Dimerization of Ethynylcyclopentadienylmetal Complexes

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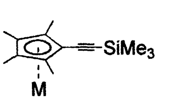
Heating of bulky ethynyltetramethylcyclopentadienylmetal complexes, $RC{\equiv}CH$ (R= Me_4C_5Rh(cod), Me_4C_5Ir(cod), $Me_4C_5Fe(C_5Me_4H)$), in the presence of catalytic amounts of $Ru(H)_2(CO)(PPh_3)_3$ afforded the corresponding butatriene, $RCH{=}C{=}C{=}CHR$. The rhodium complex was stepwise hydrogenated by $Ru(H)_2(CO)(PPh_3)_3$ to give a butadiene complex, $RCH{=}CH{-}CH{=}CHR$, whose molecular structure was determined by X-ray diffraction analysis.

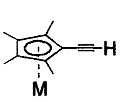
The transition metal-catalyzed dimerization of terminal alkynes has been known for many years.[1] The formations of 1,3-disubstituted enynes from the head-to-tail coupling and of 1,4-disubstituted enynes from the tail-to-tail coupling of terminal alkynes have been extensively reported. However, there are few reports about the formation of butatriene from the formal coupling of two vinylidene moieties derived from a terminal alkyne. Examples are only limited to the dimerization of *tert*-butylacetylene and trimethylsilylacetylene into 1,4-di-*tert*-butylbutatriene and 1,4-bis(trimethylsilyl)butatriene by $Ru(H)_2(CO)(PPh_3)_3$ and [Ru(cod)(cot)] / PR_3, respectively,[2] and benzylacetylene into 1,4-dibenzylbutatriene by $Ru(H)_3(C_5Me_5)(PR_3)$.[3] It is suggested that the formation of butatriene is largely controlled by the bulkiness of both the starting alkyne and the ancillary ligands linked to the ruthenium center.[2,3] In this context, we attempted the synthesis of the terminal alkynes substituted with bulky tetramethylcyclopentadienylmetal moieties and the dimerization to the corresponding butatrienes.

$RC{\equiv}C{-}CH{=}CHR$	$RC{\equiv}C{-}CR{=}CH_2$	$RCH{=}C{=}C{=}CHR$
cis, trans-enyne	*gem*-enyne	*cis, trans*-butatriene

The treatment of (trimethylsilylethynyl)tetramethylcyclopentadiene[4] with butyllithium and the subsequent reaction with $[MCl(cod)]_2$ (M=Rh, Ir) gave the corresponding cyclopentadienyl-metal complexes, $(Me_3SiC{\equiv}CC_5Me_4)M$(cod) (M= Rh (**1a**), Ir (**1b**)) in good yield(~60%). Hydrolysis with KOH afforded the terminal alkynes, $(HC{\equiv}CC_5Me_4)M$(cod) (M= Rh (**2a**), Ir (**2b**)), in reasonable yields.[5] Octamethylethynylferrocene $(HC{\equiv}CC_5Me_4)Fe(C_5Me_4H)$ (**3**) and ethynylferrocene $(HC{\equiv}CC_5H_4)Fe(C_5H_5)$ (**4**) were prepared according to the literature.[4,6]

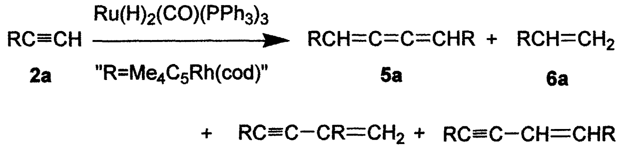


1a : M= Rh(cod)
1b : M= Ir(cod)



2a : M= Rh(cod)
2b : M= Ir(cod)
3 : M= Fe(Me_4C_5H)

The heating of **2** in toluene at 80 °C in the presence of $Ru(H)_2(CO)(PPh_3)_3$ (monomer/catalyst=20/1) afforded the butatriene dimer, $RCH{=}C{=}C{=}CHR$ (R= Me_4C_5Rh(cod) (**5a**), Me_4C_5Ir(cod) (**5b**))[7], along with small amounts of the geminal enyne, trans enyne and cis enyne, and a hydrogenation product of the starting alkynes $(H_2C{=}CHC_5Me_4)M$(cod) (M= Rh (**6a**), Ir (**6b**))[8] which were identified from the proton nmr spectra (entries 1 and 7 in Table 1) (Scheme 1). It is deduced from the proton nmr spectra showing two broad singlets of vinylic protons at δ ~6.1 and ~6.2 that **5a** and **5b** consisted of an approximate 3:1 mixture of *cis* and *trans* isomers, although the stereochemistry could not be unequivocally determined. The turnover number of this catalytic reaction is low (~5) but a higher number (15) is obtained by using an excess of **2a** (entry 2). An increase in the ratio resulted in the concomitant formation of the butadiene complex, $RCH{=}CH{-}CH{=}CHR$ (R= Me_4C_5Rh(cod) (**7a**)) (entry 3).[9] A further increase in the catalyst ratio (1/1) resulted in the exclusive formation of **6a**, suggesting that the initial step of the catalysis is the generation of a zero-valent ruthenium species by consuming two hydride ligands (entry 4). In order to confirm the origin of **7a**, **5a** was treated with $Ru(H)_2(CO)(PPh_3)_3$ at 80 °C and followed by proton nmr. The stepwise hydrogenations of **5a** to **7a** and then to a butene complex, $RCH{=}CH{-}CH_2{-}CH_2R$ (R= Me_4C_5Rh(cod) (**8a**))[11], were observed, suggesting the formation of **7a** through **5a**. The *trans, trans* stereochemistryof **7a** was determined by X-ray diffraction analysis and is depicted in Figure 1.[10] The molecule has a crystallographic center of symmetry. The cyclopentadienyl ring and the diene moiety are nearly coplanar.



$$\underset{\mathbf{2a}}{RC{\equiv}CH} \xrightarrow[\text{"R=Me}_4\text{C}_5\text{Rh(cod)"}]{Ru(H)_2(CO)(PPh_3)_3} \underset{\mathbf{5a}}{RCH{=}C{=}C{=}CHR} + \underset{\mathbf{6a}}{RCH{=}CH_2} + RC{\equiv}C{-}CR{=}CH_2 + RC{\equiv}C{-}CH{=}CHR$$

Scheme 1. Dimerization of **2a** catalyzed by $Ru(H)_2(CO)(PPh_3)_3$.

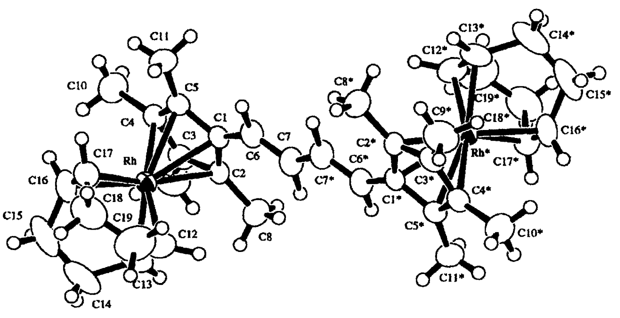


Figure 1. ORTEP view of **7a**.

The [Ru(cod)(cot)] / PPh_3 (1/3) system was also found to catalyze the formation of **5a** although the yield is rather low (entry 5). Dimerization of the bulky ethynylferrocene **3** by $Ru(H)_2(CO)(PPh_3)_3$ similarly proceeded and produced the expected butatriene, $RCH{=}C{=}C{=}CHR$ (R= $Me_4C_5Fe(C_5Me_4H)$ (**9**))[11] (entry 8). However, the dimerization of the simple ethynylferrocene **4** by the same catalyst produced only enynes (gem : trans : cis = 1.25 : 1 : 2.25) in very low yield. (entry 9). In contrast to these ruthenium catalysts, even a bulky terminal alkyne **2a** was dimerized by $Rh(PPh_3)_3Cl$ to give enynes (gem : trans : cis = 2.8 : 2.4 : 1) without forming the butatriene **5a**

Table 1. Dimerization of terminal alkynes [a]

Entry	Monomer	Catalyst	Monomer /catalyst	Product /%				
				Butatriene [d]	Butadiene [d]	Enyne [e]		
						geminal	trans	cis
1	**2a**	$Ru(H)_2(CO)(PPh_3)_3$	20:1	45	0	tr	tr	tr
2[b]	**2a**	$Ru(H)_2(CO)(PPh_3)_3$	100:1	28	0	tr	tr	tr
3	**2a**	$Ru(H)_2(CO)(PPh_3)_3$	7:1	22	21	tr	tr	tr
4[c]	**2a**	$Ru(H)_2(CO)(PPh_3)_3$	1:1	0	tr	0	0	0
5	**2a**	[Ru(cod)(cot)] / PPh_3(1/3)	20:1	10	0	tr	tr	tr
6	**2a**	$Rh(PPh_3)_3Cl$	10:1	0	0	28	24	10
7	**2b**	$Ru(H)_2(CO)(PPh_3)_3$	20:1	48	0	tr	tr	tr
8	**3**	$Ru(H)_2(CO)(PPh_3)_3$	20:1	53	0	0	0	0
9	**4**	$Ru(H)_2(CO)(PPh_3)_3$	20:1	0	0	5	4	8

[a]Reaction condition: 80 °C in toluene. [b]**2a** was recovered in 40% yield. [c]$R-CH=CH_2$ was formed in 40% yield. [d]Isolated yield. [e]Determined from the ^1H NMR spectrum.

(entry 6).

In conclusion, we have shown that the dimerization of terminal alkynes having bulky tetramethylcyclopentadienylmetal moieties by ruthenium complexes, $Ru(H)_2(CO)(PPh_3)_3$ or [Ru(cod)(cot)] / PPh_3, proceeds to give the corresponding novel butatriene dimer complexes. The same mechanisum as already suggested for the dimerization of *t*-butylacetylene may also be operative in this case.

References and Notes

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5 Satisfactory elemental analyses were obtained for all the new complexes mentioned in this paper.

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7 **5a**: red crystals. FT-IR(KBr); ν (C=C) 1604 cm^{-1}. ^1H NMR ($CDCl_3$); δ (ppm) 1.80 (s, 3H), 1.82 (bs, 12H), 1.88 (bs, 9H), 1.93 (m, 8H), 2.15 (m, 8H), 3.14 (m, 8H), 6.10 (bs, 1.5H), 6.15 (bs, 0.5H). M^+ = 712.2. **5b**: orange crystals. FT-IR(KBr); ν (C=C) 1610 cm^{-1}. ^1H NMR ($CDCl_3$); δ (ppm) 1.83 (m, 8H), 1.90 (s, 3H), 1.91 (bs, 12H), 1.92 (bs, 9H), 2.02 (m, 8H), 2.97 (m, 8H), 6.13 (bs, 1.5H), 6.20 (bs, 0.5H).

8 **6a**: ^1H NMR ($CDCl_3$); δ (ppm) 1.77 (s, 6H), 1.86 (s, 6H), 1.91 (m, 4H), 2.14 (m, 4H), 3.00 (m, 4H) 5.02, 5.05 (d, 1H, *J*=2.0 Hz), 5.15, 5.19 (d, 1H, *J*=2.0 Hz), 6.49, 6.54 (d, 1H, *J*=11.5 Hz). **6b**: ^1H NMR ($CDCl_3$); δ (ppm) 1.80 (m, 4H), 1.86 (s, 6H), 1.90 (s, 6H), 2.00 (m, 4H), 2.83 (m, 4H) 5.14, 5.17 (d, 1H, *J*=1.9 Hz), 5.20, 5.25 (d, 1H, *J*=1.9 Hz), 6.41, 6.45 (d, 1H, *J*=11.2 Hz).

9 **7a**: yellow-orange crystals. FT-IR(KBr); ν (C-H) 3038 cm^{-1}, ν (C=C) 1610 cm^{-1}. ^1H NMR ($CDCl_3$); δ (ppm) 1.82 (s, 12H), 1.87 (s, 12H), 1.91 (m, 8H), 2.14 (m, 8H), 3.04 (m, 8H), 6.28~6.42 (m, 4H).

10 Crystallographic data. **7a**: $C_{38}H_{52}Rh_2$, Fw = 714.64; monoclinic, space group $P2_1/n$ (#14); a = 8.260(3) Å, b = 14.311(4) Å, c = 14.266(6) Å, β= 103.84(5)°, V = 1637(1) $Å^3$; Z = 2; D_{calc}= 1.449 $g{\cdot}cm^{-3}$; R = 0.035, Rw = 0.036.

11 **8a**: yellow crystals. ^1H NMR ($CDCl_3$); δ (ppm) 1.75 (s, 6H), 1.77 (s, 6H), 1.81 (s, 6H), 1.84 (s, 6H), 1.90 (m, 8H), 2.13 (m, 8H), 2.29 (m, 4H), 2.94 (m, 8H), 5.69 (dt, 1H) 6.11 (d, 1H).

12 **9**: dark purple crystals. FT-IR(KBr); ν (C=C) 1605 cm^{-1}. ^1H NMR ($CDCl_3$); δ (ppm) 1.67 (s, 1.2H), 1.68 (s, 10.8H), 1.73 (bs, 12H), 1.81 (bs, 12H), 1.95 (bs, 12H), 3.30 (s, 2H), 6.05 (bs, 1.8H), 6.16 (bs, 0.2H).