of ether, and the precipitated imine was removed by passage through a pad of 20 g of silica gel in a sintered-glass funnel. The filtrate was stirred with 1.0 g of Amberlyst 15 ion-exchange resin for 30 min and filtered and the solvent removed under vacuum. Flash chromatography (silica gel G) of the residue eluting with 1:1 ethyl acetate/*n*-hexane (1:1) gave 0.19 g (58% based on the amount of **3**) of (2*S*,3*R*)-**2a**: mp 99-100 °C (lit.[11a] mp 103 °C); $[\alpha]^{23}_D$ -6.24° (*c* 4.0, $CHCl_3$) [lit.[11a] $[\alpha]^{23}_D$ -10.7° (*c* 1.0, $CHCl_3$)]. Two crystallizations from ethyl ether improved the ee to >95%: $[\alpha]^{23}_D$ -10.03° (*c* 2.6, $CHCl_3$). Spectroscopic properties were identical with reported values.

(2*R*,3*S*)-(+)-Verrucarinolactone (2c). This material was prepared in a similar manner from oxaziridine (+)-**3a** to give 0.15 g (55%) of **2c**: mp 98-99 °C; $[\alpha]^{23}_D$ = +6.07° (*c* 2.6, $CHCl_3$).

Addition of BF_3·OEt_2 or LiCl. Enolate oxidations were carried out as described above except that 1.0 equiv of BF_3·OEt_2 or LiCl was added to the preformed enolate of (±)-**1** at -78 °C prior to addition of the oxaziridine.

Determination of the Enantiomeric Purity of 2a and 2c. The enantiomeric purity was determined by integration of the OMe group of the Mosher ester of **2**. The Mosher ester was prepared by stirring 26 mg (0.2 mmol) of **2** with 70.2 mg (0.3 mmol) of (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid, 82.5 mg (0.4 mmol) of 1,3-dicyclohexylcarbodiimide, and 10 mg (0.08 mmol) of 4-(dimethylamino)pyridine in 3 mL of dry dichloromethane for 2 days. The product was purified by preparative chromatography eluting with 1:1 ethyl acetate/*n*-hexane.

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by National Institutes of Health (Institute of General Medical Sciences) through Grant GM 34014.

Cobaloxime-Catalyzed Hydroperfluoroalkylation of Electron-Deficient Alkenes with Perfluoroalkyl Halides: Reaction and Mechanism

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Received January 2, 1992

Direct hydroperfluoroalkylation of electron-deficient alkenes—ethyl acrylates **4**, **7**, and **8**, acrylonitrile (**5**), and methyl vinyl ketone (**6**)—with perfluoroalkyl halides R_fX (**1**, X = I; **2**, X = Br) in the presence of cobaloxime(III) (**3**) and zinc gives 1:1 hydroperfluoroalkylation adducts in good yields. This reaction provides a convenient synthesis of β-(perfluoroalkyl)carboxylic esters **9**, **12**, and **13**, nitriles **10**, and ketones **11**. Details of the reaction including effect of solvent, temperature, and ratio of reagents were examined. The reaction is proposed to proceed via a radical mechanism initiated by low-valent cobalt.

Numerous reports have been focused on introduction of per(poly)fluoroalkyl groups into organic molecules via either radical or carbanion route by reduction, photolysis, or thermolysis of perfluoroalkyl halides or under catalysis of transition-metal complexes.[1] C-C multiple bonds are used extensively as acceptors for this purpose. However, the addition of perfluoroalkyl radical $R_f^{\bullet}$ to alkenes connected with a electron-withdrawing group like acrylates is inefficient by routine heat,[2] light,[3] and electrochemical methods[4] because (a) the electrophilic $R_f^{\bullet}$[5] has to attack the electron-deficient C-C multiple bonds, (b) the reaction can not be controlled to a 1:1 addition stage, and (c) certain substrates are not stable enough under such reaction conditions. Therefore, searching for more efficient synthetic methods has been the subject of much interest. Radical reactions of perfluoroalkanesulfonyl halides (iodide,[6] bromide,[7] and chloride[8]) with acrylates initiated by thermal, peroxide, or Ru(II)-complex catalysts were reported, but the procedures were rather tedious. Thus, an alternative route to the synthesis of β-(perfluoroalkyl)-carboxylic ester has been just appeared.[9]

We have reported that a bimetal redox couple, cobaloxime(III)/Zn, promoted hydroperfluoroalkylation of acrylate **4** in a preliminary paper.[10] Here a full account of this reaction system, its further application to hydroperfluoroalkylation of other electron-deficient alkenes, and a possible mechanism are described.

Results and Discussion

The cobaloxime(III) **3**, a well-studied model compound of coenzyme vitamin B_{12}[11] can be reduced electrochemically or chemically to low-valent cobalt species,[12] which exhibit powerful nucleophilic reactivity in the carbon-carbon bond formation via several pathways ranging from S_N2 to single-electron transfer mechanisms.[13] We hypothesize that

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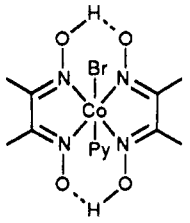
0022-3263/92/1957-3339$03.00/0



$BrCo(dmgH)_2Py$

3

under reductive conditions it might promote perfluoroalkylation of alkenes by way of electron transfer to perfluoroalkyl halides. Zinc powder was chosen as reducing agent to constitute a redox couple with cobaloxime 3.

In fact, into a green slurry of cobaloxime (0.02 mmol) and Zn powder (20 mmol) in ethanol were added acrylate 4 (15 mmol) and R_fI 1f (10 mmol) successively, and stirring at 20 °C for 1 h gave ethyl β-(perfluorohexyl)carboxylate 9f (eq 1, where R_f = straight-chain alkyl; (a) ClC_4F_8; (b) ClC_6F_{12}; (c) ClC_8F_{16}; (d) C_2F_5; (e) C_4F_9; (f) C_6F_{13}; (g) C_8F_{17}; (h) $C_{10}F_{21}$) in 72% yield after workup.

$$\begin{array}{lll} R_fX + & R_1CH{=}CR_2Z \rightarrow & R_fCHR_1CHR_2Z + R_fH \\ 1\ (X = I) & 4\ (R_1 = R_2 = H,\ Z = CO_2Et) & 9 \qquad 14 \\ 2\ (X = Br) & 5\ (R_1 = R_2 = H,\ Z = CN) & 10 \\ & 6\ (R_1 = R_2 = H,\ Z = C(O)CH_3) & 11 \\ & 7\ (R_1 = H,\ R_2 = CH_3,\ Z = CO_2Et) & 12 \\ & 8\ (R_1 = CH_3,\ R_2 = H,\ Z = CO_2Et) & 13 \end{array} \qquad (1)$$

The mild reaction conditions and good yield encouraged us to extend such a reaction to acrylonitrile (5) and methyl vinyl ketone (6). Experiments showed that the above initiating system works well except a higher temperature and a longer reaction time were required. The reactivity of electron-deficient alkenes with perfluoroalkyl halides decreases in the order 4 > 5 > 6. The methacrylate 7 and crotonate 8 could also be effectively perfluoroalkylated, while 8 gave reduced yields for the steric effect. It was also found that perfluoroalkyl bromides 2 could be used successfully in the present reaction, giving even better yields than the corresponding iodides 1. The reaction proceeded smoothly and usually was complete within a short period. The results are summarized in Tables I and II.

All the products formed were 1:1 hydroperfluoroalkylated adducts of the alkenes. No telomer could be detected. The main byproduct was α-hydroperfluoroalkanes R_fH 14. The perfluoroalkylzinc reagents (which could be observed in ^{19}F NMR) might be formed to some extent. With methyl vinyl ketone 6, some dimer of 6 was formed under the reaction conditions.

Several reaction parameters were examined. The catalyst, cobaloxime(III) (3), is indispensable for this reaction. Parallel experiments revealed that reaction of the very reactive perfluoroalkyl iodides 1 with alkenes could be initiated by Zn alone with dramatically reduced yields, giving mainly R_fH 14. Satisfactory yields were obtained even in presence of 0.5 mol % of 3. Perfluoroalkyl bromides 2 undergo successful reaction only in the presence of both cobaloxime and Zn.

Excess Zn is necessary for efficient and rapid conversion. At least 1 equiv of Zn was required to accomplish a complete conversion of R_fX with acrylate 4, and 1- to 2-fold excess of Zn was required with acrylonitrile 5 and methyl vinyl ketone 6.

The effect of solvents on the yield of products is obvious; ethanol is a better choice. The reaction proceeded smoothly at 20 °C, while higher or lower temperature would lead to a reduced yield.

Table I. Hydroperfluoroalkylation of Electron-Deficient Alkenes with R_fI 1 in EtOH[a]

entry	R_fI	alkenes	temp (°C)	time (h)	product[b]	(%)
1	1a	4	25	1	9a	75
2	1b	4	15	0.5	9b	56
3	1c	4	15	1	9c	50
4	1d	4	5	1	9d	53
5	1e	4	20	0.5	9e	71
6	1f	4	20	0.5	9f	72
7	1g	4	20	1	9g	75
8	1h	4	25	1	9h	65
9	1a	5	30	2	10a	61
10	1b	5	30	2	10b	67
11	1c	5	30	3	10c	70
12	1d	5	30	3	10d	37
13	1e	5	30	1.5	10e	69
14	1f	5	30	2.5	10f	71
15	1g	5	30	3	10g	69
16	1h	5	25	4	10h	60
17	1a	6	30	4	11a	55
18	1b	6	30	5	11b	45
19	1c	6	30	4	11c	60
20	1d	6	30	4	11d	35
21	1e	6	25	4	11e	49
22	1f	6	30	3.5	11f	64
23	1g	6	30	4	11g	56
24	1h	6	30	4.5	11h	50
25	1b	7	20	1	12b	61
26	1c	7	15	1	12c	65
27	1f	7	25	1	12f	71
28	1a	8	25	1.5	13a	50
29	1b	8	25	2	13b	45
30	1c	8	15	1	13c	41
31	1f	8	25	0.5	13f	56

[a] The reaction was performed on a 5–10 mmol scale with a molar ratio of 1:alkene:3:Zn = 1:1.5:0.02–0.05:1.5. [b] Isolated yield based on 1.

Table II. Hydroperfluoroalkylation of Electron-Deficient Alkenes with R_fBr 2 in EtOH[a]

entry	R_fBr	alkenes	temp (°C)	time (h)	product[b]	(%)
1	2f	4	30	4	9f	80
2	2f	5	30	3.5	10f	75
3	2f	6	45	5	11f	72
4	2f	7	30	2	12f	81
5	2f	8	30	2.5	13f	56
6	2g	4	30	3	9g	79
7	2g	5	30	4	10g	70
8	2g	6	45	5	11g	53
9	2g	7	30	3	12g	78
10	2g	8	30	2.5	13g	60
11	2h[c]	4	30	3.5	9h	74
12	2h[c]	5	30	5	10h	75
13	2h[c]	6	45	6	11h	50

[a] The reaction was performed on a 2–3 mmol scale with a molar ratio of 2:alkene:3:Zn = 1:1.5:0.02:1.5–4. [b] Isolated yield based on 2. [c] The solvent used was 1:1 $EtOH/Et_2O$.

Mechanistic Discussion

Cobaloxime 3 itself could not initiate the reaction. Perfluoroalkylated cobaloxime $C_6F_{13}Co(dmgH)_2Py$ 15 (prepared according to Schrauzer[11] from $C_6F_{13}I$ (1f), $Co(OAc)_2$, dimethylglyoxime, and pyridine) was proven to be too stable to react with acrylate 4 even in the presence of Zn.

In the presence of 3, the zinc reagent $ClC_6F_{12}ZnX$ (prepared according to Miller et al. from $ClC_6F_{12}I$ and Zn[14])

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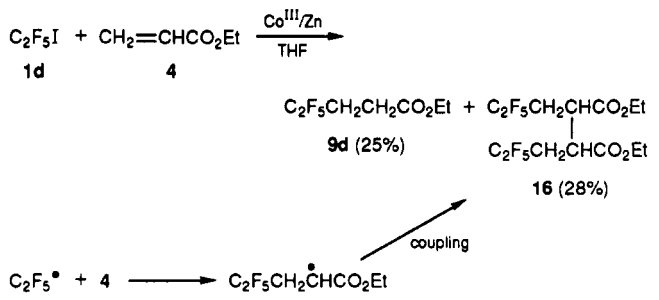
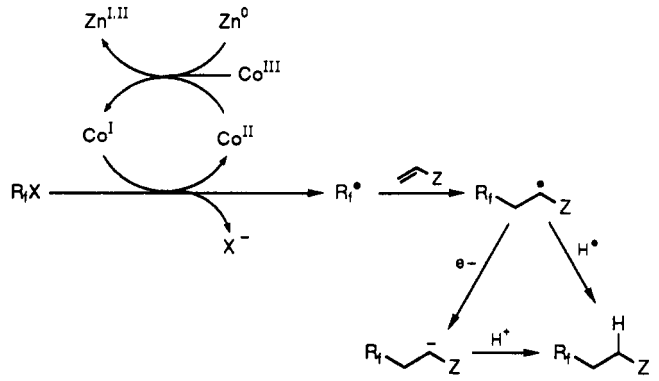
Scheme I



Scheme II



did not react with 4 in a parallel experiment (eq 2). This fact excluded it as an active intermediate for the present hydroperfluoroalkylation.

$$\underset{X = I \text{ or } ClC_6F_{12}}{ClC_6F_{12}ZnX} + \underset{4}{CH_2{=}CHCO_2Et} \xrightarrow[\text{dioxane/EtOH}]{3/15\text{–}50\ ^\circ C} \text{no reaction} \quad (2)$$

The $R_f^\bullet$ was trapped by the addition of *t*-BuN=O to the reaction system ($C_6F_{13}I$ (**1f**) initiated by Co[III]/Zn), and the adduct *t*-BuN(O)C_6F_{13} displayed a well-separated and typical ESR spectrum with g = 2.0053, a_N = 11.43, and a_F = 19.55G.

When C_2F_5I (**1d**) reacted in THF with acrylate **4** initiated by Co[III]/Zn, dimer **16** was formed in 28% yield together with the usual adduct **9d** (yield 25%). Similar results were obtained when the solvent was CH_3CN or DMF. Obviously, compound **16** was produced by coupling of the secondary radical $C_2F_5CH_2\dot{C}HCO_2Et$. This revealed that the above reaction might proceed via a radical addition as shown in Scheme I.

It is likely the low-valent cobalt which was in situ generated by the Co[III]/Zn catalytic cycle initiated the above perfluoroalkyl radical addition (see Scheme II) through ET to iodides or bromides. Adding 5 mol % of *p*-dinitrobenzene suppressed the reaction completely.

To a certain extent, the intermediate $R_f^\bullet$ and $R_fCH_2\dot{C}HZ$ might exist in the form of radical pairs[15] with •Co[II] which were responsible for the mild reaction conditions.

In conclusion, we describe a cobaloxime/Zn bimetal redox system which is able to perform direct hydroperfluoroalkylation of electron-deficient alkenes—acrylates, acronitrile, and methyl vinyl ketone—with perfluoroalkyl iodides and bromides. The mild reaction conditions make it a convenient approach to the synthesis of β-(perfluoroalkyl)carboxylic esters, nitriles, and ketones.

Experimental Section

General Comments. Boiling points and melting points are uncorrected. ^1H NMR spectra were measured with external TMS standard by a Varian EM-360A spectrometer at 60 MHz. ^{19}F NMR spectra were measured with an external CF_3COOH standard by a Varian EM-360L spectrometer at 56.4 MHz. ^1H NMR and ^{19}F NMR were recorded with neat samples without additional solvents unless otherwise indicated. IR spectra were recorded as films for liquid samples with a Shimadzu IR-440 spectrometer. Mass spectra were recorded with a Finnigan GC-MS-4021 mass spectrometer.

Methyl vinyl ketone (**6**) was freshly distilled before use. All other chemicals were of analytical grade and were used without further purification.

Hydroperfluoroalkylation of Acrylates 4, 7, and 8, Acrylonitrile (5), and Methyl Vinyl Ketone (6). General Procedure. A suspension of cobaloxime (**3**) (0.2–0.5 mmol) and Zn powder (15–40 mmol) in 25 mL of EtOH was stirred at room temperature under N_2 for about 0.5 h. When the mixture turned green, alkene (15 mmol) and then perfluoroalkyl halide were added dropwise over 0.5 h with cooling (usually an ice–water bath was sufficient). Then the contents were reacted at the temperature and time cited in Tables I and II. After that, the mixture was poured onto ice–water (10 mL) and filtered. The residue was washed, and the filtrate was extracted with ether (3 × 15 mL). After being washed with water and brine, the combined etheral extract was dried over Na_2SO_4. Removal of the solvent and distillation or sublimation gave the corresponding product.

Ethyl 7-chloro-4,4,5,5,6,6,7,7-octafluorooctanoate (9a): bp 82–83 °C (6 mmHg); IR 1740 (C=O) cm^{-1}; ^1H NMR δ 4.02 (q, 2 H, $^3J_{HH}$ = 7.0 Hz), 1.83–2.88 (m, 4 H), 1.12 (t, 3 H, $^3J_{HH}$ = 7.0 Hz); ^{19}F NMR δ −7.5 (s, 2 F), 39.6 (t, 2 F, $^3J_{HF}$ = 15.5 Hz), 44.6 (s, 2 F), 47.5 (s, 2 F); *m/e* 337 (M + 1, 100). Anal. Calcd for $C_9H_9ClF_8O_2$: C, 32.11; H, 2.70; F, 45.15. Found: C, 31.66; H, 2.49; F, 45.58.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoate (9f): bp 78–79 °C (5 mmHg); IR 1740 (C=O) cm^{-1}; ^1H NMR δ 3.99 (q, 2 H, $^3J_{HH}$ = 7.0 Hz), 1.93–2.88 (m, 4 H), 1.18 (t, 3 H, $^3J_{HH}$ = 7.0 Hz); ^{19}F NMR δ 6.0 (s, 3 F), 39.8 (t, 2 F, $^3J_{HF}$ = 17.1 Hz), 47.0 (s, 2 F), 48.0 (s, 4 F), 51.3 (s, 2 F); *m/e* 421 (M + 1, 100). Anal. Calcd for $C_{11}H_9F_{13}O_2$: C, 31.44; H, 2.16; F, 58.78. Found: C, 31.17; H, 1.96; F, 59.72.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoate (9g): bp 92–93 °C (5 mmHg); IR 1740 (C=O) cm^{-1}; ^1H NMR δ 4.09 (q, 2 H, $^3J_{HH}$ = 7.0 Hz), 1.85–2.79 (m, 4 H), 1.17 (t, 3 H, $^3J_{HH}$ = 7.0 Hz); ^{19}F NMR δ 5.5 (s, 3 F), 39.5 (t, 2 F, $^3J_{HF}$ = 14.6 Hz), 46.0 (s, 8 F), 47.7 (s, 2 F), 50.7 (s, 2 F); *m/e* 521 (M + 1, 100). Anal. Calcd for $C_{13}H_9F_{17}O_2$: C, 30.02; H, 1.74; F, 62.09. Found: C, 29.56; H, 1.54; F, 62.77.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heneicosafluorotridecanoate (9h): mp 57–58 °C; IR 1740 (C=O) cm^{-1}; ^1H NMR (CCl_4) δ 4.05 (q, 2 H, $^3J_{HH}$ = 7.0 Hz), 1.83–2.90 (m, 4 H), 1.12 (t, 3 H, $^3J_{HH}$ = 7.0 Hz); ^{19}F NMR δ 3.0 (s, 3 F), 38.1 (t, 2 F, $^3J_{HF}$ = 16.2 Hz), 45.1 (s, 12 F), 46.8 (s, 2 F), 49.5 (s, 2 F); *m/e* 621 (M + 1, 73.99). Anal. Calcd for $C_{15}H_9F_{21}O_2$: C, 29.05; H, 1.46; F, 64.33. Found: C, 29.02; H, 1.19; F, 64.32.

11-Chloro-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-hexadecafluoroundecanenitrile (10c): mp 75–76 °C; IR 2250 (C≡N) cm^{-1}; ^1H NMR δ 1.8–3.0 (m); ^{19}F NMR δ −7.8 (s, 2 F), 39.0 (t, 2 F, $^3J_{HF}$ = 14.5 Hz), 43.8 (s, 2 F), 45.2 (s, 8 F), 47.2 (s, 2 F); *m/e* 490 (M + 1, 10.84). Anal. Calcd for $C_{11}H_4ClF_{16}N$: C, 26.99; H, 0.82; F, 62.09; N, 2.86. Found: C, 26.73; H, 0.67; F, 62.00; N, 2.77.

4,4,5,5,5-Pentafluoropentanenitrile (10d): bp 61–62 °C (20 mmHg); IR 2250 (C≡N) cm^{-1}; ^1H NMR δ 1.8–3.0 (m); ^{19}F NMR δ 10.3 (s, 3 F), 43.8 (t, 2 F, $^3J_{HF}$ = 17.5 Hz); *m/e* 174 (M + 1, 3.62). Anal. Calcd for $C_5H_4F_5N$: C, 34.70; H, 2.33; F, 54.88; N, 8.09. Found: C, 34.73; H, 2.33; F, 54.55; N, 7.29.

4,4,5,5,6,6,7,7,7-Nonafluoroheptanenitrile (10e): bp 60–61 °C (10 mmHg); IR 2250 (C≡N) cm^{-1}; ^1H NMR δ 1.5–2.7 (m); ^{19}F NMR δ 6.5 (s, 3 F), 40.4 (t, 2 F, $^3J_{HF}$ = 13.5 Hz), 49.5 (s, 2 F), 51.1 (s, 2 F); *m/e* 274 (M + 1, 28.35). Anal. Calcd for $C_7H_4F_9N$: C,

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30.79; H, 1.48; F, 62.61; N, 5.13. Found: C, 30.61; H, 1.34; F, 62.15; N, 5.17.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononanenitrile (10f): bp 56–57 °C (4 mmHg); IR 2250 (C≡N) cm^{-1}; ^1H NMR δ 1.8–3.0 (m); ^{19}F NMR δ 5.3 (s, 3 F), 39.6 (t, 2 F, $^3J_{HF}$ = 14.0 Hz), 46.0 (s, 2 F), 47.2 (s, 4 F), 50.6 (s, 2 F); *m/e* 374 (M + 1, 15.57). Anal. Calcd for $C_9H_4F_{13}N$: C, 28.97; H, 1.08; F, 66.19; N, 3.75. Found: C, 28.97; H, 0.96; F, 65.85; N, 3.74.

8-Chloro-5,5,6,6,7,7,8,8-octafluoro-2-octanone (11a): bp 66–67 °C (8 mmHg); IR 1730 (C=O) cm^{-1}; ^1H NMR δ 1.9–3.0 (m, 4 H), 2.15 (s, 3 H); ^{19}F NMR δ −7.9 (s, 2 F), 38.7 (t, 2 F, $^3J_{HF}$ = 15.0 Hz), 44.2 (s, 2 F), 47.2 (s, 2 F); *m/e* 307 (M + 1, 3.70). Anal. Calcd for $C_8H_7ClF_8O$: C, 31.34; H, 2.30; F, 49.57. Found: C, 31.39; H, 2.17; F, 49.54.

10-Chloro-5,5,6,6,7,7,8,8,9,9,10,10-dodecafluoro-2-decanone (11b): bp 70–71 °C (4 mmHg); IR 1730 (C=O) cm^{-1}; ^1H NMR δ 1.8–3.0 (m, 4 H), 2.08 (s, 3 H); ^{19}F NMR δ −8.5 (s, 2 F), 37.6 (t, 2 F, $^3J_{HF}$ = 15.0 Hz), 43.8 (s, 2 F), 44.8 (s, 4 F), 47.2 (s, 2 F); *m/e* 407 (M + 1, 7.44). Anal. Calcd for $C_{10}H_7ClF_{12}O$: C, 29.54; H, 1.73; F, 56.07. Found: C, 29.45; H, 1.59; F, 55.56.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-2-decanone (11f): bp 55–56 °C (5 mmHg); IR 1730 (C=O) cm^{-1}; ^1H NMR δ 1.9–3.0 (m, 4 H), 2.07 (s, 3 H); ^{19}F NMR δ 5.6 (s, 3 F), 40.0 (t, 2 F, $^3J_{HF}$ = 17.0 Hz), 46.6 (s, 2 F), 48.2 (s, 4 F), 52.0 (s, 2 F); *m/e* 391 (M + 1, 35.15). Anal. Calcd for $C_{10}H_7F_{13}O$: C, 30.79; H, 1.81; F, 63.30. Found: C, 30.83; H, 1.63; F, 62.80.

5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluoro-2-dodecanone (11g): mp 35–36 °C; IR 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9–3.0 (m, 4 H), 2.13 (s, 3 H); ^{19}F NMR δ 3.9 (s, 3 F), 37.5 (t, 2 F, $^3J_{HF}$ = 16.5 Hz), 45.0 (s, 8 F), 46.5 (s, 2 F), 49.3 (s, 2 F); *m/e* 491 (M + 1, 17.96). Anal. Calcd for $C_{12}H_7F_{17}O$: C, 29.40; H, 1.44; F, 65.89. Found: C, 29.25; H, 1.36; F, 66.04.

Ethyl 9-chloro-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-2-methylnonanoate (12b): bp 94–95 °C (5 mmHg); IR 1740 (C=O) cm^{-1}; ^1H NMR δ 4.12 (q, 2 H, $^3J_{HH}$ = 6.5 Hz), 1.8–3.4 (m, 3 H), 1.2 (m, 6 H); ^{19}F NMR δ −8.3 (s, 2 F), 37.0 (s, 2 F), 43.7 (s, 2 F), 44.8 (s, 4 F), 47.0 (s, 2 F); *m/e* 451 (M + 1, 100). Anal. Calcd for $C_{12}H_{11}ClF_{12}O_2$: C, 31.98; H, 2.46; F, 50.59. Found: C, 32.23; H, 2.27; F, 48.27.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-methylundecanoate (12g): bp 102–103 °C (2.5 mmHg); IR 1740 (C=O) cm^{-1}; ^1H NMR δ 4.13 (q, 2 H, $^3J_{HH}$ = 7.0 Hz), 1.8–2.3 (m, 3 H), 1.20 (m, 6 H); ^{19}F NMR δ 5.6 (s, 3 F), 38.0 (t, 2 F), 46.1 (s, 8 F), 48.1 (s, 2 F), 50.9 (s, 2 F); *m/e* 535 (M + 1, 18.28). Anal. Calcd for $C_{14}H_{11}F_{17}O_2$: C, 31.48; H, 2.07; F, 60.46. Found: C, 31.42; H, 1.98; F, 60.00.

Ethyl 3-methyl-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoate (13f): bp 87–88 °C (5 mmHg); IR 1740 (C=O) cm^{-1}; ^1H NMR δ 4.13 (q, 2 H, $^3J_{HH}$ = 7.8 Hz), 1.9–3.2 (m, 3 H), 1.2 (m, 6 H); ^{19}F NMR ($CDCl_3$) 2.0 (s, 3 F), 41.2 (AB, 2 F, J_{AB} = 141 Hz), 44.0 (m, 2 F), 46.3 (m, 4 F), 50.0 (m, 2 F); *m/e* 435 (M + 1, 100). Anal. Calcd for $C_{12}H_{11}F_{13}O_2$: C, 33.20; H, 2.55; F, 56.88. Found: C, 33.16; H, 2.30; F, 56.53.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-3-methylundecanoate (13g): bp 91–92 °C (2 mmHg); IR 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.13 (q, 2 H, $^3J_{HH}$ = 6.6 Hz), 1.8–3.6 (m, 3 H), 1.20 (m, 6 H); ^{19}F NMR δ 5.8 (s, 3 F), 41.8 (AB, 2 F, J_{AB} = 133 Hz), 42.4 (m, 2 F), 46.2 (s, 8 F), 51.0 (s, 2 F); *m/e* 535 (M + 1, 100). Anal. Calcd for $C_{14}H_{11}F_{17}O_2$: C, 31.48; H, 2.07; F, 60.46. Found: C, 31.22; H, 1.77; F, 61.05.

Perfluorohexyl(pyridino)bis(dimethylglyoximato)cobalt(III) (15): mp 195–196 °C; ^1H NMR ($CDCl_3$) δ 8.70 (m, 2 H, α-Py), 7.62 (m, 1 H, γ-Py), 7.23 (m, 2 H, β-Py), 2.07 (s, 12 H, 4 × CH_3); ^{19}F NMR ($CDCl_3$) δ 3.60 (s, 3 F), 17.9 (s, 2 F), 41.0 (s, 2 F), 43.3 (s, 2 F), 45.2 (s, 2 F), 48.8 (s, 2 F); MS (FAB) *m/e* 686 (M − 1), 654 (M − 2 × H_2O + 1), 608 (M − Py), 591 (M − H_2O −Py + 1), 319 (C_6F_{13}), 288 (M − Py − C_6F_{13} − 1). Anal. Calcd for $C_{19}H_{19}CoF_{13}N_5O_4$: C, 33.20; H, 2.79; N, 10.19. Found: C, 33.09; H, 2.69; N, 10.27.

Diethyl 2,3-bis(2,2,3,3,3-pentafluoropropyl)succinate (16): bp 78–80 °C (2 mmHg); IR 1740 (C=O) cm^{-1}; ^1H NMR δ 4.24 (q, 4 H, $^3J_{HH}$ = 7.2 Hz), 1.70–3.40 (m, 6 H), 1.36 (t, 6 H, $^3J_{HH}$ = 7.2 Hz); ^{19}F NMR δ 9.6 (s, 6 F), 41.3 (s, 4 F); *m/e* 439 (M + 1, 33.17), 393 (M − OEt, 67.64), 365 (M − CO_2Et, 18.10), 291 (M − 2 × CO_2Et − 1, 23.42). Anal. Calcd for $C_{14}H_{16}F_{10}O_4$: C, 38.37; H, 3.68; F, 43.35. Found: C, 38.91; H, 3.74; F, 43.21.

Acknowledgment. Helpful discussions with professor Jiang Xi-Kui are gratefully acknowledged. We also acknowledge the Hoechst for gifts of R_fI and the National Natural Science Foundation of China for financial support.

Registry No. **1a**, 5848-38-4; **1b**, 16486-97-8; **1c**, 16486-98-9; **1d**, 354-64-3; **1e**, 423-39-2; **1f**, 355-43-1; **1g**, 507-63-1; **1h**, 423-62-1; **2f**, 335-56-8; **2g**, 423-55-2; **2h**, 307-43-7; **3**, 23432-34-0; **4**, 140-88-5; **5**, 107-13-1; **6**, 78-94-4; **7**, 97-63-2; **8**, 10544-63-5; **9a**, 136905-33-4; **9b**, 136905-34-5; **9c**, 136905-35-6; **9d**, 136905-36-7; **9e**, 136905-37-8; **9f**, 60023-26-9; **9g**, 40599-19-7; **9h**, 60023-27-0; **10a**, 140834-57-7; **10b**, 140834-58-8; **10c**, 119898-51-0; **10d**, 13265-56-0; **10e**, 26649-23-0; **10f**, 26649-25-2; **10g**, 26649-26-3; **10h**, 140834-59-9; **11a**, 140834-60-2; **11b**, 140834-61-3; **11c**, 140834-62-4; **11d**, 140834-63-5; **11e**, 140834-64-6; **11f**, 110388-12-0; **11g**, 82486-22-4; **11h**, 140834-65-7; **12b**, 140834-66-8; **12c**, 140834-67-9; **12f**, 140834-68-0; **12g**, 126331-02-0; **13a**, 140834-69-1; **13b**, 140834-70-4; **13c**, 140834-71-5; **13f**, 140834-72-6; **13g**, 140834-73-7; **15**, 140834-75-9; **16**, 140834-74-8.

Supplementary Material Available: Data for effect of cobaloxime (3) (Table III), solvent (Table IV), and temperature (Table V) on the reaction, spectral data, and micro analyses for compounds **9b–e**, **10a–b**, **10g–h**, **11c–e**, **11h**, **12c**, **12f**, and **13a–c**, and ^1H NMR spectrum of compound **9e** (5 pages). Ordering information is given on any current masthead page.