Rhodium Complexes of 1,4-Disubstituted-1,2,3-butatrienes: Their Preparation and Reactivity

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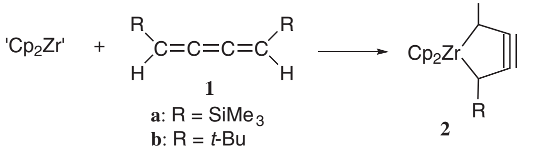
The 1,4-disubstituted butatrienes, (*Z*)-R-CH=C=C=CH-R (**1**, R = $SiMe_3$, *t*-Bu), reacted with $RhCl(PAr_3)_3$ (Ar = Ph, *p*-tolyl) to give rhodium-(*Z*)-butatriene complexes **3**. The butatrienes coordinated to Rh with the central double bond in an η^2-fashion. (*Z*)-Butatrienes on **3** isomerized to (*E*)-form at 70 °C to afford (*E*)-butatriene complexes **4** with excellent *E*/*Z* ratios (*E*/*Z* = 97/3–99/1). The molecular structure of **4b** (R = $SiMe_3$, Ar = *p*-tolyl) was determined by X-ray diffraction analysis. Hydrosilation of **1** was catalyzed by rhodium complexes to give allenes as major products accompanied by 1,3-dienes as minor ones, which are results of 2,1-addition and 2,3-*anti*-addition of the silane.

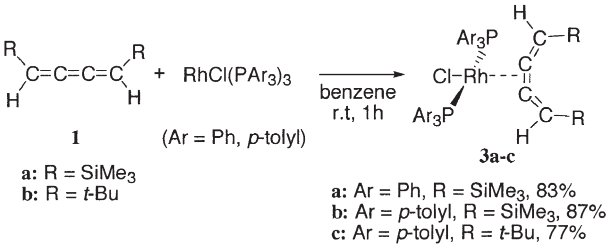
1,2,3-Butatrienes have long attracted organometallic chemists because of their highly unsaturated structure.[1–4] However, reactivity and transformation of the coordinated butatrienes on metal complexes have been rarely described,[5,6] although some catalytic reactions were reported.[7–9] Besides, most examples described transition metal complexes of 1,1,4,4-tetrasubstituted butatrienes. There have been only a few reports on transition metal complexes of 1,4-disubstituted butatrienes probably because of their unavailability.[10] Straightforward and highly selective synthesis of (*Z*)-R–CH=C=C=CH–R (**1a**: R = Me_3Si, **1b**: R = *t*-Bu) from 1-alkynes in the presence of ruthenium catalysts was reported from our laboratory.[11–13] This prompted us to study the reactivity of (*Z*)-1,4-disubstituted butatrienes with transition metal complexes.



(1)

We recently reported the preparation of zirconocene complexes of **1**. Their structures are 1-zirconacyclopent-3-ynes (**2**) that are the first isolated and structurally characterized five-membered cyclic alkynes (Eq 1).[14] In the most of known mononuclear butatriene complexes, butatrienes coordinated to metals in an η^2-π-coordination mode.[15] It must be of interest to examine if **1** gives a metallacyclopentyne or an η^2-π-complex with other metals, in particular, late-transition metals. Herein we report the synthesis of rhodium-1,4-disubstituted butatriene complexes, *E*/*Z* isomerization of **1** on the metal, and rhodium-catalyzed reactions of **1**.

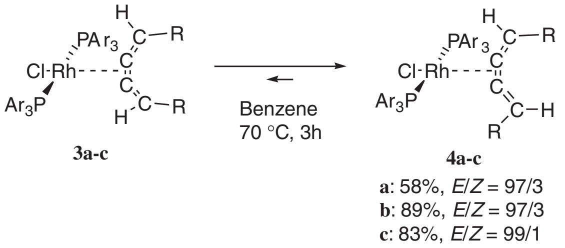
Butatriene **1** was mixed with an equimolar rhodium complex, $RhCl(PAr_3)_3$ (Ar = Ph, *p*-tolyl), in benzene at room temperature. After stirring for 1 h, the formation of butatriene complex **3** was observed by NMR spectroscopy in good yields (Scheme 1).[16]



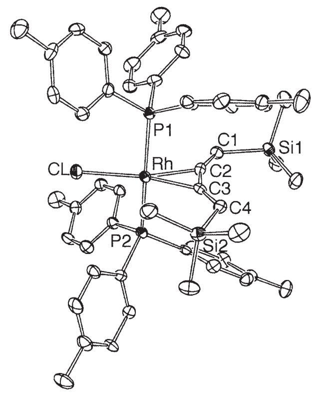
Scheme 1. Formation of Rh-(*Z*)-butatriene complexes.

Quaternary cumulene carbons (^{13}C NMR: **1a**: 182.99, **1b**: 160.17 ppm) appeared upfield owing to coordination to rhodium (**3a**: 156.97, **3b**: 158.60, **3c**: 131.47 ppm), and methines in the butatrienes at the sp^2-carbon region. Two trimethylsilyl (**3a**,**b**) or *tert*-butyl (**3c**) groups, methines, and quaternary carbons in **3** were observed as single signals showing their symmetrical structure. These results indicated that butatrienes **1** coordinated to rhodium with the central double bond in an η^2-fashion as well as the known rhodium-butatriene complexes.[3,17–19] X-ray diffraction analysis of **3b** supported this structure although the refinement was not satisfactory because of disorder observed in the solvated diethyl ether molecule. The butatriene moiety was slightly bent out and the trimethylsilyl groups were located away from the metal.

To our interest, coordinated (*Z*)-butatriene moieties in **3** isomerized to an (*E*)-form by heating in benzene at 70 °C for 3 h to give (*E*)-butatriene complexes **4** (Scheme 2). ^1H and ^{13}C NMR spectroscopy showed that four carbons in the butatriene unit are unequivalent.[20] Figure 1 illustrates the molecular structure of **4b**.[21] The butatriene bonds to rhodium in an η^2-fashion as well as **3b**, and other structural features were similar to the reported complexes. It should be noted that the *E*/*Z* ratios (**4**/**3**) in equilibria are extremely high (97/3–99/1). Similar equilibrium was also observed in the zirconium complexes **2**. The ratio, however, was 3/1–9/1. It is probably due to steric repulsion between bulky trimethylsilyl or *tert*-butyl groups in **3**. To the best of our knowledge, this is the first example of *E*/*Z* isomerization of π-coordinated butatrienes on transition metals, although its mechanism is still vague.



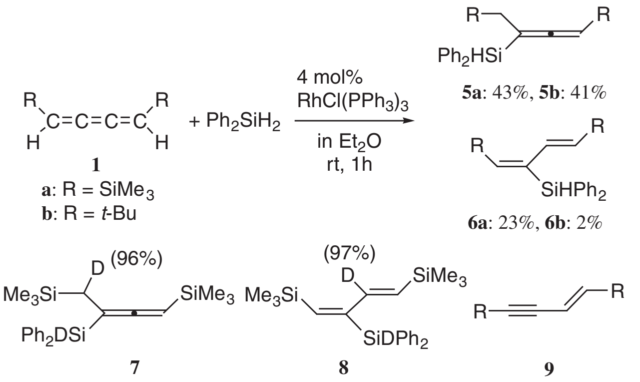
Scheme 2. Isomerization of butatrienes on Rh complexes.



Rh-C2 2.016(5)
Rh-C3 2.021(5)
C1-C2 1.338(7)
C2-C3 1.372(6)
C3-C4 1.322(7)
C1-C2-C3 150.3(5)
C2-C3-C4 153.5(5)

Figure 1. Molecular structure of **4b**; selected bond lengths (Å) and angles (deg).

Hiyama reported that hydrosilation of 1,1,4,4-tetrakis(trimethylsilyl)butatriene catalyzed by rhodium complexes gave 1,2-addition products in which a silyl group attached at the terminal position.[8] When **1** was treated with diphenylsilane in the presence of a catalytic amount of $RhCl(PPh_3)_3$, hydrosilated products were obtained in moderate yields (Scheme 3).[22] Contrary to the previous results, allenes **5** were obtained as major products. These have a silyl group at the internal position as a result of 2,1-addition, while 2,3-addition gave 1,3-dienes **6** as minor products. Interestingly, **6** is formally an *anti*-addition product. A reaction of **1a** using Ph_2SiD_2 (97%D) gave deuterated products **7** and **8**. Deuterium was incorporated at C1 in **7** and C3 in **8** (96 and 97%D). It should be noted that D was not attached at the other carbons. The possibility that (*Z*)-**1** isomerized to 1,3-enyne **9** and this accepted hydrosilation to give **6** can be ruled out. However, it is not clear yet whether **6** formed via direct *anti*-addition of Si–H on (*Z*)-**1** or *syn*-addition to (*E*)-**1** that was isomerized from (*Z*)-**1**. Further investigation is now in progress.



Scheme 3. Hydrosilation of butatrienes catalyzed by Rh complexes.

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References and Notes

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16 **3a**: ^{1}H NMR (C_6D_6, Me_4Si) $\delta = -0.14$ (s, 18H), 6.71 (d, $^3J_{\text{Rh-H}} = 2.6$ Hz, 2H), 7.01–7.13 (m, 18H), 7.90–7.97 (m, 12H). ^{13}C NMR (C_6D_6, Me_4Si) $\delta = -0.67$, 124.34, 127.77 ($^3J_{\text{P-C}} = 5.0$ Hz), 129.45, 132.95 ($^1J_{\text{P-C}} = 21.2$ Hz), 135.15 ($^2J_{\text{P-C}} = 6.1$ Hz), 156.97 (q, $^1J_{\text{Rh-C}} = 12.9$, $^2J_{\text{P-C}} = 3.4$ Hz). ^{31}P NMR (C_6D_6, H_3PO_4) $\delta = 31.2$ (d, $^1J_{\text{P-Rh}} = 138.1$ Hz). ^{29}Si NMR (C_6D_6, Me_4Si) $\delta = -11.5$ (d, $^3J_{\text{Si-Rh}} = 3.2$ Hz). Anal. Calcd for $C_{46}H_{50}ClP_2RhSi_2$: C 64.29 H 5.86, Found: C 64.72, H 5.84. Yield 83% by ^{1}H NMR (35% isol.).

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20 **4a**: ^{1}H NMR (C_6D_6, Me_4Si) $\delta = -0.18$ (s, 9H), 0.33 (s, 9H), 5.71 (dd, $^5J_{\text{H-H}} = 3.0$, $^3J_{\text{Rh-H}} = 3.0$ Hz, 1H), 6.02 (dd, $^5J_{\text{H-H}} = 3.0$, $^3J_{\text{Rh-H}} = 3.0$ Hz, 1H), 7.06 (m, 18H), 7.90 (m, 12H). ^{13}C NMR (C_6D_6, Me_4Si) $\delta = -0.40$, 0.40, 116.22, 122.16, 127.66 ($^3J_{\text{P-C}} = 4.5$ Hz), 129.69, 131.85 ($^1J_{\text{P-C}} = 21.2$ Hz), 135.21 ($^2J_{\text{P-C}} = 5.9$ Hz), 154.66 (q, $^1J_{\text{Rh-C}} = 13.4$, $^2J_{\text{P-C}} = 3.7$ Hz), 157.07 (q, $^1J_{\text{Rh-C}} = 15.1$, $^2J_{\text{P-C}} = 3.9$ Hz). ^{31}P NMR (C_6D_6, H_3PO_4) $\delta = 39.3$ (d, $^1J_{\text{P-Rh}} = 134.3$ Hz). ^{29}Si NMR (C_6D_6, Me_4Si) $\delta = -4.9$ (d, $^3J_{\text{Si-Rh}} = 3.7$ Hz), -8.0 (d, $^3J_{\text{Si-Rh}} = 1.8$ Hz). Anal. Calcd for $C_{46}H_{50}ClP_2RhSi_2$: C 64.29, H 5.86, Found: C 64.04, H 5.87. Yield 58% by ^{1}H NMR (17% isol.).

21 **4b**: Crystal data: $C_{52}H_{62}ClP_2RhSi_2$, fw=943.50, orthorhombic, space group = *Pna*2(1), $a = 33.305(4)$, $b = 11.4630(12)$, $c = 12.9333(13)$ Å, $V = 4937.5(9)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.269$ g/cm^3, $R = 0.057$, $R_w = 0.125$. Data were collected on Bruker APEX diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation at 110 K. A total of 37042 reflections was measured. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The final cycle of least-squares refinement was based on 14067 observed reflections ($I \geq 2\sigma(I)$) with 535 variable parameters. The data were deposited in Cambridge Crystallographic Data Centre (CCDC 191256).

22 Typically, to a solution of $RhCl(PPh_3)_3$ (18.5 mg, 0.02 mmol) in diethyl ether (0.5 mL) were added **1a** (99 mg, 0.5 mmol) and diphenylsilane (184 mg, 1 mmol). The mixture was stirred at room temperature for 1 h. Usual workup gave **5a** and **6a** (Y. 35% and 16% isolated). Yields were determined by GC. **5a**: ^{1}H NMR (C_6D_6) $\delta = -0.01$ (s, 9H), 0.06 (s, 9H), 1.37 (dd, $J = 15$, 2.8 Hz, 1H), 1.48 (dd, $J = 15$, 2.8 Hz, 1H), 4.5 (t, $J = 2.8$ Hz, 1H), 5.38 (s, 1H, Si-*H*), 7.1–7.2 (m, 6H), 7.65–7.69 (m, 4H). ^{13}C NMR (C_6D_6) $\delta = -0.77$, -0.64, 17.57, 75.96, 78.15, 128.24, 129.98, 133.98, 135.99, 211.41. **6a**: ^{1}H NMR (C_6D_6) $\delta = 0.07$ (s, 9H), 0.22 (s, 9H), 5.33 (s, 1H, Si-*H*), 6.05 (d, $J = 19.0$ Hz, 1H), 6.49 (d, $^4J = 1.0$ Hz, 1H), 7.16 (dd, $^3J = 19.0$, $^4J = 1.0$ Hz, 1H), 7.39 (m, 4H), 7.42 (m, 2H), 7.58 (dd, $J = 7.8$, 1.5 Hz, 4H). ^{13}C NMR (C_6D_6) $\delta = -1.32$, 0.46, 128.32, 130.00, 134.23, 136.22, 136.25, 147.44, 153.73, 155.65.