidative Addition of Cl_3CCOCl with $RhCl(CO)(PMe_3)_2$



attempted reaction of $RhCl(CO)(PMe_3)_2$ with Cl_3CCOCl (1.0 equiv) at 0 °C in $CDCl_3$ furnished, after 15 min, a mixture that displayed, in ^{31}P NMR spectroscopy, two doublets, major one centered at −1.27 ppm ($^1J_{Rh-P} = 72.8$ Hz) arising from known *fac*,*cis*-$RhCl_3(CO)(PMe_3)_2$ (***fac*,*cis*-5**)[21] and the other minor one at −0.91 ppm ($^1J_{Rh-P} = 76.3$ Hz), in addition to two more even minor doublets. However, the doublet at −0.91 ppm, which we presume was arising from $Cl_3CC(O)RhCl_2(CO)(PMe_3)_2$ disappeared after additional 1 h at the temperature, and the major doublet became more intense. When the same reaction was run at room temperature, only signals due to ***fac*,*cis*-5** were observed.[22] Another reaction run at −30 °C for 1 h provided a ^{31}P NMR spectrum similar to that obtained at 0 °C after 15 min. A 10 μL portion of the resulting mixture was evaporated *rapidly* on a NaCl disk and was subjected to IR spectroscopy, which showed an absorption band at 1681 cm^{-1}, reasonable for $\nu_{C=O}$ due to $Cl_3CC(O)Rh$ species. A third support for $Cl_3CC(O)RhCl_2(CO)(PMe_3)_2$ has come from FAB-MS measurement; to a solution of $RhCl(CO)(PMe_3)_2$ in CH_2Cl_2 cooled at 0 °C was added Cl_3CCOCl (1.0 equiv) *in front of a mass spectrometer* to instantaneously develop a red-orange solution, and the mixture was injected *immediately* to the spectrometer to furnish satisfactory HRMS *m*/*z* values with the expected isotope distribution pattern for $[M - 2Cl + H]^+$,

(17) (a) Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. *J. Org. Chem.* **1996**, *61*, 6941. (b) Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478.

(18) (a) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147. (b) Sargent, G. D.; Browne, M. W. *J. Am. Chem. Soc.* **1967**, *89*, 2788. (c) Jenkins, P. R.; Symons, M. C. R.; Booth, S. E.; Swain, C. J. *Tetrahedron Lett.* **1992**, *33*, 3543. (d) Galli, C.; Guarnieri, A.; Koch, H.; Mencarelli, P.; Rappoport, Z. *J. Org. Chem.* **1997**, *62*, 4072.

(19) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321.

(20) (a) Hua, R.; Shimada, S.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 12365. (b) Hua, R.; Onozawa, S.-y.; Tanaka, M. *Chem.—Eur. J.* **2005**, *11*, 3621. (c) Kashiwabara, T.; Kataoka, K.; Hua, R.; Shimada, S.; Tanaka, M. *Org. Lett.* **2005**, *7*, 2241.

(21) Browing, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061.

(22) Another reaction at room temperature was run in toluene (5 mL) using $RhCl(CO)(PMe_3)_2$ (38.0 mg, 0.119 mmol) and Cl_3CCOCl (50 μL, 0.45 mmol) for 1 h to afford a near-quantitative yield of *mer*,*trans*-$RhCl_3(CO)(PMe_3)_2$ (***mer*,*trans*-5**, yellow powder), which was confirmed to be identical with an authentic sample prepared via separate route (ref 21). The formation of *mer*,*trans*-isomer in this experiment is associated with the polarity of the solvent (vide infra).

i.e., HRMS (FAB, matrix = 2-nitrobenzyl alcohol) calcd for $C_9H_{19}{}^{35}Cl_2{}^{37}ClO_2P_2Rh$ ($[M - 2Cl + H]^+$) m/z 430.8952, found 430.8962; calcd for $C_9H_{19}{}^{35}Cl^{37}Cl_2O_2P_2Rh$ ($[M - 2Cl + H]^+$) m/z 432.8924, found 432.8929.

Mechanistic detail of the transformation from $Cl_3CC(O)RhCl_2(CO)(PMe_3)_2$ to ***fac*,*cis*-5** (Scheme 3), or to $RhCl_3L_n$ in a broader sense with Scheme 2 in mind (route 2), is uncertain at this time. It may involve β-chlorine abstraction with concomitant formation of dichloroketene, similar to the chemistry of α-iodoacetylrhodium complex as Cole-Hamilton reported,[23] although we have been unable to detect any species derived from dichloroketene.

To discuss the next insertion step (route 3), it is worth noting beforehand that coordinatively saturated complex **5**, either *cis* or *trans*, is also labile in two directions (Scheme 3). One is its configurational lability. According to Goggin and co-workers,[21] the stereochemistry of the major product formed in chlorination of *trans*-$RhCl(CO)(PMe_3)_2$ with chlorine depends on the polarity of the solvent, benzene preferring *mer,trans*-$RhCl_3(CO)(PMe_3)_2$ (***mer*,*trans*-5**) and dichloromethane ***fac*,*cis*-5**.[21,24] In our experiment, an authentic sample of ***fac*,*cis*-5** (synthesized in dichloromethane) dissolved in benzene displayed ^1H and ^{31}P NMR signals identical with those of ***mer*,*trans*-5**, and ***mer*,*trans*-5** (synthesized in benzene) dissolved in $CDCl_3$ displayed signals assignable to ***fac*,*cis*-5**, suggesting that *cis*-*trans* isomerization had taken place rapidly. The other lability we encountered is facile formation of a dinuclear rhodium complex. Upon recrystallization in a dichloromethane/hexane mixture, ***fac*,*cis*-5** and ***mer*,*trans*-5** were converted near quantitatively to known dimeric rhodium complex $[Rh(\mu\text{-}Cl)Cl_2(PMe_3)_2]_2$ (**6**),[25] the structure of which is interesting in that one rhodium has two mutually *cis* phosphines and the other *trans*, as verified unequivocally by X-ray diffraction as illustrated in Figure 1 although it displays a disorder at PMe_3 ligands.[26]

The *cis*−*trans* interconversion is envisaged to involve dissociation of a ligand, which provides an unoccupied coordination site, a prerequisite for alkyne insertion. Likewise, the formation of **5** proceeds via dissociation of CO leaving a vacant site. In the dinuclear rhodium complex formation, the vacant site is satisfied by bridging chlorines, but in the present catalysis, the site is available for an alkyne molecule toward insertion. Although we do not have convincing evidence for insertion of alkyne into a Cl−Rh bond, our previous observations[14,20] and following two experiments combined together indicate that route 3-i (Scheme 2) is reasonable. Thus, we ran a catalytic reaction under the standard conditions (130 °C, 12 h, in ethylbenzene) using a yellow powder obtained by mixing $RhCl_3$ and 2 equiv of P(*o*-Tol)$_3$ in ethanol and subsequent evaporation to see if the material could initiate the catalysis. The yield of **3a** was 28%, which was lower than that obtained using the $[RhCl(CO)_2]_2$ + 4P(*o*-Tol)$_3$ catalyst system (40%; entry 11, Table 1), but not too low to consider that even the chlororhodium species

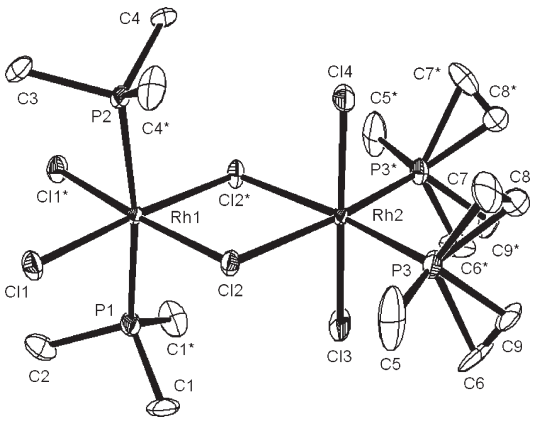


FIGURE 1. Molecular structure of **6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms were omitted for clarity.

is able to participate in the catalysis, if we admit the chlororhodium species being ill-defined.[27] In the other experiment, a solution of ***fac*,*cis*-5** and 1-octyne (approximadely 3 equiv) in chlorobenzene was heated at 130 °C for 3 h. Although PMe_3 was not a better perfoming ligand in the present catalysis (entry 18, Table 1), **3a** was formed in 27% yield based on Rh.[28,29]

As for the dimerization of the rhodium-bound β-chloroalkenyl ligand leading to 1,4-dichloro-1,3-butadiene formation, one can think mainly of the following two possibilities. First, the transformation is realized by reductive elimination of two β-chloroalkenyl ligands bonded to the same rhodium center. The pioneering work by Beletskaya and co-workers on metal-catalyzed halogenative dimerization of alkynes suggested such transformation of two β-iodo-(*E*)-alkenyl ligands bound to a single platinum center to (*E*,*E*)-1,4-diiodo-1,3-butadienes, although the β-iodo-(*E*)-alkenyl ligand in this case was formed via external attack of iodine to the coordinated triple bond.[13a,c] These authors were also able to cleanly generate [β-iodo-(*E*)-alkenyl]platinum

(23) Weston, W. S.; Cole-Hamilton, D. J. *Inorg. Chim. Acta* **1998**, *280*, 99.

(24) A similar observation was also reported by Intille for somewhat different rhodium complexes. See: Intille, G. M. *Inorg. Chem.* **1972**, *11*, 695.

(25) This compound appeared to be the same as a rhodium complex reported without detailed information of the stereochemistry. See ref 24.

(26) For similar complexes ligated by other phophine ligands, see: (a) Cotton, F. A.; Kang, S.-J.; Mandal, S. K. *Inorg. Chim. Acta* **1992**, *206*, 29. (b) Cotton, F. A.; Eglin, J. L.; Kang, S. J. *Inorg. Chem.* **1993**, *32*, 2332.

(27) In view of the yellow color of the material we obtained, we presume that it contained Rh(III) species, but the material might not be pure, which can be the origin of the somewhat low yield of **3a** as compared with the $[RhCl(CO)_2]_2$ + 4P(*o*-Tol)$_3$ catalyst system. Formation of Rh(II) species, which should be blue-green, can be generated even by a slight modification of the procedure and appears dependent on the ligand used. For instance, treatment of $RhCl_3$ with PPh(*o*-Tol)$_2$ was assumed to generate a dimeric Rh(II) species $[RhCl_2\{PPh(o\text{-}Tol)_2\}_2]_2$ or, less probably, a chlorine-bridged Rh(I)−Rh(III) mixed valence dinuclear species, like $[\{PPh(o\text{-}Tol)_2\}_2Rh(\mu\text{-}Cl)_2RhCl_2\{PPh(o\text{-}Tol)_2\}_2]$. On the other hand, another similar treatment with PPh_2(*o*-Tol) may have afforded a chlorine-bridged Rh(I) dimer $[RhCl\{PPh_2(o\text{-}Tol)\}_2]_2$. For details, see: (a) Sacco, A.; Ugo, R.; Moles, A. *J. Chem. Soc., A* **1966**, 1670. (b) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266. Even if the yellow powder we generated contains a dimeric Rh(II) species, one can anticipate that the dimeric Rh complex undergoes "oxidative addition" with Cl_3CCOCl to afford Cl-Rh(III) and $Cl_3CC(O)$-Rh(III) species, which are envisioned to enter the proposed catalytic cycle. Similar arguments are also possible for a chlorine-bridged Rh(I)−Rh(III) mixed valence dinuclear species and also for a chlorine-bridged Rh(I) dimer.

(28) Somewhat puzzling is the formation of another product, which appeared, in GCMS analysis, to be an isomer of **3a**, in some 5%. Although its structure has not been fully characterized, this is the only case where an regio- or stereoisomer of **3a**, if any, was formed.

(29) In a similar experiment, to $[Rh(\mu\text{-}Cl)Cl_2(PMe_3)_2]_2$ (**6**) (8.2 mg, 0.046 mmol with respect to rhodium atom) and toluene-d_8 (0.5 mL) placed in an NMR tube was added 1-octyne (7 μL, 0.046 mmol) and the mixture was heated at 110 °C for 15 h. Analysis by ^1H NMR spectroscopy, after addition of 1,1,2,2-tetrachloroethane (5.4 mg) as internal standard, revealed (*Z*,*Z*)-7,10-dichlorohexadeca-7,9-diene (**3a**) being formed in 4% yield.

and bis[β-iodo-(*E*)-alkenyl]platinum complexes as discrete intermediates, which clearly indicates high stereospecificity of the reductive elimination. The other possibility is disproportionation of (β-chloroalkenyl)$RhCl_2$ species, which produces (β-chloroalkenyl)$_2$RhCl and $RhCl_3$ species. There have been a plethora of publications reporting disproportionation of this type.[30] Whitesides and co-workers reported stereospecific thermolysis of (*E*)- and (*Z*)-propen-1-yl copper and silver complexes forming 2,4-hexadiene with retention of configuration at the double bonds. They have proposed disproportionation and other possibilities like bimolecular reductive elimination.[31] The latter possibility cannot be excluded in our reaction and remains to be studied further.

In conclusion, the reaction of terminal alkynes with trichloroacetyl chloride has proved to provide an operationally easy and high yielding access to (*Z*,*Z*)-1,4-dichloro-1,3-butadienes stereo- and regioselectively. Further mechanistic study on this and related catalysis is in progress.

Experimental Section

Typical Procedure for the Reaction of Alkyne with Trichloroacetyl Chloride: The Reaction with 1-Octyne Affording (*Z*,*Z*)-7,10-Dichlorohexadeca-7,9-diene (3a). To a mixture of $[RhCl(CO)_2]_2$ (9.7 mg, 0.025 mmol), $PMes_3$ (39 mg, 0.10 mmol), and chlorobenzene (1.0 mL) placed in a 5 mL Schlenk tube were added trichloroacetyl chloride (180 mg, 1.0 mmol) and 1-octyne (110 mg, 1.0 mmol). The mixture was heated at 130 °C for 3 h. After being cooled to room temperature, the resulting mixture was analyzed by ^{1}H NMR spectroscopy after addition of 1,1,2,2-tetrachloroethane (24.3 mg) as internal standard and $CDCl_3$ (1.0 mL) to reveal the formation of (*Z*,*Z*)-7,10-dichlorohexadeca-7,9-diene **3a** in 91% NMR yield. Evaporation left a brown residue, which was subjected to preparative TCL (silica gel, hexane), leading to isolation of **3a** (127.6 mg, 88%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (s, 1H), 2.39 (t, J = 7.54 Hz, 4H), 1.54 (quart, J = 7.26 Hz, 4H), 1.29−1.09 (m, 12H), 0.86 (t, J = 6.80 Hz, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 133.7, 120.3, 39.9, 31.5, 28.3, 27.5, 22.5, 14.1; IR (neat, cm^{-1}) 1605; GCMS (70 eV) *m*/*z* (relative intensity) 290 ([M]$^+$, 100), 255 (4), 206 (8), 185 (12), 149 (14), 135 (18), 109 (40), 95 (21), 81 (21), 67 (13); HRMS (EI) calcd for $C_{16}H_{28}Cl_2$ *m*/*z* 290.1568, found 290.1566.

(*Z*,*Z*)-1,4,7,10-Tetrachloro-4,6-decadiene (3c). Isolated by preparative TLC (silica gel, hexane): colorless oil; bp 210−215 °C/0.1 mmHg (Kugelrohr); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (s, 2H), 3.55 (t, J = 6.31 Hz, 4H), 2.59 (t, J = 7.08 Hz, 4H), 2.07 (quint-like, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 136.1, 121.4, 43.5, 36.9, 30.0; IR (neat, cm^{-1}) 1604; GCMS (70 eV) *m*/*z* (relative intensity) 276 ([M]$^+$, 100), 239 (27), 211 (34), 175 (17), 167 (29), 139 (78), 113 (15), 108 (23). Anal. Calcd for $C_{10}H_{14}Cl_4$: C, 43.51; H, 5.11. Found: C, 43.41; H, 4.91.

(*Z*,*Z*)-5,8-Dichloro-5,7-dodecadienedinitrile (3d). Isolated by preparative TLC (silica gel, hexane/acetone = 90/10): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.49 (s, 2H), 2.58 (t, J = 7.12 Hz, 4H), 2.36 (t, J = 7.08 Hz, 4H), 1.98 (quart-like, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 135.5, 121.9, 118.9, 38.2, 23.0, 15.9. IR (neat, cm^{-1}) 2247, 1604. GCMS (70 eV) *m*/*z* (% relative intensity) 256 ([M]$^+$, 65), 221 (39), 185 (40), 180 (100), 166 (17), 144 (35). HRMS (EI) calcd for $C_{12}H_{14}Cl_2N_2$ *m*/*z* 256.0534, found 256.0530.

Dimethyl (*Z*,*Z*)-5,8-dichloro-5,7-dodecadienedioate (3e). Isolated by preparative TLC (silica gel, hexane/acetone = 95/5), pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (s, 2H), 3.64 (s, 6H), 2.43 (t, J = 7.16 Hz, 4H), 2.30 (t, J = 7.40 Hz, 4H), 1.89 (m, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 173.4, 136.6, 121.1, 51.5, 38.9, 32.5, 22.5; IR (neat, cm^{-1}) 1734, 1603; GCMS (70 eV) *m*/*z* (relative intensity) 322 ([M]$^+$, 57), 286 (28), 255 (60), 219 (100), 186 (29), 174 (31), 139 (26), 117 (26); HRMS (EI) calcd for $C_{14}H_{20}Cl_2O_4$ *m*/*z* 322.0739, found 322.0732.

(*Z*,*Z*)-1,6-Diphenyl-2,5-dichloro-2,4-hexadiene (3f). Isolated by column chromatography (silica gel, hexane/methyl *tert*-butyl ether = 10/1): colorless solid; mp 125.9−126.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.23 (m, 10H), 6.52 (s, 2H), 3.71 (s, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.3, 137.2, 129.4, 128.9, 127.4, 122.2, 46.5; IR (KBr, cm^{-1}) 1603; GCMS (70 eV) *m*/*z* (relative intensity) 302 ([M]$^+$, 100), 267 (20), 231 (26), 211 (22), 125 (22), 91 (97); HRMS (EI) calcd for $C_{18}H_{16}Cl_2$ *m*/*z* 302.0629, found 302.0630.

(*Z*,*Z*)-1,4-Dichloro-1,4-bis(trimethylsilyl)-1,3-butadiene (3g). Isolated by preparative TLC (silica gel, hexane): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (s, 2H), 0.23 (s, 18H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.6, 130.5, −2.4; ^{29}Si{^{1}H} NMR (60 MHz, $CDCl_3$) δ 0.17; IR (neat, cm^{-1}) 1604. GCMS (70 eV) *m*/*z* (relative intensity) 266 ([M]$^+$, 26), 143 (33), 123 (42), 93 (63), 73 (100); HRMS (EI) calcd for $C_{10}H_{20}Cl_2Si_2$ *m*/*z* 266.0481, found 266.0480.

(*Z*,*Z*)-1,4-Dichloro-1,4-bis(1-cyclohexenyl)-1,3-butadiene (3h). Isolated by preparative TLC (silica gel, hexane): colorless solid; mp 95.8−97.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 2H), 6.48 (t, J = 1.8 Hz, 2H), 2.34−2.20 (m, 8H), 1.74−0.58 (m, 8H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.1, 133.6, 130.6, 119.1, 31.6, 26.3, 26.1, 22.7; IR (KBr, cm^{-1}) 1633; GCMS (70 eV) *m*/*z* (relative intensity) 282 ([M]$^+$, 55), 247 (100), 211 (89), 179 (91), 131 (15), 81 (49); HRMS (EI) calcd for $C_{16}H_{20}Cl_2$ *m*/*z* 282.0942, found 282.0940.

(*Z*,*Z*)-1,4-Dichloro-1,4-di(4-methoxyphenyl)-1,3-butadiene (3j). The reaction mixture was evaporated, and the residue was extracted with hot hexane. Evaporation of the extract gave an analytically pure sample: pale yellow solid; mp 193.2−194.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 7.2 Hz, 4H), 7.21 (s, 2H), 6.92 (d, J = 7.2 Hz, 4H), 3.85 (s, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 160.3, 135.0, 130.2, 127.8, 120.4, 113.8, 55.4; IR (neat, cm^{-1}) 1605. GCMS (70 eV) *m*/*z* (relative intensity) 334 ([M]$^+$, 77), 299 (44), 264 (100); HRMS (EI) calcd for $C_{18}H_{16}Cl_2O_2$ *m*/*z* 334.0527, found 334.0528. Anal. Calcd for $C_{18}H_{16}Cl_2O_2$: C, 64.49; H, 4.81. Found: C, 64.18; H, 5.23.

(*Z*,*Z*)-1,4-Dichloro-1,4-di(4-fluorophenyl)-1,3-butadiene (3l). Isolated by exactly the same procedure as for **3j**: colorless needles; mp 143.2−144.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (AB spin system, $^3J_{H-H}$ = 7.70 Hz, $^4J_{H-F}$ = 4.9 Hz, 4H), 7.22 (s, 2H), 7.09 (dd, $^3J_{H-H}$ = 7.70 Hz, $^3J_{F-H}$ = 8.61 Hz, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.3 (d, J = 252.2 Hz), 135.0, 133.3 (d, J = 3.54 Hz), 128.4 (d, J = 8.45 Hz), 121.6, 115.5 (d, J = 20.6 Hz); IR (neat, cm^{-1}) 1597; GCMS (70 eV) *m*/*z* (relative intensity) 310 ([M]$^+$, 100), 275 (51), 240 (94), 220 (18). Anal. Calcd for $C_{16}H_{10}Cl_2F_2$: C, 61.76; H, 3.24. Found: C, 61.96; H, 3.54.

(*Z*,*Z*)-1,4-Dichloro-1,4-di(2-thienyl)-1,3-butadiene (3m). Isolated by preparative TLC (silica gel, hexane), yellow needles, mp 127.3−127.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (dd, J = 1.15, 3.77 Hz, 2H), 7.30 (dd, J = 1.15, 5.02 Hz, 2H), 7.18 (s, 2H), 7.03 (dd, J = 3.77, 5.02 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.5, 129.2, 128.2, 127.2, 126.3, 120.2. IR (neat, cm^{-1}) 1575. GCMS (70 eV) *m*/*z* (% relative intensity) 286 ([M]$^+$,

(30) (a) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547. (b) Carvajal, J.; Muller, G.; Sales, J.; Solans, X.; Miravitlles, C. *Organometallics* **1984**, *3*, 996. (c) Ozawa, F.; Fujimori, .; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144. (d) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253. (e) van Asselt, R.; Elsevier, C. J. *Organometallics* **1994**, *13*, 1972. (f) Suzaki, Y.; Yagyu, T.; Osakada, K. *J. Organomet. Chem.* **2007**, *692*, 326. (g) Wakioka, M.; Nagao, M.; Ozawa, F. *Organometallics* **2008**, *27*, 602.

(31) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.

39), 251 (35), 216 (100), 171 (15). HRMS (FAB, matrix = 2-nitrobenzyl alcohol) calcd for $C_{12}H_9Cl_2{}^{32}S_2$ (value for $[M + H]^+$) m/z 286.9523, found 286.9523.

***mer*,*trans*-RhCl$_3$(CO)(PMe$_3$)$_2$ (*mer*,*trans*-5).** ^{1}H NMR (400 MHz, C_6D_6) δ 1.31 (t, J_{P-H} = 3.91 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ −2.28 (d, J_{Rh-P} = 72.3 Hz); IR (KBr, cm^{-1}) 2085 (ν_{CO}). An authentic sample synthesized by us according to the Goggin's procedure[21] displayed ^{1}H and $^{31}P\{^1H\}$ NMR signals at δ 1.31 (t, J_{P-H} = 4.00 Hz) and at δ −2.30 (d, J_{Rh-P} = 72.3 Hz), respectively.

Conversion of *mer*,*trans*-RhCl$_3$(CO)(PMe$_3$)$_2$ (*mer*,*trans*-5) to [Rh(μ-Cl)Cl$_2$(PMe$_3$)$_2$]$_2$ (6). *mer*,*trans*-RhCl$_3$(CO)(PMe$_3$)$_2$ (***mer*, *trans*-5**) obtained by the reaction of *trans*-RhCl(CO)(PMe$_3$)$_2$ with trichloroacetyl chloride[22] was recrystallized from dichloromethane/hexane (95/5) to afford brown crystals. The solvent was removed with a syringe, and the crystals were rinsed with hexane and dried to furnish [Rh(μ-Cl)Cl$_2$(PMe$_3$)$_2$]$_2$ (**6**; 37.8 mg, 88%), brown crystals, mp 248.3 °C (under nitrogen, dec) (lit.[24] mp 250−254 °C dec).

[Rh(μ-Cl)Cl$_2$(PMe$_3$)$_2$]$_2$ (6). This compound has been documented without spectral data,[24] which are as follows: ^{1}H NMR 400 MHz, $CDCl_3$) δ 1.87 (virtual t, J_{P-H} = 3.92 Hz, 18H), 1.64 (d, J_{P-H} = 11.7 Hz, 18H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 15.7 (d, J_{C-P} = 20.6 Hz), 12.6 (virtual t, J_{C-P} = 15.8 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 25.1 (d, J_{Rh-P} = 113.1 Hz), −4.5 (d, J_{Rh-P} = 80.1 Hz).

X-ray Analysis of [Rh(μ-Cl)Cl$_2$(PMe$_3$)$_2$]$_2$ (6). Single crystals were obtained from a CH_2Cl_2/hexane (95/5) solution. A brown crystal (= 0.20 × 0.10 × 0.10 mm) was used for X-ray diffraction data collection on a diffractometer with Mo Kα radiation (= 0.7107 Å). Atom C8 was refined isotropically. Crystal data for **5**: $C_{12}H_{30}Cl_6P_4Rh_2$, M = 716.79, orthorhombic, *Pnma* (#62), a = 11.217(5) Å, b = 13.036(6) Å, c = 17.985(9) Å, V = 2360(2) Å^3, Z = 4, D_{calc} = 1.810 g/cm^3. GOF = 0.883, R ($I > 3.00\sigma(I)$) = 0.0416, Rw ($I > 3.00\sigma(I)$, all reflections) = 0.0602. Selected bond distances and angles are summarized in Tables S2-1 and S2-2 in the Supporting Information.

Reaction of *fac*,*cis*-RhCl$_3$(CO)(PMe$_3$)$_2$ (*fac*,*cis*-5) with 1-Octyne. A mixture of the rhodium complex (3.8 mg, 9.8 × 10^{-3} mmol) and 1-octyne (3.1 mg, 0.028 mmol) in chlorobenzene (0.5 mL) was heated at 130 °C for 3 h in an NMR tube, cooled to room temperature, and analyzed, after addition of *n*-tetradecane (3.0 μL; internal standard), by ^{1}H NMR spectroscopy to reveal **3aA** and **3aA′** being formed in 27 and 5% yield, respectively.

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Supporting Information Available: Experimental details, NMR spectra of **3a**−**m** and crystallographic data for **3f** and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.