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A New Entry to π-Allylcobalt Tricarbonyls Using $(CH_3)_3SiCo(CO)_4$

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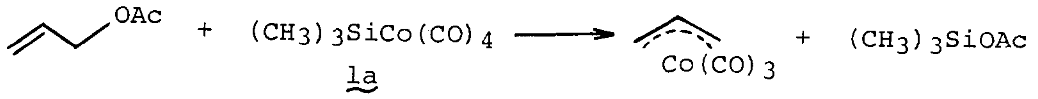
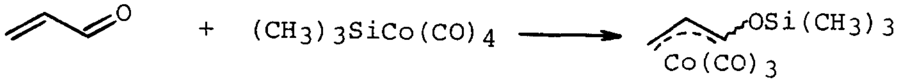
Abstract: The reactions of $(CH_3)_3SiCo(CO)_4$ with allyl acetates, enones, and a diene monoepoxide gave corresponding π-allylcobalt tricarbonyls.

In the new $Co_2(CO)_8$-catalyzed reactions of various oxygenated compounds with $HSiR_3$ and CO, incorporation of CO takes place with cleavage of the carbon-oxygen bonds in the substrates.[1] Silylcobalt carbonyl, $R_3SiCo(CO)_4$ (**1**), generated in situ has been suggested as the key catalyst species responsible for the formation of carbon-cobalt bond which is required for the incorporation of CO. Although some silylcobalt carbonyl complexes **1** have long been known, their chemistry has not been well explored yet.[2] We have now studied the stoichiometric reaction of **1** with some oxygenated compounds (vide infra) with the expectation that the known oxygenophilicity of silicon in **1** would bring about cleavage of carbon-oxygen bond in the substrate with concomitant formation of carbon-cobalt bond. The reactions of $(CH_3)_3SiMn(CO)_5$ with ethers and aldehydes have been recently reported by Gladysz.[3]

The reactions of readily available $(CH_3)_3SiCo(CO)_4$[4] (**1a**) with allyl acetates, enones, and a diene monoepoxide have given the results which constitute a new entry to and a complementary preparative method of π-allylcobalt tricarbonyl complexes,[6] as outlined in eq 1-3. π-Allylcobalt complexes have been demonstrated recently by Hegedus to be promising discrete intermediates in organic synthesis.[7]



(1)



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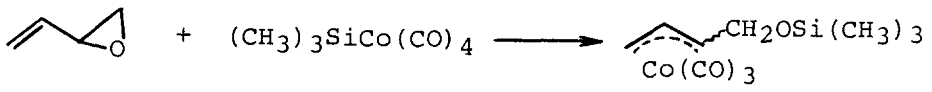
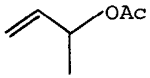
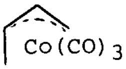
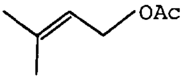
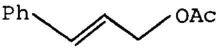
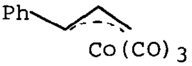
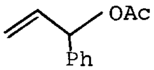
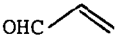
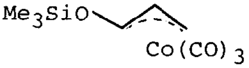
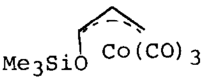
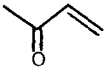
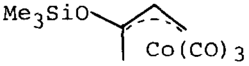
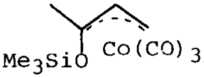
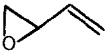
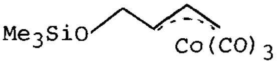


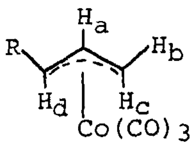
(3)

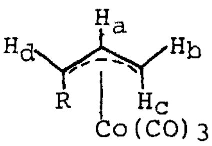
Table 1. The Reaction of $(CH_3)_3SiCo(CO)_4$ with Allyl acetates, Enones, and a Diene Monoepoxide[a)]

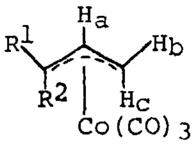
entry	substrate	π-allylcobalt tricarbonyl[b)]				ref.
1			80 %			c)
2			52 %		28 %	d)
3			44 %			d)
4			63 %			e) f)
5			56 %			e) f)
6			44 %		20 %	
7			12 %		46 %	g)
8			50 %			f)

a) Reaction conditions: The reaction was conducted with substrate(0.5 mmol), $(CH_3)_3SiCo(CO)_4$(0.7-0.9 mmol), and C_6D_6(0.5 mL) under N_2 and at 50°C for 1-1.5 h in a NMR tube. b) NMR yields based on the substrates. Yields were calculated on the basis of known quantities of an added standard (C_6H_6, C_6H_{12}) or $CH_3COOSi(CH_3)_3$ formed. c) Ref 8. d) J.A.Bertrand, H.B.Jonassen, and D.W.Moore, Inorg. Chem., 2, 601(1963). e) H.Alper, H.Des Abbayes, and D.Des Roches, J. Organomet. Chem., 121, C31(1976). f) NMR analysis of the reaction mixture showed the absence of the anti-isomer. g) The stereochemistry was tentatively assigned on the basis of NMR chemical shifts. See also Table 2.

Table 2. ^1H NMR Data for π-Allylcobalt Tricalbonyls (C_6D_6, TMS)


(I)


(II)


(III)

R	H_a	H_b	H_c	H_d	R	J_{ab}	J_{ac}	J_{ad}	J_{dR}	J_{bc}	J_{bd}
H(I or II)	4.40(tt)	2.68(d)	1.85(d)			6	11			~0	
CH_3(I)	4.26(dt)	2.55(d)	1.64(d)	2.72(dq)	1.23(d)	6	10	10	6	~0	~0
CH_3(II)	4.48(dt)	2.94(d)	2.47(d)	3.89(quint)	0.83(d)	6.5	12	6.5	6.5	~0	~0
Ph(I)	5.06(dt)	2.69(d)	1.84(d)	3.67(d)	7.04-7.12(m)	6	10	10		~0	~0
$OSi(CH_3)_3$(I)	4.59(ddd)	2.38(dd)	1.33(dd)	5.01(d)		6	10	7		1	~0
$OSi(CH_3)_3$(II)	4.07(ddd)	3.06(dd)	3.18(d)	6.17(dd)		6	10.5	3.5		~0	1.5
$CH_2OSi(CH_3)_3$(I)	4.52(dt)	2.56(d)	1.72(d)	2.80(ddd)	3.60(ABqd)[a]	6	10	10	4, 5	~0	~0

R^1, R^2	H_a	H_b	H_c	R^1	R^2	J_{ab}	J_{ac}	J_{bc}
CH_3, CH_3(III)	4.28(dd)	2.74(d)	2.17(d)	1.38(s)	0.90(s)	7	12	~0
$OSi(CH_3)_3$, CH_3(III)[b]	4.56(dd)	2.60(d)	ca. 1.7[c]		1.29(s)	6.5	10.5	2
CH_3, $OSi(CH_3)_3$(III)[b]	4.04(dd)	2.94(d)	2.86(d)	1.70(s)		6	10	~0

a) J_{AB}=12 Hz. b) The assignment is a tentative one on the basis of NMR chemical shift; H_a syn to the siloxy group would be at lower field than H_a anti to the siloxy group. Compare the chemical shift with those H_a in R=$OSi(CH_3)_3$(I) and R=$OSi(CH_3)_3$(II). The assignment is also supported by CH_3 shift data.
c) Overlapped with the $CH_3(R^1)$ group signal of another isomer (R^1=CH_3, R^2=$OSi(CH_3)_3$).

To a solution of $(CH_3)_3SiCo(CO)_4$ (1.0 g, 4.2 mmol) in C_6H_6 (2.5 mL) was added $CH_2=CH-CH_2OAc$ (0.27 g, 2.5 mmol) at 15°C, and the solution was heated at 50°C for 1.5 h. The formation of π-allylcobalt tricarbonyl in the solution was evident from ^1H NMR (80% yield). Distillation (bulb-to-bulb, ~30°C/3 torr)[8] allowed the isolation (52% yield) of the pure cobalt complex as a pale yellow liquid.

The reaction of the silylcobalt **1a** can be conducted conveniently in a NMR tube using C_6D_6 as a solvent. These results and ^1H NMR data for the products are given in Tables 1 and 2, respectively. The type of the products or the product distribution may suggest that these products have been derived *via* thermodynamically controlled processes.[9,10]

References and Notes

1) (a) N. Chatani, S. Murai, and N. Sonoda, J. Am. Chem. Soc., 105, 1370(1983).
(b) Review: S. Murai and N. Sonoda, Angew. Chem., Int. Ed. Engl., 18, 837(1979).

2) A. J. Chalk and J. F. Harrod, J. Am. Chem. Soc., 87, 1133(1965); ibid., 89, 1640(1967). Y. L. Baay and A. G. MacDiarmid, Inorg. Chem., 8, 986(1969). H. G. Ang and P. T. Lau, Organomet. Chem. Rev. A 8, 235(1972). C. S. Cundy, B. M. Kingston, and M. F. Lappert, Adv. Organomet. Chem., 11, 235(1973). F. Hofler, Topics Curr. Chem., 50, 129(1974). See also references cited in 1b.

3) M. Marsi and J. A. Gladysz, Organometallics 1, 1467(1982) and references cited therein.

4) The reported method for **1a**[5] was modified. To $Co_2(CO)_8$ (0.68 g, 2 mmol) in a 10 mL flask equipped with dry ice condenser was added $HSi(CH_3)_3$ (3.5 mL, 30 mmol) at -78°C. The mixture was warmed to 25°C with stirring over 1 h. The excess $HSi(CH_3)_3$ was removed in a stream of N_2. The residual black solid was sublimed at 40-45°C (0.5 torr) into a flask (-78°C) to give $(CH_3)_3SiCo(CO)_4$ (0.78-0.83 g, 80-85%, pale pink, ^1H NMR (C_6D_6, TMS) δ 0.45 ppm, s).

5) D. L. Morrison and A. P. Hagen, Inorg. Synth., 13, 65(1972).

6) Known methods involve: $CH_2=CH-CH_2X$ + $NaCo(CO)_4$ (or $KCo(CO)_4$), C=C-C=C + $HCo(CO)_n$ and CH_3I + $NaCo(CO)_4$ + C=C-C=C. For a review, see: R. D. W. Kemmitt and D. R. Russell, "Comprehensive Organometallic Chemistry", Ed. G. Wilkinson, Pergamon Press, Oxford, 1982, vol. 5, pp 211-222.

7) L. S. Hegedus and Y. Inoue, J. Am. Chem. Soc., 104, 4917(1982).

8) Lit. 39°C(15 torr), W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, J. Am. Chem. Soc., 83, 1601(1961).

9) In each case transient signals in NMR were observed before they collapsed to the final product. However, the assignment of these transient signals has not been established yet.

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