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Regioselective hydrosilylation of terminal acetylenes via acetylene–Co$_2$(CO)$_4$dppm complex: effects of the ligands in acetylenedicobalt complex

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Abstract—The regioselective hydrosilylation of the acetylenedicobalt complex on the terminal acetylene with special reference to the ligands to produce a vinylsilane is described. It was found that the use of the ligands exchanged dicobalttetracarbonyl bis(diphenylphosphino)methane complex dramatically changed the regioselectivity compared to the corresponding dicobalthexacarbonyl complex.
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Vinylsilanes are very useful intermediates in synthetic organic chemistry.[1] The hydrosilylation of an acetylenic compound is one of the general methods to produce a vinylsilane.[2] We have developed the reductive decomplexation of the acetylenedicobalthexacarbonyl complex with a trialkylsilane to produce the corresponding vinylsilane (hydrosilylation).[3] In the course of the syntheses of marine natural products, the hydrosilylations of the internal acetylenedicobalt complexes such as **1** and **3** usually exhibited an extremely high regioselectivity (Scheme 1).[3a,4] However, the same hydrosilylation reaction of the terminal acetylene with an acetylene–Co$_2$(CO)$_4$dppm complex. We found a significant improvement in the regioselectivity by changing

to a dicobalttetracarbonyl bis(diphenylphosphino)methane (Co$_2$(CO)$_4$dppm) complex from a dicobalthexacarbonyl (Co$_2$(CO)$_6$) complex in the terminal acetylene.

The results of hydrosilylations with the Co$_2$(CO)$_6$ complexes and Co$_2$(CO)$_4$dppm complexes[5] are shown in Table 1. In all cases, the results of the Co$_2$(CO)$_4$dppm complexes exhibited high regioselectivity. The Co$_2$(CO)$_6$ complexes of the sugar acetylene derivatives **11**, **15**, **18**, **22**, **26**, and **30** were readily prepared by mixing the corresponding sugar acetylene compounds[6–8] with Co$_2$(CO)$_8$. The dppm complexes were prepared by the following sequence (Scheme 2).
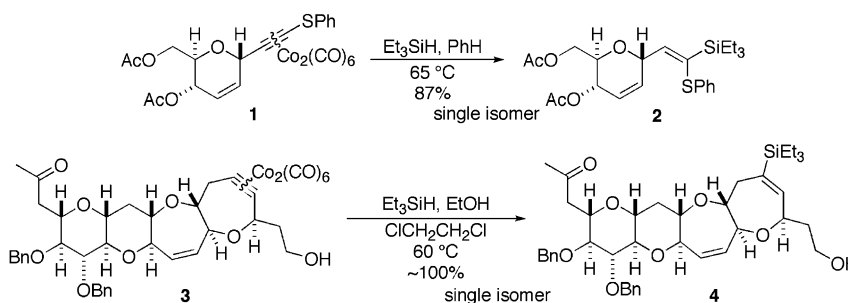
Scheme 1. Hydrosilylations of internal acetylene Co$_2$(CO)$_6$ complexes.
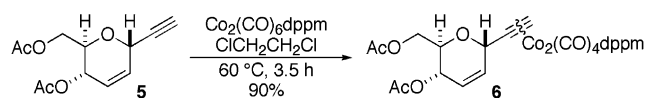
Scheme 2. Preparation of $Co_2(CO)_4$dppm complex.

The complex **6** could be directly obtained from sugar acetylene **5**[6] by treating with $Co_2(CO)_6$dppm, which was easily prepared by $Co_2(CO)_8$ and dppm,[9] therefore **6**[10] was cleanly produced as a single diastereomer in 90% yield.

We first examined the hydrosilylation with the $Co_2(CO)_6$ complexes (Table 1, entries 1, 3, 5, 7, 9, 11, 13, and 15). In every case, the hydrosilylations were completed in 1–3 h by heating at 65 °C with triethylsilane and bis(trimethylsilyl)acetylene (BTMSA)[3d] to give the vinylsilanes

as a mixture of regioisomers in high yields. However, the regioselectivity was low, and most of the major products were vinylsilane **A** which has an internal silyl group.

Next, we investigated the reaction with the ligands exchanged $Co_2(CO)_4$dppm complexes (Table 1, entries 2, 4, 6, 8, 10, 12, 14, and 16). The reaction of a simple aliphatic compound **8** and triethylsilane in 1,2-dichloroethane with BTMSA[3d] at reflux for 16 h gave **9** and **10** as an inseparable mixture with the ratio of 6:94 in 70% yield (entry 2). For the sugar acetylene complexes **12**, **6**, **19**, **23**, **27**, and **31**, which were prepared from the corresponding sugar acetylene, the reactions proceeded very slowly to give the vinylsilanes with high regioselectivity in moderate yields (entries 4, 6, 8, 10, 12, and 14). The moderate yields may be responsible for the instability of the dppm complexes under the heating conditions.

Table 1. Hydrosilylations with acetylenedicobalt complexes

Entry	Substrate	X	Temp (°C)	Time (h)	Products[a] A	Products[a] B	Yield (%)	Ratio (A:B)[b]
1		**7**: $Co_2(CO)_6$	65	1	**9**	**10**	99	55:45
2		**8**: $Co_2(CO)_4$dppm	Reflux[d]	16			70	6:94
3		**11**: $Co_2(CO)_6$	65	1	**13**	**14**	90	56:44
4		**12**: $Co_2(CO)_4$dppm[c]	Reflux[d]	27			44	7:93
5		**15**: $Co_2(CO)_6$	65	1.5	**16**	**17**	95	63:37
6		**6**: $Co_2(CO)_4$dppm[c]	Reflux[d]	23			70	8:92
7		**18**: $Co_2(CO)_6$	65	2	**20**	**21**	97	55:45
8		**19**: $Co_2(CO)_4$dppm[c]	Reflux[d]	25			49	6:94
9		**22**: $Co_2(CO)_6$	65	2	**24**	**25**	83	87:13
10		**23**: $Co_2(CO)_4$dppm[c]	Reflux[d]	46			56	2:98
11		**26**: $Co_2(CO)_6$	65	2	**28**	**29**	96	71:29
12		**27**: $Co_2(CO)_4$dppm[c]	Reflux[d]	64			54	0:100
13		**30**: $Co_2(CO)_6$	65	2.5	**32**	**33**	97	57:43
14		**31**: $Co_2(CO)_4$dppm[c]	Reflux[d]	63			44	0:100
15		**34**: $Co_2(CO)_6$	65	3	**36**	**37**	89	26:74
16		**35**: $Co_2(CO)_4$dppm	Reflux[d]	35			80	15:85

BTMSA = bis(trimethylsilyl)acetylene.[3d]

[a] All products were inseparable mixtures.

[b] The ratios of the products were determined from the ^{1}H NMR data (400 MHz).

[c] Dppm complexes were unstable under the heating condition.

[d] Reflux temperature is 83 °C.

The regioselectivity was pronounced in entries 10, 12, and 14, particularly **27** and **31** afforded **29**[11] and **33** as a single regioisomer. In the reaction of an aromatic compound **35** (entry 16), no dramatic effect of the ligands was observed, which might be probably attributed to an electronic factor of the aromatic ring.

In a hydrosilylation, platinum or rhodium catalysts have often been used with a trialkylsilane to produce a vinylsilane.[1,2] Therefore, we also examined the reaction of **38**, **39**, and **40** with a platinate catalyst (Na_2PtCl_6) as the most typical catalyst (Table 2). The reactions were completed in 10–30 min by heating with triethylsilane at 65 °C to afford the vinylsilanes **9**, **10**, **24**, **25**, **36**, and **37**. In these cases, the major products were vinylsilane **B** which has a terminal silyl group, and the regioselectivity was low, especially in entry 2. This system was usually carried out by simple heating of the reaction mixture under air atmosphere,[12] but various side reactions occasionally occurred, such as the intramolecular isomerization of an olefin, and the silylation of a free alcohol, thus a mild condition which is applicable to complex compounds is desired. The fact that the small amount of some products should be generated by the side reactions was observed in entry 2.

The hydrosilylation mechanism via the acetylenedicobalt complex has not yet been clarified, however the significant difference in the selectivity between the $Co_2(CO)_6$ and $Co_2(CO)_4$dppm complexes should be explained on the basis of the configuration of the reactant system. The configurations of **8**, **26**, and **27** were confirmed by the NOESY spectra (Fig. 1). The terminal position of the $Co_2(CO)_4$dppm complex in **8** is very hindered, judging from the NOE's correlations between the ligand-aromatic protons of dppm and the terminal proton of the cobalt complex. Furthermore, in the case of **27**, the terminal proton had correlations at the ligand-methylene protons of dppm as well as the C6 position on the dihydropyran ring. Thus, as a plausible explanation, the hydride should approach the less hindered internal carbon to produce a vinylsilane **B** as **29**. While, the terminal proton of $Co_2(CO)_6$ complex in **26** had a correlation at the C2 position on the dihydropyran ring. Thus, the terminal carbon should be attacked by the hydride in the $Co_2(CO)_6$ complexes,

Table 2. Hydrosilylations with Na_2PtCl_6

Entry	Substrate	Temp (min)	Products[b]		Yield (%)	Ratio (A:B)[c]
			A	**B**		
1	TBDPSO‑‑‑‑ **38**	10	**9** +	**10**	94	22:88
2	AcO‑‑‑ **39** OH	30	**24** +	**25**	80	31:69
3	**40**	30	**36** +	**37**	89	13:87

[a] Na_2PtCl_6 was added as a 0.01 M solution in 2-propanol.
[b] All products were inseparable mixtures.
[c] The ratios of the products were determined from the ^1H NMR data (400 MHz).
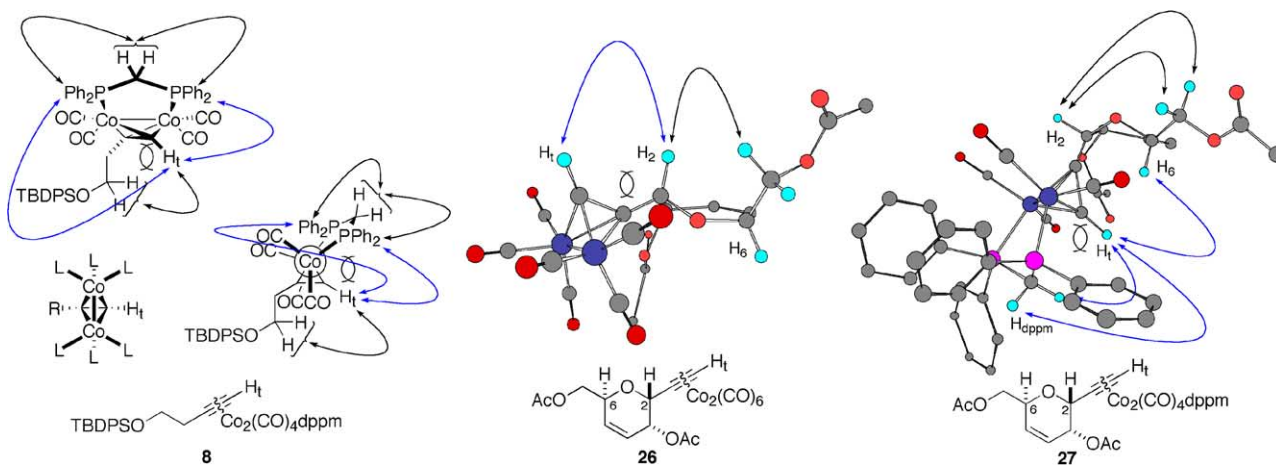

Figure 1. NOE's correlations observed in **8**, **26**, and **27**.

since the internal carbon would be hindered by the dihydropyrane ring. However, the steric hindrance of the $Co_2(CO)_6$ complex was smaller than that of the $Co_2(CO)_4$dppm complex, therefore the regioselectivity of the $Co_2(CO)_6$ complex may be slightly lower than that of the $Co_2(CO)_4$dppm complex.

In conclusion, we have successfully improved the regioselectivity of the hydrosilylation by using a $Co_2(CO)_4$dppm complex on the terminal acetylene derivatives. Further developments of this reaction, such as catalytic reactions and synthetic applications, are now in progress.

Acknowledgements

References and notes

1. For reviews, see: (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic: London, 1988; (b) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, M. B., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8, p 763.

2. For general method, see: *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon: Oxford, 1992.

3. (a) Hosokawa, S.; Isobe, M. *Tetrahedron Lett.* **1998**, *39*, 2609; (b) Isobe, M.; Nishizawa, R.; Hosokawa, S.; Nishikawa, T. *Chem. Commun.* **1998**, 2665; (c) Isobe, M.; Nishizawa, R.; Nishikawa, T.; Yoza, K. *Tetrahedron Lett.* **1999**, *40*, 6927; BTMSA was added as a trapping reagent of active cobalt catalyst to avoid the side reactions: (d) Kira, K.; Tanda, H.; Hamajima, A.; Baba, T.; Takai, S.; Isobe, M. *Tetrahedron* **2002**, *58*, 6485.

4. (a) Kira, K.; Isobe, M. *Tetrahedron Lett.* **2001**, *42*, 2821; (b) Baba, T.; Isobe, M. *Synlett* **2003**, 547, and references therein.

5. About the selection of ligand and the other application of $Co_2(CO)_4$dppm complexes, see: Hamajima, A.; Isobe, M., in preparation.

6. Hosokawa, S.; Kirschbaum, B.; Isobe, M. *Tetrahedron Lett.* **1998**, *39*, 1917.

7. Ichikawa, Y.; Isobe, M.; Konobe, M.; Goto, T. *Carbohydr. Res.* **1987**, *171*, 193.

8. Tsukiyama, T.; Isobe, M. *Tetrahedron Lett.* **1992**, *33*, 7911.

9. (a) Lisic, E. C.; Hanson, B. E. *Inorg. Chem.* **1986**, *25*, 812; (b) Chia, L. S.; Cullen, W. R. *Inorg. Chem.* **1975**, *14*, 482.

10. *For compound* **6**: as a reddish-brown amorphous; ^{1}H NMR (CDCl$_3$, 400 MHz), δ 7.44–7.16 (20H, m), 6.16–6.12 (1H, m), 5.79 (1H, br d, $J = 10.2$ Hz), 5.59–5.52 (2H, m), 5.36–5.31 (1H, m), 4.61–4.55 (1H, m), 4.37 (1H, dd, $J = 4.7, 12.0$ Hz), 4.27 (1H, dd, $J = 2.0, 12.0$ Hz), 3.63 {1H, td, $J = 10.0$ (*H–P*), 13.2 Hz}, 3.09 {1H, td, $J = 9.6$ (*H–P*), 13.2 Hz}, and 2.08 (6H, s); ^{13}C NMR (CDCl$_3$, 100 MHz), δ 203.10–202.80 (m), 171.25, 170.61, 137.00–136.00 (m), 132.69–132.63 (m), 132.00–131.34 (m), 129.71–129.61 (m), 128.43–128.14 (m), 123.87, 77.20, 76.31, 72.65–72.60 (m), 68.51, 65.08, 63.36, 42.02 (t, $J = 19.8$ Hz), 21.12, and 20.83; ^{31}P NMR (CDCl$_3$, 162 MHz), δ 40.67 (2P, br s); IR (neat), v_{max} 3057, 2931, 2022, 1992, 1965, 1733, 1435, 1371, 1235, 1096, 1042, 782, 739, and 694 cm^{-1}; FAB-MS-HR, found: 853.0573, calcd for $C_{41}H_{37}O_9P_2Co_2$ (M+H)$^+$: 853.0577.

11. *For compound* **29**: as a colorless oil; $[\alpha]_D^{25}$ -74.6 (*c* 0.67, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 400 MHz), δ 6.08 (1H, ddd, $J = 2.2, 4.9, 10.2$ Hz), 6.02–5.94 (3H, m), 5.20–5.17 (1H, m), 4.58–4.54 (1H, m), 4.49 (1H, br t, $J = 3.4$ Hz), 4.37 (1H, dd, $J = 7.6, 11.7$ Hz), 4.05 (1H, dd, $J = 3.9, 11.7$ Hz), 2.08 (3H, s), 2.03 (3H, s), 0.93 (9H, t, $J = 8.1$ Hz), and 0.57 (6H, q, $J = 8.1$ Hz); ^{13}C NMR (CDCl$_3$, 100 MHz), δ 170.76, 170.52, 141.88, 130.29, 129.49, 125.24, 77.23, 73.25, 70.87, 65.36, 63.53, 20.86, 7.29, and 3.30; IR (neat), v_{max} 2954, 2912, 2876, 1748, 1457, 1372, 1232, 1119, 1024, 943, 786, and 722 cm^{-1}; Anal. Calcd for $C_{32}H_{48}O_5Si_3$: C, 67.56; H, 8.50. Found: C, 67.54; H, 8.69; EI-MS-HR, found: 325.1476, calcd for $C_{16}H_{25}O_5Si$ (M−Et)$^+$: 325.1471.

12. Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694.