CHEMISTRY LETTERS, pp. 1163-1166, 1989.

First Isolation of a π-Perfluoroallylic Complex from a Transition Metal Hydride with Hexafluorobuta-1,3-diene

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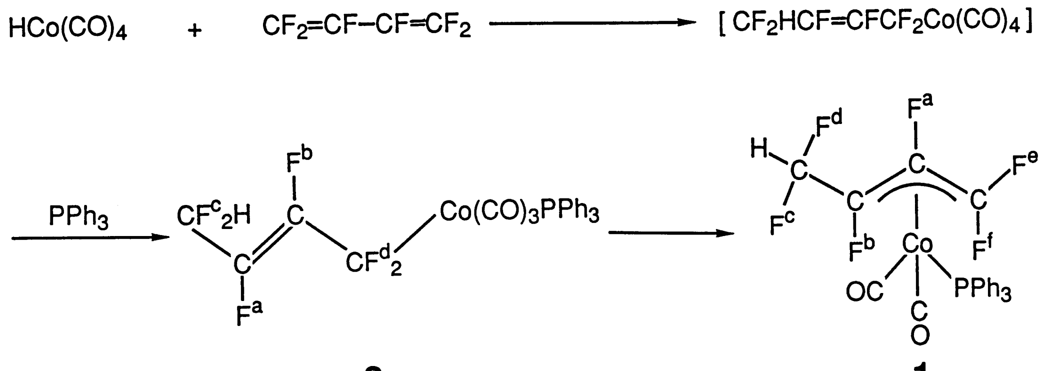
Dicarbonyl(η^3-1,1,2,3,4,4-hexafluoro-2-butenyl)(triphenylphosphine)cobalt(I) was isolated at the first time from the reaction of tetracarbonylhydridocobalt(I) with hexafluorobuta-1,3-diene and triphenylphosphine.

Organometallic chemistry of butadiene has been studied extensively and the application of butadiene to organic syntheses are widely achieved.[1)] However there are a few reports on the reaction of hexafluorobutadiene with organometallic complexes.[2)] π-Perfluoroallylic derivatives of transition metals are of special interest because the hydrocarbon analogues show high reactivities toward a variety of nucleophiles and may be converted to many useful chemicals. Though π-allylic complexes are known for almost all of transition metals, the perfluoro analogues have been limited to tricarbonyl(η^3-pentafluoroallyl)cobalt(I)[3)] and perfluorocyclic derivatives of iron,[4)] cobalt,[5)] and rhodium.[5)] π-Allylic complexes are easily formed from the reaction of metal hydrides with butadiene, whereas no example with hexafluorobutadiene has been reported so far.[2a)]
We now report the formation of a π-perfluoroallylic cobalt(I) complex starting from hexafluorobutadiene.

The reaction of tetracarbonylhydridocobalt(I) with excess hexafluorobutadiene in hexane at -50 °C for 3 h, followed by an addition of triphenylphosphine under reflux to give dicarbonyl(η^3-1,1,2,3,4,4-hexafluoro-2-butenyl)(triphenylphosphine)cobalt(I), (**1**), in 18% isolated yield along with hexacarbonylbis(triphenylphosphine)dicobalt(0) as an undesired product(60%). The latter product was also formed in the same reaction of tetracarbonylhydoridocobalt with butadiene. trans-Tricarbonyl(σ-E-1,1,2,3,4,4-hexafluoro-2-butenyl)(triphenylphosphine)cobalt(I), (**2**), was isolated in 16% yield from the reaction performed at room temperature. Complexes **1** and **2** were obtained as pale yellow crystals by recrystallization from hexane and characterized by elemental analyses, NMR and IR spectra.[6)]



2 **1**

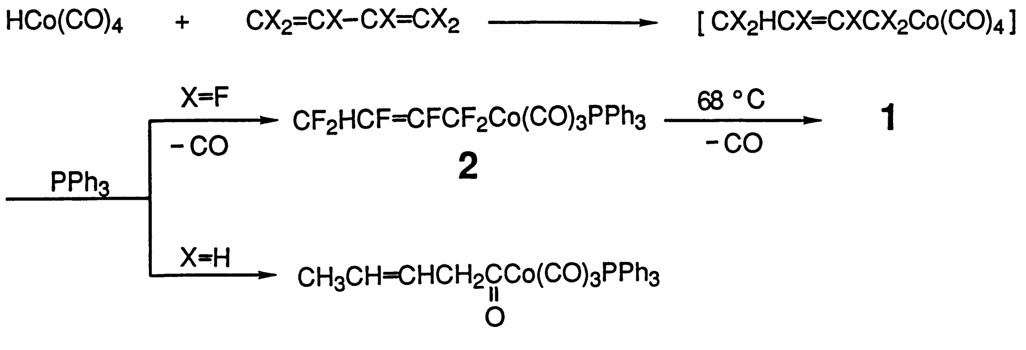
Table 1. Selected $^{19}F\{^1H\}$ and ^1H NMR Spectral Data of **1** and **2**$^{a)}$

	F^a	F^b	F^c	F^d	F^e	F^f	$-CF_2\underline{H}$
1	190.0	172.2	123.0	106.9	97.2	81.3	5.49(td)$^{b)}$
2	173.1	153.5	124.9	50.1			6.00(tdd)$^{c)}$

a) Measured in C_6D_6. ^{19}F chemical shifts(ppm) are refered to internal $CFCl_3$, increasing to high field.
b) $J_{H-F^c}=J_{H-F^d}=53$, $J_{H-F^b}=18$ Hz. c) $J_{H-F^c}=52$, $J_{H-F^a}=16$, $J_{H-F^b}=3$ Hz.

The $^{19}F\{^1H\}$ and ^1H NMR data of **1** and **2** are summarized in Table 1. The $^{19}F\{^1H\}$ NMR of **1** showed six multiplets with the same intensity. Chemical shifts (F^a, F^e, F^f) and coupling constants ($J_{F^a-F^e}=25$, $J_{F^a-F^f}=71$, $J_{F^e-F^f}=148$ Hz) are similar to those of tricarbonyl(η^3-pentafluoroallyl)cobalt(I).[3)] The relatively large coupling constant ($J_{F^a-F^b}=47$ Hz) suggests the syn configuration of the π-perfluoroallylic moiety as compared with the reported configuration of the hydrocarbon analogue.[7)] The resonances of diastereotopic $-C\underline{F}_2H$ are separated with a large coupling constant and the assignment was confirmed by ^1H nondecoupled measurement. The ^1H NMR of **1** exhibited resonances of $-CF_2\underline{H}$ at 5.49 ppm coupled with the two geminal fluorines and one vicinal fluorine. The $^{19}F\{^1H\}$ NMR of **2** showed four resonances with relative intensity 1:1:2:2 with chemical shifts decreasing to the low field. Among them, two resonances with relative intensity one have in common a large coupling constant ($J_{F^a-F^b}$=132 Hz) which is indicative of E-alkenyl group. The $^{31}P\{^1H\}$ NMR of **2** showed a triplet due to PPh_3 ligand at 58.6 ppm ($^3J_{P-F^d}$=31 Hz) which indicates a trans configuration about the cobalt atom as reported on $R_fCo(CO)_3PPh_3$ complexes.$^{3,8)}$ The IR spectrum of **2** showed a very weak ν(C=C) band at 1712 cm^{-1} and three ν(CO) bands (2067(w), 2004(s), 1997(s) cm^{-1}) which are also consistent with a trans configuration. (C_{3v} symmetry, A_1+E)$^{3,8)}$

It is well known that the reaction of tetracarbonylhydridocobalt with butadiene at low temperature, followed by the reaction with triphenylphosphine to give an acyl complex, tricarbonyl(σ-3-pentenoyl)(triphenylphosphine)cobalt(I) via 1,4-addition and then CO insertion.$^{9)}$ In contrast, CO insertion did not occur in the present reaction, i.e., σ-perfluoroallylic complex **2** could be isolated. This may be attributed to high stability of the metal-perfluorocarbon bond compared with that of the hydrocarbon analogue. McBride et al. reported that the addition of triphenylphosphine to tricarbonyl(η^3-pentafluoroallyl)cobalt(I) caused a fluorine migration and resulted in a rearrangement to tricarbonyl(σ-pentafluoro-1-propenyl)cobalt(I); π-perfluoroallyl complexes having a triphenylphosphine ligand could not be isolated.$^{3)}$ However, we confirmed that **2** was converted to the stable π-perfluoroallylic complex **1** by the loss of carbon monoxide on heating. Complex **1** provides the first example of π-perfluoroallylic complex having a phosphine ligand as well as demonstrates the first formation of π-allylic complex starting from metal hydride with hexafluorobutadiene.



We thank Dr. Masayoshi Tatemoto, Daikin Industries, Ltd., for the gift of 1,2-dichloro-1,2,2-trifluoroiodoethane, and the Material Analysis Center, I.S.I.R., Osaka University for spectral measurements and microanalyses.

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6) **1**: Anal. Found: C, 53.55; H, 3.00; F, 21.05; P, 5.78%. Calcd for $C_{24}H_{16}F_6O_2PCo$: C, 53.35; H, 2.98; F, 21.00; P, 5.73%. Mp(dec.) 113 °C. $^{19}F\{^1H\}$ NMR (C_6D_6) δ 81.3(m, F^f), 97.2(m, F^e), 106.9(m, F^d), 123.0(m, F^c), 172.2(m, F^b), 190.0(m, F^a); $J_{F^a\text{-}F^b}=47$, $J_{F^a\text{-}F^c}=7$, $J_{F^a\text{-}F^d}\simeq 0$, $J_{F^a\text{-}F^e}=25$, $J_{F^a\text{-}F^f}=71$, $J_{F^a\text{-}P}=7$, $J_{F^b\text{-}F^c}=19$, $J_{F^b\text{-}F^d}=14$, $J_{F^b\text{-}F^e}=9$, $J_{F^b\text{-}F^f}\simeq 0$, $J_{F^b\text{-}P}=20$, $J_{F^c\text{-}F^d}=282$, $J_{F^c\text{-}P}=7$, $J_{F^d\text{-}P}=25$, $J_{F^e\text{-}F^f}=148$, $J_{F^e\text{-}P}=50$, $J_{F^f\text{-}P}\simeq 0$ Hz.
2: Anal. Found: C, 53.02; H, 2.81; F, 20.00; P, 5.66%. Calcd for $C_{25}H_{16}F_6O_3PCo$: C, 52.84; H, 2.84; F, 20.06; P, 5.45%. Mp(dec.) 98-99 °C. $^{19}F\{^1H\}$ NMR (C_6D_6) δ 50.1(m, F^d), 124.9(d, F^c), 153.5(dt, F^b), 173.1(m, F^a); $J_{F^a\text{-}F^b}=132$, $J_{F^a\text{-}F^c}=19$, $J_{F^b\text{-}F^d}=21$, $J_{F^d\text{-}P}=31$ Hz. $^{31}P\{^1H\}$ NMR (C_6D_6) δ (from external PPh_3) 58.6(t, PPh_3); $J_{P\text{-}F^d}=31$ Hz.

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(Received April 3, 1989)