Organometallics 1983, *2*, 1382-1385

Cumulenes as Ligands. Heterobimetallic η^2-Butatriene Complexes Containing both a Main-Group Metal and Rhodium

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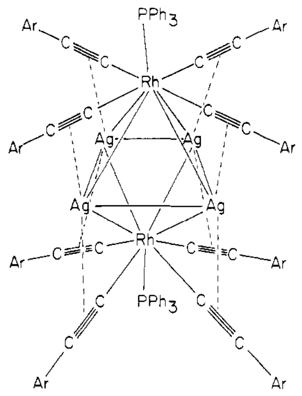
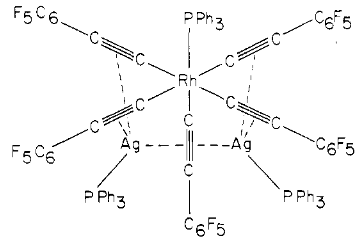
The interaction of Si-, Ge-, and Sn-functionalized butatrienes with Wilkinson's catalyst produced five new rhodium π complexes, in moderate to good yields. These compounds are all air-stable, crystalline solids, which exhibit some degradation in chlorocarbon solution over a period of days. The IR and ^{1}H NMR spectra of these complexes show that they are structurally analogous to the recently reported rhodium complexes of hydrocarbon butatrienes. The ^{31}P NMR spectra indicate that these complexes are in general diastereomeric mixtures. There is no evidence of insertion of the rhodium fragment into the group 4 metal–carbon bond. The butatriene ligand can be freed from the complexes by exposure to carbon monoxide. These results are discussed in detail.

In a previous paper[1] we presented a simple high-yield synthesis of (η^2-butatriene)rhodium complexes from Wilkinson's catalyst, where the butatrienes used were all hydrocarbons. Here we wish to report the application of this methodology to the formation of some novel heterobimetallic complexes from group 4 metal-substituted butatrienes.

In general, rhodium heterobimetallics (that is, complexes which have rhodium and some other metal sharing one or more carbon ligands) are quite rare. Some silver rhodium acetylide complexes have been reported by Bruce and co-workers,[2,3] with an X-ray structure of **3** having been done by Churchill and DeBoer.[2,4] Copper analogues to **1–3** are also known.[5] Abel and co-workers studied the interaction of bis(dicarbonylchlororhodium) (**4**) with 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**5**) and isolated two π complexes (**6** and **7**).[6] Several vinylsilanes have been complexed to rhodium,[7] but complexes of allenylsilanes or the analogous germanes or stannanes are unknown.



1, Ar = C_6H_5
2, Ar = C_6F_5



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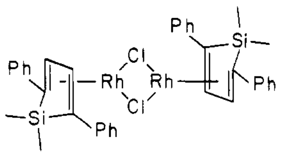

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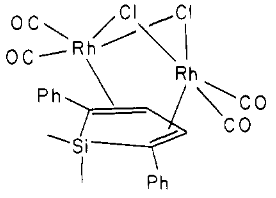

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The X-ray structure of complex **8** clearly showed that the rhodium was bound to the central bond of the butatriene.[1] Wilkinson's catalyst does not oxidatively insert into the cyclopropane ring of the butatriene, although some rhodium complexes do insert into three-membered rings.[8] The situation changes significantly when butatrienes **11–15** are considered. Not only are cumulenes **11–15** more stable than those used to produce **8–10**,[9] but also the possibility of different structures in the final complexes increases. For instance, there are three possible rhodium oxidative insertions, namely, at the (a) cumulene C–H, (b) C(sp^3)–M, or (c) C(sp^2)–M bonds (Figure 1). Likewise, π complexation can occur at more than one site. Furthermore, there is now the possibility of diastereomers from complexation about the central olefin of the cumulene (Figure 2). These varied possible outcomes provide a unique chance to test the selectivity of the rhodium(I) fragment upon encountering a multifunctional ligand.

Results and Discussion

The reaction of butatrienes **11–15** with Wilkinson's catalyst, chlorotris(triphenylphosphine)rhodium (**16**), for 1–2 h at room temperature in benzene led to the formation

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[1] Stang, P. J.; White, M. R.; Maas, G. *Organometallics* 1983, *2*, 720–725.

[2] Abu Salah, O. M.; Bruce, M. I.; Churchill, M. R.; DeBoer, B. G. *J. Chem. Soc., Chem. Commun.* 1974, 688–689.

[3] Abu Salah, O. M.; Bruce, M. I. *Aust. J. Chem.* 1977, *30*, 2639–2646.

[4] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* 1975, *14*, 2630–2639.

[5] Abu Salah, O. M.; Bruce, M. I. *Aust. J. Chem.* 1976, *29*, 531–541.

[6] Abel, E. W.; Blackmore, T.; Whitley, R. J. *J. Chem. Soc., Dalton Trans.* 1976, 2484–2489.

[7] (a) Pannell, K. H.; Bassindale, A. R.; Fitch, J. W. *J. Organomet. Chem.* 1981, *209*, C65–C68. (b) Fitch, J. W.; Osterloh, W. T. *Ibid.* 1981, *213*, 493–502.

[8] (a) Roundhill, D. M.; Lawson, D. N.; Wilkinson, G. *J. Chem. Soc. A* 1968, 845–849. (b) Cassar, L.; Halpern, J. *Chem. Commun.* 1970, 1082–1083.

[9] (a) Stang, P. J.; White, M. R. *J. Am. Chem. Soc.* 1981, *103*, 5429–5433. (b) Stang, P. J.; Fisk, T. E. *Ibid.* 1980, *102*, 6813–6816.

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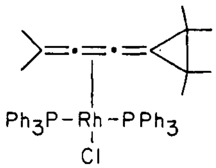

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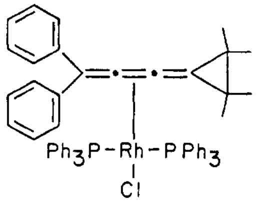

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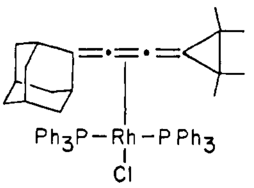

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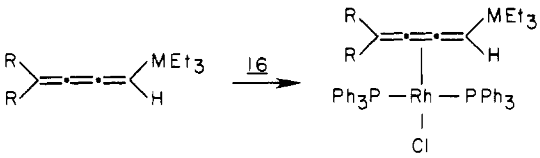
of complexes **17–21**. These compounds are all air-stable, crystalline solids and are isolated by chromatography on unactivated silica gel using chloroform/carbon tetrachloride mixtures. They are further purified by recrystallization from benzene/hexanes, where no care is taken to exclude oxygen. Table I summarizes the properties of complexes **17–21**.



11: R = CH_3 ; M = Si
12: R = C_6H_5 ; M = Si
13: R = CH_3 ; M = Ge
14: R = C_6H_5 ; M = Ge
15: R = C_6H_5 ; M = Sn

17: R = CH_3 ; M = Si
18: R = C_6H_5 ; M = Si
19: R = CH_3 ; M = Ge
20: R = C_6H_5 ; M = Ge
21: R = C_6H_5 ; M = Sn

16 = $[(C_6H_5)_3P]_3RhCl$

The yields are generally moderate to high (71–94%), with the lowest being 44% for the tin-containing compound **21**. The complexes all exhibit a weak absorption in the IR in the region of 2100–2360 cm^{-1}, as well as the usual absorptions due to coordinated triphenylphosphine. The fast atom bombardment (FAB) mass spectra of complexes **17–21** give some useful structural information. Four of the five spectra show a weak but distinct molecular ion, and all show ions that indicate loss of chlorine and also loss of the butatriene. The isotopic abundance patterns in **19–21** can be clearly seen in the $(M - Cl)^+$ region. The base peak in each spectrum is due to the ion $((C_6H_5)_3P)_2Rh^+$ (m/z 627). The ^1H NMR spectra clearly show the ethyl groups of the triethylmetal functions, the methyl groups of complexes **17** and **19**, and the hydrogen attached to the end of the cumulene. However, in **18**, **19**, and **20**, this single proton manifests itself by several peaks, and in **18** and **20** there is some apparent coupling.

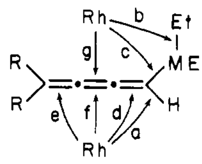


Figure 1. Possible sites for the rhodium fragment from Wilkinson's catalyst to attach to butatrienes **11–15**. The insertion modes are a, b, and c, while the π complexation ones are d through g.

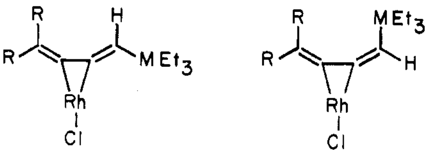


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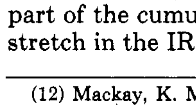
Figure 2. Possible diastereomers of complexes **17–21**. Structure **22** is the *Z* isomer, while **23** is the *E* isomer. The triphenylphosphines are above and below the rhodium.

The question of oxidative insertions of the rhodium can now be addressed. The first possibility, namely, C–H insertion, is ruled out by the ^1H NMR spectra, since the product of such an insertion must be a rhodium hydride species. Although the apparent small coupling constants in complexes **18** and **20** are about the right value for a $^1J(Rh–H)$,[10] the shift of the lone proton in **17–21** is about 15 ppm too far downfield to be directly attached to rhodium(III).[11] The other insertion possibilities are analogous to the insertion of rhodium or iridium into M–H bonds (M = Si, Ge, Sn)[12] or of platinum into Sn–C(sp^2) bonds.[13] Although the ^1H NMR spectra do not give any definitive clues about whether the rhodium fragment has oxidatively inserted into one of the main-group metal–carbon bonds, the FAB mass spectra do. The lack of any apparent loss of C_2H_5 or $M(C_2H_5)_3$ from any of these complexes argues against insertion structure, while the pattern that does emerge from the FAB spectra (molecular ion, loss of chloride, loss of butatriene, loss of triphenylphosphine) indicates that the butatriene ligand is structurally intact while bound to rhodium. Indeed, this is the case, since the cumulene ligand can be released intact upon exposure of complexes **17–21** to carbon monoxide for a few minutes. This last result clearly rules out the oxidative addition possibilities.

The choices that remain include π complexes **22–25**. One of these (**24**) is ruled out by the ^1H NMR spectra, since having the rhodium bound to the same double bond as the lone hydrogen should induce a considerable upfield shift of this proton, as in rhodium–ethylene π complexes.[14] In structure **25**, one would predict that the uncomplexed part of the cumulene backbone would exhibit an allenic stretch in the IR, but in **17–21** no such absorption is ap-



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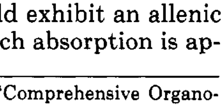

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[11] Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1971**, *15*, 59–61.

[12] Mackay, K. M.; Nicholson, B. K. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 43, pp 1091–1094.

[13] (a) Cardin, C. J.; Cardin, D. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 767–779. (b) Eaborn, C.; Odell, K. J.; Pidcock, A. *Ibid.* **1978**, 357–368. (c) Eaborn, C.; Odell, K. J.; Pidcock, A. *Ibid.* **1978**, 1288–1294. (d) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Organomet. Chem.* **1978**, *146*, 17–21. (e) Eaborn, C.; Kundu, K.; Pidcock, A. *Ibid.* **1979**, *170*, C18–C20.

[14] For low-valent, uncharged rhodium–ethylene complexes, the hydrogens are found at δ 0.9–4.6, while free ethylene is at δ 5.3. One example: Herberhold, M.; Kreiter, C. G.; Widerstaz, G. O. *J. Organomet. Chem.* **1976**, *120*, 103–130.

Table I. Properties of (Cumulene)rhodium Complexes 17-21

compd	yield,[a] %	mp,[b] °C	IR,[c] ν_{max}, cm^{-1}	FAB MS,[d] *m/z* (%)	^{1}H NMR,[e] δ (H's, mult)
17	62.4	154-156	3055, 2955, 2905, 2875, 2235, 1805, 1585, 1480, 1435, 1095, 920, 735, 695	856 (M^+, 1), 821 (26), 662 (56), 627 (100), 595 (2)	0.30 (6, m), 0.67 (9, t), 1.17 (3, s), 1.82 (3, s), 5.43 (0.2, s), 5.72 (0.8, s), 7.3-8.0 (30, m)
18	75.1	158-160	3055, 2950, 2870, 2105, 1765, 1480, 1435, 1095, 745, 695	980 (M^+, 4), 945 (34), 419 (3), 662 (29), 627 (100)	−0.21-1.0 (m, 15), 5.28 (0.3, d, J = 3 Hz), 5.93 (0.7, d, J = 4 Hz), 7.0-7.9 (40, m)
19	94.3	185.5-188	3050, 2950, 2900, 2870, 2360, 1800, 1585, 1480, 1435, 1095, 745, 695	902 (M^+, 2), 867 (27), 662 (46), 627 (100)	0.43-1.0 (15, m), 1.18 (3, s), 1.82 (3, s), 5.11 (0.25, s), 5.82 (0.75, s), 7.3-8.1 (30, m)
20	71.0	163-165	3050, 2945, 2865, 2220, 1770, 1480, 1435, 1095, 745, 695	1024 (M^+, 4), 991 (23), 662 (45), 627 (100)	0.13 (6, q), 0.71 (9, t), 6.21 (0.8, d, J = 3 Hz), 6.46 (0.2, d, J = 2 Hz), 7.2-8.0 (40, m)
21	44.0	112-115	3050, 2960, 2920, 2860, 2100, 1725, 1480, 1430, 1260, 1095, 745, 695	1037 (16), 662 (24), 627 (100)	0.15-1.10 (15, m), 6.05 (1, s), 7.05-7.65 (40, m)

[a] Isolated yields. [b] All dec. [c] KBr pellet. [d] 18-Crown-6 and tetraglyme (4:1) dispersant. [e] $CDCl_3$, Me_4Si internal standard.

parent. Furthermore, an inspection of molecular models quickly leads to the conclusion that the two R groups of **25** would lie well within the steric exclusion cones of the triphenylphosphines,[15] regardless of the orientation of the ligand with respect to the coordination plane. These two facts combine to exclude structure **25** from consideration.

The question of stereoisomers in complexes **17–21** is not a trivial consideration, since the central π bond is in the same plane as the four substituents of the butatriene. A simplistic steric argument would lead one to conclude that the rhodium would approach the central double bond from the side which has the hydrogen substituent, leading to the *E* isomer **23** (Figure 2). Initially this is the result we expected, but an inspection of molecular models with a nonlinear complexed butatriene[16] suggests that the trialkylmetal substituent is being forced near the methyl or phenyl substituent on the other end of the ligand in the *E* isomer. The *Z* isomer **22** brings a hydrogen toward the methyl or phenyl group but leaves the trialkylmetal group near the steric cones of the two triphenylphosphines.

The ^{1}H NMR spectra of complexes **17–21** indicate that some of these compounds do exist as diastereomeric mixtures. Although complex **21** shows only one isomer to the limit of NMR determination, the other four compounds each show two isomers in varying ratios.

The ^{1}H NMR spectra were very encouraging, but we sought corroboration in the ^{31}P NMR spectra. These data are listed in Table II. Figure 3 shows a typical ^{31}P NMR spectrum, in this case of complex **19**. This spectrum can best be explained as a mixture of diastereomers, where each isomer has the coordination plane of the rhodium perpendicular to the plane of the cumulene. This would lead to enantiotopic phosphorus atoms in the two phosphine ligands and a two-line spectrum for each stereoisomer due to the ^1J(Rh–P) coupling (^{103}Rh has a spin of $^1/_2$). Thus, the actual spectrum in Figure 3 arises from a superposition of two two-line spectra, with the integrated intensities giving the relative abundances of the two isomers. The same analysis for the remaining complexes gives the data in Table II.

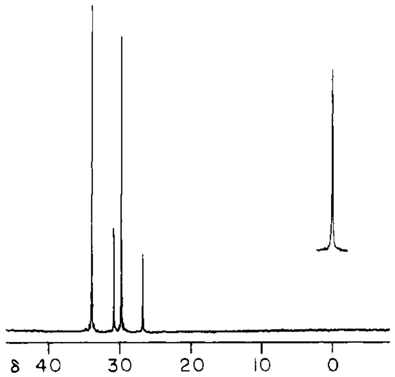

Figure 3. The 32.203-MHz ^{31}P NMR spectrum of complex **19**. Zero reference is external H_3PO_4 (85%).

Table II. ^{31}P NMR Characteristics of Complexes 17-21

	diastereomer A			diastereomer B		
compd	%	δ[a]	$^1J_{Rh-P}$[b]	%	δ	$^1J_{Rh-P}$
17	81	31.73	134.0	19	28.69	131.2
18	60	30.04	134.9	40	25.95	131.6
19	74	31.64	134.0	26	28.56	131.8
20	16	30.13	132.9	84	25.94	129.1
21	100	30.29	132.6			

[a] Shifts downfield relative to 85% H_3PO_4.

The question of which diastereomer gives rise to specific signals in the ^{1}H and ^{31}P NMR spectra of these complexes is more difficult to answer. Considering the trends from Table II, it becomes apparent that as the substituents on C-4 of the cumulene are changed from methyl to phenyl, the ratio of the two isomers shifts in favor of isomer B. In fact, in complexes **19** and **20** the predominant isomer switches from A to B. Since phenyl is larger than methyl, it would appear that this shift points toward isomer B as being the *Z* isomer of Figure 2. This assertion is supported by the ^{31}P NMR shifts and coupling constants in the following way. If one considers the *Z* isomer, then it is clear that the two phosphine ligands are crowded near the trialkylmetal group and might seek relief of this steric interference by increasing the Rh–P bond length slightly. This would lead to a slightly more "free ligand", with the

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[15] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956–2965.

[16] All of the known X-ray structures of η^2-butatriene complexes show that a complexed butatriene becomes bent by about 30° at each originally sp carbon. (a) Hagelee, L.; West, R.; Calabrese, J.; Norman, J. *J. Am. Chem. Soc.* **1979**, *101*, 4888–4892. (b) Bright, D.; Mills, O. S. *J. Chem. Soc. A* **1971**, 1979–1982.

shift becoming more like the shift in free triphenylphosphine (δ 7)[17] and the coupling constant tending toward zero. This argument does not take into account any possible hybridization changes around rhodium, however. Nonetheless, these arguments are consistent with and suggest, albeit do not prove, that diastereomer A of Table II is the *E* isomer, with isomer B being the *Z* one. Verification of the initial assignment awaits resolution of the mixtures and the appropriate X-ray crystallographic studies.

The structural details of the complexes **17**–**21** are thus completely described from the spectra. The rhodium atom is formally rhodium(I), with the chloride ligand trans to the butatriene ligand in a square-planar coordination scheme. Further, the butatriene is oriented perpendicular to the coordination plane of the rhodium, so that the two triphenylphosphines are enantiotopically related. The rhodium is bound to the central bond of the cumulene ligand, as one would expect from the known X-ray structures of butatriene complexes.[1,16] Thus, in spite of the potential for varied chemistry provided by butatrienes **11**–**15** in their interaction with Wilkinson's catalyst, the rhodium turns out to be quite selective, choosing only one type of reaction, namely, π complexation, and only one site, the central olefin of the butatriene. However, in at least four instances (**17**–**20**), the diastereoselection seems to be low, giving mixtures.

In conclusion, we have demonstrated an extension of our previously reported rhodium–butatriene complex synthesis into the area of heteroatom-substituted butatrienes and in doing so have simultaneously entered the realm of rhodium heterobimetallics and entered into questions of complex stereoisomerism. Complexes **17**–**21** are readily formed, air-stable, and in all but one case, a mixture of diastereomers. There is no evidence that the rhodium has inserted into the M–C(sp^2) (M = Si, G, Sn) bond, and all the spectral data are consistent with previously reported information. Further chemistry of these systems as well as extensions to other transition metals will be discussed in future reports.

Experimental Section

General Data. Melting points were recorded on a Mel-Temp capillary apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer and referenced to the 1601-cm^{-1} absorption of polystyrene. The ^{1}H NMR spectra were recorded on a Varian EM-390, FT-80, or SC-300 spectrometer, and ^{13}C NMR and ^{31}P NMR spectra were recorded on a Varian FT-80 or SC-300 spectrometer. Routine mass spectra were recorded on a VG Micromass 7070 mass spectrometer with DS2050 data system. Low-resolution, positive-ion fast atom bombardment (FAB) mass spectra were recorded on either a VG Micromass ZAB reverse-geometry mass spectrometer with a DS2035 data system, a Kratos MS950 mass spectrometer, or a Varian MAT 731 spectrometer fitted with an Iontech FAB gun. All FAB spectra were confirmed by oscillographic chart output. Elemental analyses for carbon, hydrogen, and phosphorus were performed by Galbraith Labs.

Materials. All commercial reagents were ACS reagent grade. Solvents were purified and rigorously dried immediately prior to use. Rhodium chloride hydrate was purchased from Strem Chemicals and used to make Wilkinson's catalyst.[18]

The Silicon-, Germanium-, and Tin-Functionalized Butatrienes (11–15). These compounds were prepared as reported by Stang and White.[9a] The only new compound in this series is 4,4-diphenyl-1-(triethylsilyl)-1,2,3-butatriene (**12**), which was prepared from the interaction of diphenylallenylidenecarbene with triethylsilane (5 equiv), yield 56% of a yellow-orange oil which freezes on standing at −10 °C: IR (neat film) 3055, 2955, 2910, 2875, 2040, 1595, 1445, 1240, 1005, 735, 695, 625 cm^{-1}; MS, *m/z* (%) 318 (M$^+$, 20.4), 289 (15.4), 261 (13.0), 233 (20.1), 231 (18.0), 217 (17.1), 182 (36.0), 105 (100); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 7.53–7.03 (m, 10 H), 5.97 (s, 1 H), 1.20–0.43 (m, 15 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 170.8, 163.7, 139.3, 132.4, 130.2, 129.5, 129.3, 128.6, 128.5, 128.2, 108.8, 7.24, 3.81.

General Procedure for the Formation of Rhodium π Complexes. The five complexes described below were prepared according to the general procedure reported recently.[1] The reaction times varied from 1 to 2 h. These complexes were chromatographed as described in the general procedure, but all were recrystallized from benzene/hexane at room temperature, due to the sensitivity of these compounds to extended contact with chlorocarbon solvents. All physical and spectral properties are reported in Tables I and II.

Bis(triphenylphosphine)chloro(4-methyl-1-(triethylsilyl)-1,2,3-pentatriene)rhodium (17). This complex was prepared from 185 mg (200 μmol) of **16** and 40.8 mg (210 μmol) of **11** by using the general procedure. The yield was 107 mg (62.4%) of yellow, feathery crystals: ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 134.87, 134.57, 134.26, 132.84, 131.77, 130.71, 129.87, 129.29, 128.57, 127.91, 127.60, 127.35, 127.11, 123.00, 109.48, 25.92, 25.00, 7.09, 4.28. Anal. Calcd for $C_{48}H_{52}ClP_2RhSi$: C, 67.25; H, 6.11; P, 7.18. Found: C, 67.56; H, 6.36; P, 7.18.

Bis(triphenylphosphine)chloro(4,4-diphenyl-1-(triethylsilyl)-1,2,3-butatriene)rhodium (18). This complex was prepared from 185 mg (200 μmol) of **16** and 66.9 mg (210 μmol) of **12**, yielding 142 mg (75.1%) of bright yellow needles. Anal. Calcd for $C_{58}H_{56}ClP_2RhSi$: C, 70.98; H, 5.75; P, 6.31. Found: C, 71.18; H, 6.01; P, 6.17.

Bis(triphenylphosphine)chloro(4-methyl-1-(triethylgermyl)-1,2,3-pentatriene)rhodium (19). This complex was prepared from 185 mg (200 μmol) of **16** and 50.2 mg (210 μmol) of **13**, yielding 170 mg (94.3%) of yellow-orange needles. Anal. Calcd for $C_{48}H_{52}ClGeP_2Rh$: C, 63.93; H, 5.81; P, 6.87. Found: C, 63.99; H, 5.82; P, 7.08.

Bis(triphenylphosphine)chloro(4,4-diphenyl-1-(triethylgermyl)-1,2,3-butatriene)rhodium (20). This complex was prepared from 185 mg (200 μmol) of **16** and 76.2 mg (210 μmol) of **14**, giving 144 mg (71.0%) of bright yellow, fine needles. Anal. Calcd for $C_{58}H_{56}ClGeP_2Rh$: C, 67.93; H, 5.50; P, 6.04. Found: C, 68.10; H, 5.40; P, 6.20.

Bis(triphenylphosphine)chloro(4,4-diphenyl-1-(triethylstannyl)-1,2,3-butatriene)rhodium (21). This complex was prepared from 185 mg (200 μmol) of **16** and 85.9 mg (210 μmol) of **15**, yielding 96 mg (44.0%) of deep red needles.

Reaction of Complexes 17–21 with Carbon Monoxide. These complexes were exposed to carbon monoxide as described previously.[1] In a typical reaction, 60 mg of complex **17** was used, giving 11 mg (79%) of butatriene **11** and 41.8 mg (91%) of bis(triphenylphosphine)carbonylrhodium. All complexes showed satisfactory release of the butatriene.

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Registry No. **11**, 79085-45-3; **12**, 86374-30-3; **13**, 79073-92-0; **14**, 79073-90-8; **15**, 79073-87-3; **16**, 14694-95-2; (*E*)-**17**, 86374-25-6; (*Z*)-**17**, 86420-13-5; (*E*)-**18**, 86374-26-7; (*Z*)-**18**, 86420-14-6; (*E*)-**19**, 86374-27-8; (*Z*)-**19**, 86420-15-7; (*E*)-**20**, 86374-28-9; (*Z*)-**20**, 86420-16-8; (*E*)-**21**, 86374-29-0.

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