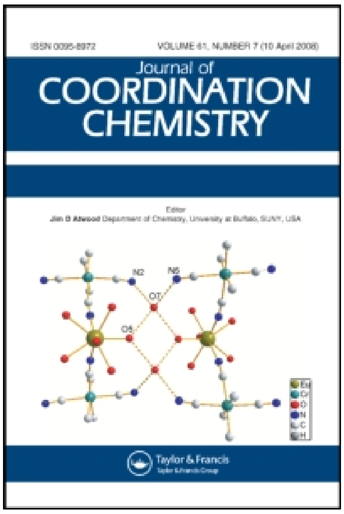

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SYNTHESIS AND STRUCTURAL CHARACTERIZATIONS OF {μ_3-H(Ph)C=C} $FeCo_2(CO)_7$dppfe (dppfe = 1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE): INTRAMOLECULAR π-πINTERACTION BETWEEN THE APICAL PHENYL GROUP OF THE CLUSTER AND A PHENYL GROUP IN DPPFE

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SYNTHESIS AND STRUCTURAL CHARACTERIZATIONS OF {μ_3-H(Ph)C=C} $FeCo_2(CO)_7$dppfe (dppfe = 1,1′-BIS(DIPHENYLPHOSPHINO)FERROCENE): INTRAMOLECULAR π-π INTERACTION BETWEEN THE APICAL PHENYL GROUP OF THE CLUSTER AND A PHENYL GROUP IN DPPFE

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Thermal reaction of {μ_3–H(Ph)C=C} $FeCo_2(CO)_9$ (1) with dppfe in benzene affords dark green {μ_3-H(Ph)C=C} $FeCo_2(CO)_7$dppfe (2). The molecular structures of 1 and 2 have been determined by single crystal x-ray analysis; dppfe replaces two equatorial carbonyls from two $Co(CO)_3$ groups. Thus, dppfe approaches the apical phenyl group. This unusual conformation has been analyzed by computer visualization of the π electrons of the apical phenyl group and one of the phenyl groups in dppfe to indicate an intramolecular π-π interaction between these two phenyl groups. Atomic charge analysis by Extended Hückel (E.H.) calculation suggests why dppfe coordinates to Co atoms preferentially. Cyclic voltammetric behavior for these compounds is interpreted in terms of HOMO and LUMO, which have also been analyzed by E.H. calculations.

Keywords: mixed metal cluster; 1,1′-bis(diphenylphosphino)ferrocene; intramolecular π-π interaction; E.H. calculation; CV; HOMO-LUMO

INTRODUCTION

1,1′-Bis(diphenylphosphino)ferrocene (abbreviated as dppfe hereafter) is a fascinating ligand not only from the catalytic importance of its metal complexes[1] but also from a synthetic prospective due to its flexible coordination to the metal(s) as demonstrated in our previous papers.[2–4] We have also shown that

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dppfe gives significant effects on the redox potential of the metal center to which dppfe is coordinated.[5] Recently our interest in the construction of higher-nuclearity clusters led to the formation of $[RCCo_3(CO)_8]_2(\mu\text{-dppfe})$ in which dppfe bridges two cobalt cluster units, $RCCo_3(CO)_8$.[6] As a logical extension of this finding, we have attempted to synthesize $[\{\mu_3\text{-H(Ph)C}{=}C\}\ FeCo_2(CO)_8]_2$ (μ-dppfe) by thermal decarbonylation of $\{\mu_3\text{-H(Ph)C}{=}C\}\ FeCo_2(CO)_9$ (1); the reason why we expected that dppfe might bridge two cluster units by thermal decarbonylation is that **1** possesses a bulky apical substituent, H(Ph)C=C and this bulky substituent should prevent dppfe from bridging two metal sites in one cluster unit as observed for $CH_3CCo_3(CO)_7$dppfe.[3] Herein is reported the result of the reaction, molecular structure analyses of the product and **1**, and CV for these compounds.

EXPERIMENTAL

Materials and General Procedures

Syntheses and manipulations were made under a nitrogen atmosphere with standard Schlenk-line techniques. Solvents were purified by standard procedures before use. Dppfe was purchased from Strem Chemicals and was used as received. $\{\mu_3\text{-H(Ph)C}{=}C\}\ FeCo_2(CO)_9$ (**1**) was synthesized by the literature method.[7] IR spectra were recorded on a JASCO Valor-III FT-IR spectrometer. ^{31}P-NMR spectra were measured on a Varian XL-200 spectrometer operated at 80.984 MHz with Fourier transform mode and were referenced to external H_3PO_4. A positive chemical shift designates a resonance to a lower field than the resonance of the standard.

Synthesis of $\{\mu_3\text{-H(Ph)C}{=}C\}FeCo_2(CO)_7$ *dppfe*

A benzene solution (40 mL) of **1** (350 mg, 0.663 mmol) and dppfe (368 mg, 0.663 mmol) was heated at 80 °C for 3.5 h under N_2. The solvent was vacuum-stripped from the resulting dark brown solution. A dark brown residue was dissolved into a minimum amount of dichloromethane and the solution was subjected to a Yamazen YFLC-700 medium pressure liquid chromatography (Wako-gel C-200). A purple-red band was eluted with a petroleum ether-hexane (1:1) solution. Then a green band and a dark green band were eluted with a hexane-benzene (1:1) solution. The second green band was collected and the solvent was rotary-evaporated to leave a dark-green solid. Pure samples were obtained by recrystallizing this solid from petroleum ether-chloroform. Yield

245 mg (36%). IR(v(CO)) (Nujol mull) 2041(s), 1999(vs), 1985(vs), 1957(m), 1948(s), 1940(m), 1919(m) cm^{-1}; ^{31}P NMR ($CDCl_3$ soln, –50 °C) δ 39.3 and 50.6 (each peak consists of 8 lines due to coupling with Co nucleus, I = 7/2). *Anal* Calcd for $C_{49}H_{34}Co_2FeO_7P_2$(%): C, 57.34; H, 3.34. Found: C, 57.75; H, 3.59.

X-Ray Data Collection and Structure Determination

A dark green crystal of **2** with approximate dimensions of 0.80 × 0.50 × 0.20 mm^3 and a dark brown crystal of **1** with approximate dimensions of 0.55 × 0.50 × 0.40mm^3 (both of which were grown from CH_2Cl_2-hexane) were mounted on a MAC MXC^3 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal data for these compounds are given in Table I. The structures were solved by a direct method (SHELXS 86) and refined by a full-matrix least-squares method on a Sun SP/Classic work station with a Crystan program package provided by MAC Science. Refinements were made anisotropically for nonhydrogen atoms for **2**. However, strong correlation among the parameters prevented anisotropical refinements for **1** and final parameters obtained are based on isotropical refinements. The molecular structures of **2** and **1** are shown in Figure 1 and 2. The atomic coordinates are listed in Table II and selected bond lengths and angles are given in Table III. The $|F_0|-|F_c|$ tables and anisotropic temperature factor tables are available from the author.

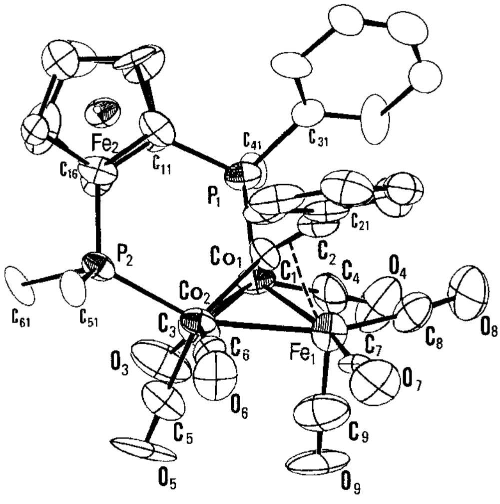

FIGURE 1 Molecular structure of {μ_3-H(Ph)C=C} $FeCo_2(CO)_7(\mu$-dppfe) (**2**). Phenyl carbons of the dppfe group except ipso-carbons are omitted for clarity.

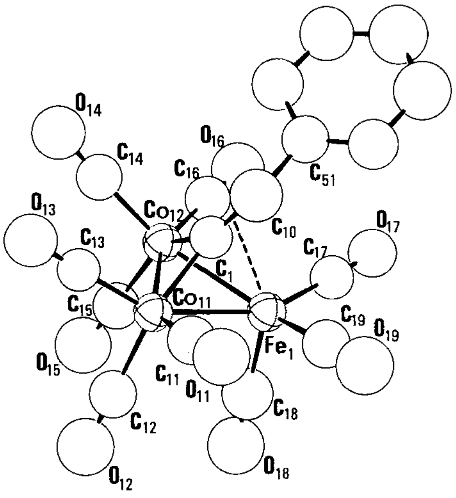

FIGURE 2 Molecular structure of the molecule 1 of {μ_3-H(Ph)C═C} $FeCo_2(CO)_9$ (**1**).

TABLE I Crystal data

Compound	*{μ_3-H(Ph)C═C} $FeCo_2(CO)_7$ dppfe(**2**)*	*{μ_3-H(Ph)C═C} $FeCo_2(CO)_9$ (**1**)*
Formula	$C_{49}H_{34}Co_2Fe_2O_7P_2$	$C_{17}H_6Co_2FeO_9$
Formula weight	1026.3	527.93
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	12.095(4)	15.407(5)
b/Å	16.774(7)	28.639(5)
c/Å	12.035	9.444(2)
α/deg	104.56(3)	90.73(1)
β/deg	110.12(3)	104.31(2)
γ/deg	85.09(3)	96.97(2)
V/Å^3	2219(1)	4004(1)
Z	2	8
d_{calcd}/gcm^{-3}	1.54	1.75
Crystal dimens/mm^3	0.80 × 0.70 × 0.55	0.55 × 0.50 × 0.40
μ(Mo kα)/cm^{-1}	10.1	14.2
Scan type	2θ-ω	2θ-ω
Scan range	1.36 + 0.35tanθ	1.60 + 0.35tanθ
Scan speed/deg.min^{-1}	5.0	6.0
$2\theta_{max}$/deg	45	45
Temperature (K)	298	298
Unique reflections	5784	10454
Reflections with $\|F_o\|>3\sigma\|F_o\|$	3420	7461
No. of parameters refined	568	471
R	0.095	0.125
Rw	0.066	0.126

Mo Kα radiation (λ=0.71073 Å); $R = ||F_o|-|F_c||/|F_o|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma(F_o)^2]^{1/2}$ where $w = 1/\sigma^2(F)$.

TABLE II Atomic coordinates and isotropic thermal parameter, Beq(A^2)

$\{\mu_3$-H(Ph)C=C$\}$ $FeCo_2(CO)_7$dppfe (*2*)					$\{\mu_3$-H(Ph)C=C$\}FeCo_2(CO)_9$ (*1*)				
atom	*x*	*y*	*z*	*B (eq)*	*atom*	*x*	*y*	*z*	*B (eq)*
Fe1	0.1490 (3)	0.2163 (2)	−0.2716 (3)	3.3 (3)	Co11	1.1002 (2)	−0.1132 (1)	−0.2079 (3)	4.43 (6)
Co1	0.1894 (2)	0.2894 (2)	−0.4158 (2)	3.1 (3)	Co2	1.2616 (2)	−0.1160 (1)	−0.0889 (3)	4.63 (6)
Co2	0.3470 (2)	0.2906 (2)	−0.2115 (2)	2.7 (3)	Fe1	1.1549 (2)	−0.0981 (1)	0.0624 (3)	4.56 (6)
Fe2	0.5268 (2)	0.2401 (2)	−0.5050 (2)	3.2 (3)	C1	1.190 (1)	−0.0671 (8)	−0.100 (2)	5.5 (5)
P1	0.2185 (5)	0.2496 (3)	−0.5929 (4)	2.7 (4)	C10	1.201 (2)	−0.022 (1)	−0.068 (3)	8.3 (7)
P2	0.5329 (5)	0.3035 (3)	−0.2099 (4)	2.6 (4)	C11	1.005 (2)	−0.0854 (9)	−0.220 (2)	6.8 (6)
C1	0.275 (2)	0.203 (1)	−0.344 (1)	2.7 (8)	C12	1.053 (2)	−0.1744 (9)	−0.222 (2)	6.4 (5)
C2	0.249 (2)	0.120 (1)	−0.361 (2)	3.6 (9)	C13	1.113 (1)	−0.1064 (8)	−0.385 (2)	5.4 (5)
C3	0.201 (2)	0.397 (1)	−0.384 (2)	3.8 (9)	C14	1.310 (1)	−0.1009 (8)	−0.235 (2)	6.0 (5)
C4	0.041 (2)	0.277 (1)	−0.482 (2)	4.0 (9)	C15	1.249 (1)	−0.1794 (9)	−0.094 (2)	6.1 (5)
C5	0.324 (2)	0.397 (1)	−0.135 (2)	3.9 (9)	C16	1.360 (1)	−0.1042 (8)	0.053 (2)	6.0 (5)
C6	0.391 (2)	0.252 (1)	−0.080 (2)	3.1 (8)	C17	1.235 (1)	−0.0797 (8)	0.228 (2)	5.4 (5)
C7	0.172 (2)	0.169 (1)	−0.145 (2)	3.8 (8)	C18	1.119 (2)	−0.157 (1)	0.101 (3)	7.5 (6)
C8	0.023 (2)	0.158 (1)	−0.359 (2)	5 (1)	C19	1.068 (2)	−0.0708 (9)	0.104 (2)	6.5 (5)
C9	0.082 (2)	0.310 (2)	−0.213 (2)	6 (1)	O11	0.943 (1)	−0.0647 (7)	−0.222 (2)	9.2 (5)
O3	0.206 (2)	0.4691 (9)	−0.366 (1)	7.3 (8)	O12	1.019 (1)	−0.2130 (7)	−0.237 (2)	9.4 (5)
O4	−0.063 (1)	0.274 (1)	−0.530 (1)	7.8 (8)	O13	1.122 (1)	−0.1005 (6)	−0.501 (2)	8.3 (4)
O5	0.306 (2)	0.462 (1)	−0.090 (1)	8.7 (9)	O14	1.342 (1)	−0.0900 (6)	−0.331 (2)	8.3 (4)
O6	0.422 (1)	0.230 (1)	0.013 (1)	5.8 (7)	O15	1.245 (1)	−0.2209 (6)	−0.100 (2)	8.8 (5)
O7	0.182 (1)	0.136 (1)	−0.070 (1)	6.9 (8)	O16	1.426 (1)	−0.0959 (6)	0.146 (2)	8.1 (4)
O8	−0.054 (1)	0.111 (1)	−0.421 (2)	7.9 (9)	O17	1.288 (1)	−0.0679 (6)	0.333 (2)	6.8 (4)
O9	0.037 (2)	0.368 (1)	−0.182 (2)	8.4 (9)	O18	1.098 (1)	−0.1950 (8)	0.128 (2)	9.6 (5)
C11	0.361 (2)	0.273 (1)	−0.598 (2)	2.4 (8)	O19	1.011 (1)	−0.0530 (7)	0.133 (2)	9.3 (5)
C12	0.417 (2)	0.230 (1)	−0.686 (2)	4.1 (9)	C51	1.274 (2)	0.0113 (8)	0.032 (3)	6.4 (5)
C13	0.522 (2)	0.277 (1)	−0.659 (2)	5 (1)	C52	1.363 (2)	0.012 (1)	0.015 (3)	7.7 (6)
C14	0.526 (2)	0.350 (2)	−0.560 (2)	5 (1)	C53	1.426 (2)	0.044 (1)	0.110 (3)	8.6 (7)
C15	0.424 (2)	0.347 (1)	−0.522 (2)	3.8 (9)	C54	1.409 (2)	0.074 (1)	0.216 (3)	10.1 (8)
C16	0.579 (2)	0.233 (1)	−0.331 (2)	2.4 (8)	C55	1.319 (2)	0.071 (1)	0.226 (3)	9.6 (8)
C17	0.681 (2)	0.249 (1)	−0.363 (2)	2.6 (8)	C56	1.251 (2)	0.038 (1)	0.130 (3)	7.3 (6)
C18	0.684 (2)	0.176 (1)	−0.460 (2)	3.6 (8)	Co21	0.1991 (2)	−0.3062 (1)	−0.5176 (3)	4.94 (6)
C19	0.585 (2)	0.122 (1)	−0.491 (2)	3.1 (8)	Co22	0.3052 (2)	−0.2860 (1)	−0.6752 (3)	4.42 (6)

TABLE II (*Continued*)

	$\{\mu_3\text{-H(Ph)C=C}\}\ \text{FeCo}_2\text{(CO)}_7\text{dppfe)}$ (2)					$\{\mu_3\text{-H(Ph)C=C}\}\text{FeCo}_2\text{(CO)}_9$ (*1*)			
atom	*x*	*y*	*z*	*B (eq)*	*atom*	*x*	*y*	*z*	*B (eq)*
C20	0.521 (2)	0.159 (1)	−0.409 (2)	2.9 (8)	Fe2	0.3679 (2)	−0.2943 (1)	−0.4061 (3)	4.40 (6)
C21	0.311 (2)	0.058 (1)	−0.296 (2)	3.4 (9)	C2	0.291 (1)	−0.3386 (7)	−0.559 (2)	4.7 (4)
C22	0.434 (2)	0.071 (1)	−0.220 (2)	4.5 (9)	C20	0.342 (1)	−0.3724 (8)	−0.511 (2)	5.7 (5)
C23	0.488 (2)	0.009 (1)	−0.156 (2)	5 (1)	C21	0.170 (1)	−0.3295 (8)	−0.363 (2)	6.0 (5)
C24	0.418 (3)	−0.062 (1)	−0.173 (2)	6 (1)	C22	0.172 (2)	−0.247 (1)	−0.501 (3)	9.1 (8)
C25	0.300 (2)	−0.072 (1)	−0.248 (2)	4 (1)	C23	0.106 (2)	−0.331 (1)	−0.646 (2)	8.2 (7)
C26	0.247 (2)	−0.014 (1)	−0.314 (2)	5 (1)	C24	0.235 (1)	−0.3051 (8)	−0.840 (2)	6.1 (5)
C31	0.186 (2)	0.140 (1)	−0.668 (2)	2.4 (8)	C25	0.405 (1)	−0.2971 (6)	−0.722 (2)	4.6 (4)
C32	0.066 (2)	0.115 (1)	−0.722 (2)	6 (1)	C26	0.309 (2)	−0.224 (1)	−0.687 (2)	7.0 (6)
C33	0.036 (2)	0.033 (1)	−0.775 (2)	6 (1)	C27	0.379 (2)	−0.2332 (9)	−0.368 (2)	6.7 (6)
C34	0.128 (2)	−0.022 (1)	−0.770 (2)	6 (1)	C28	0.482 (1)	−0.2970 (7)	−0.392 (2)	5.1 (4)
C35	0.244 (2)	−0.003 (1)	−0.721 (2)	3.7 (9)	C29	0.368 (1)	−0.3124 (8)	−0.229 (2)	5.5 (5)
C36	0.277 (2)	0.082 (1)	−0.664 (2)	2.8 (8)	O21	0.146 (1)	−0.3464 (7)	−0.266 (2)	9.8 (5)
C41	0.122 (2)	0.298 (1)	−0.715 (2)	3.2 (8)	O22	0.160 (1)	−0.2099 (8)	−0.482 (2)	11.0 (6)
C42	0.069 (2)	0.372 (1)	−0.686 (2)	3.5 (8)	O23	0.044 (1)	−0.3501 (8)	−0.736 (2)	11.5 (6)
C43	0.003 (2)	0.414 (1)	−0.772 (2)	4.3 (9)	O24	0.179 (1)	−0.3200 (6)	−0.949 (2)	8.5 (4)
C44	−0.009 (2)	0.378 (1)	−0.898 (2)	3.8 (9)	O25	0.469 (1)	−0.3041 (6)	−0.750 (2)	7.0 (4)
C45	0.045 (2)	0.300 (1)	−0.925 (2)	3.8 (9)	O26	0.312 (1)	−0.1822 (7)	−0.691 (2)	8.5 (4)
C46	0.113 (2)	0.263 (1)	−0.838 (2)	4.6 (9)	O27	0.389 (1)	−0.1928 (7)	−0.339 (2)	9.4 (5)
C51	0.638 (2)	0.280 (1)	−0.067 (2)	2.6 (8)	O28	0.557 (1)	−0.2963 (6)	−0.381 (2)	7.7 (4)
C52	0.644 (2)	0.339 (1)	0.042 (2)	3.0 (8)	O29	0.370 (1)	−0.3207 (6)	−0.109 (2)	8.6 (4)
C53	0.719 (2)	0.317 (2)	0.150 (2)	5 (1)	C61	0.323 (1)	−0.4122 (7)	−0.412 (2)	5.1 (4)
C54	0.785 (2)	0.247 (1)	0.150 (2)	4 (1)	C62	0.235 (1)	−0.4329 (8)	−0.408 (2)	6.0 (5)
C55	0.776 (2)	0.186 (1)	0.039 (2)	5 (1)	C63	0.231 (2)	−0.4690 (9)	−0.306 (3)	7.0 (6)
C56	0.697 (2)	0.206 (1)	−0.074 (2)	3.0 (8)	C64	0.306 (2)	−0.4824 (9)	−0.220 (3)	7.2 (6)
C61	0.593 (2)	0.402 (1)	−0.202 (2)	2.8 (8)	C65	0.391 (2)	−0.4626 (9)	−0.228 (3)	7.2 (6)
C62	0.712 (2)	0.416 (1)	−0.166 (2)	3.9 (9)	C66	0.399 (1)	−0.4265 (8)	−0.327 (2)	6.3 (5)
C63	0.752 (2)	0.494 (2)	−0.162 (2)	5 (1)	Co31	0.6374 (2)	−0.2225 (1)	−0.9597 (3)	4.25 (6)
C64	0.678 (3)	0.557 (1)	−0.190 (2)	6 (1)	Co32	0.8007 (2)	−0.2072 (1)	−0.8426 (3)	4.56 (6)
C65	0.553 (2)	0.547 (2)	−0.221 (2)	5 (1)	Fe3	0.6893 (2)	−0.2036 (1)	−0.6894 (3)	4.00 (6)
C66	0.512 (2)	0.468 (1)	−0.227 (2)	4.0 (9)	C3	0.709 (1)	−0.1701 (6)	−0.857 (2)	4.3 (4)

TABLE II (*Continued*)

$\{\mu_3$-H(Ph)C=C$\}$ FeCo$_2$(CO)$_7$dppfe) (*2*)					$\{\mu_3$-H(Ph)C=C$\}$FeCo$_2$(CO)$_9$ (*1*)				
atom	*x*	*y*	*z*	*B (eq)*	*atom*	*x*	*y*	*z*	*B (eq)*
H1	0.20 (1)	0.10 (1)	–0.46 (1)	2.72 (0)	C30	0.686 (2)	–0.127 (1)	–0.821 (3)	8.5 (7)
					C31	0.529 (1)	–2091 (8)	–0.966 (2)	6.1 (5)
					C32	0.616 (1)	–0.2848 (9)	–0.980 (2)	6.0 (5)
					C33	0.644 (2)	–0.2092 (9)	–1.134 (3)	6.7 (6)
					C34	0.690 (1)	–0.2633 (8)	–0.646 (2)	5.9 (5)
					C35	0.760 (1)	–0.1780 (8)	–0.529 (2)	6.1 (5)
					C36	0.590 (1)	–0.1929 (8)	–0.640 (2)	5.5 (5)
					C37	0.823 (2)	–0.267 (1)	–0.848 (3)	7.1 (6)
					C38	0.889 (2)	–0.1894 (9)	–0.696 (3)	7.2 (6)
					C39	0.842 (2)	–0.1863 (9)	–0.981 (3)	6.7 (6)
					O31	0.458 (1)	–0.2017 (7)	–0.966 (2)	9.0 (5)
					O32	0.600 (1)	–0.3250 (7)	–0.990 (2)	9.3 (5)
					O33	0.646 (1)	–0.1953 (6)	–1.253 (2)	9.4 (5)
					O34	0.689 (1)	–0.3033 (7)	–0.619 (2)	8.3 (4)
					O35	0.805 (1)	–0.1600 (6)	–0.422 (2)	9.5 (5)
					O36	0.528 (1)	–0.1859 (6)	–0.605 (2)	8.6 (4)
					O37	0.828 (1)	–0.3080 (7)	–0.858 (2)	9.7 (5)
					O38	0.955 (1)	–0.1762 (7)	–0.601 (2)	10.2 (5)
					O39	0.872 (1)	–0.1658 (8)	–1.075 (2)	11.0 (6)
					C71	0.743 (2)	–0.0878 (8)	–0.718 (2)	6.3 (5)
					C72	0.838 (2)	–0.079 (1)	–0.707 (3)	7.6 (6)
					C73	0.889 (2)	–0.040 (1)	–0.602 (3)	10.6 (9)
					C74	0.837 (2)	–0.018 (1)	–0.528 (3)	9.8 (8)
					C75	0.760 (2)	–0.026 (1)	–0.536 (3)	8.6 (7)
					C76	0.695 (2)	–0.062 (1)	–0.644 (3)	9.8 (8)
					Co41	–0.1461 (2)	–0.3929 (1)	–0.4444 (3)	4.78 (6)
					Co42	–0.1048 (2)	–0.4093 (1)	–0.1789 (3)	4.98 (6)
					Fe4	–0.2638 (2)	–0.3947 (1)	–0.2992 (3)	4.44 (6)
					C4	–0.188 (1)	–0.4417 (7)	–0.332 (2)	4.2 (4)
					C40	–0.262 (2)	–0.4739 (9)	–0.371 (2)	6.6 (5)
					C41	–0.225 (1)	–0.3982 (8)	–0.612 (2)	6.0 (5)

TABLE II (*Continued*)

{μ_3-H(Ph)C=C} FeCo$_2$(CO)$_7$dppfe) (*2*)					{μ_3-H(Ph)C=C}FeCo$_2$(CO)$_9$ (*1*)				
atom	*x*	*y*	*z*	*B (eq)*	*atom*	*x*	*y*	*z*	*B (eq)*
					C42	−0.100 (2)	−0.332 (1)	−0.444 (3)	8.0 (7)
					C43	−0.065 (2)	−0.4206 (9)	−0.496 (2)	6.6 (6)
					C44	−0.051 (2)	−0.353 (1)	−0.121 (3)	7.0 (6)
					C45	−0.133 (1)	−0.4284 (8)	−0.016 (2)	5.8 (5)
					C46	−0.016 (2)	−0.440 (1)	−0.171 (3)	9.5 (8)
					C47	−0.240 (1)	−0.3327 (9)	−0.259 (2)	5.9 (5)
					C48	−0.317 (1)	−0.411 (8)	−0.160 (2)	5.2 (4)
					C49	−0.362 (1)	−0.3956 (8)	−0.439 (2)	6.0 (5)
					O41	−0.282 (1)	−0.4025 (6)	−0.720 (2)	7.2 (4)
					O42	−0.076 (1)	−0.2923 (8)	−0.451 (2)	10.5 (6)
					O43	−0.011 (1)	−0.4406 (7)	−0.532 (2)	9.1 (5)
					O44	−0.023 (1)	−0.3126 (6)	−0.081 (2)	8.9 (5)
					O45	−0.150 (1)	−0.4378 (6)	−0.094 (2)	7.8 (4)
					O46	0.041 (1)	−0.4636 (8)	−0.162 (2)	11.8 (6)
					O47	−0.228 (1)	−0.2936 (6)	−0.230 (2)	7.8 (4)
					O48	−0.358 (1)	−0.4225 (6)	−0.073 (2)	7.5 (4)
					O49	−0.430 (1)	−0.3934 (6)	−0.527 (2)	7.7 (4)
					C81	−0.287 (2)	−0.5124 (8)	−0.267 (2)	6.4 (5)
					C82	−0.219 (2)	−0.532 (1)	−0.165 (3)	7.8 (6)
					C83	−0.266 (2)	−0.572 (1)	−0.085 (3)	10.5 (9)
					C84	−0.350 (2)	−0.578 (1)	−0.103 (3)	9.3 (8)
					C85	−0.417 (2)	−0.558 (1)	−0.197 (3)	9.8 (8)
					C86	−0.381 (2)	−0.525 (1)	−0.284 (3)	9.2 (8)

TABLE III Selected bond lengths (Å) and angles (deg)

Compound: (μ_3-H(Ph)C=C}FeCo$_2$(CO)$_7$dppfe (*2*)		(μ_3-H(Ph)C=C}FeCo$_2$(CO)$_9$ (*1*)			
Distance					
Co1—Co2	2.538(3)	Molecule 1		Molecule 3	
Co1—Fe1	2.552(5)	Co11—Co12	2.473(4)	Co31—Co32	2.467(3)

TABLE III (*Continued*)

Compound: (μ_3-H(Ph)C=C}FeCo$_2$(CO)$_7$dppfe (*2*)				(μ_3-H(Ph)C=C}FeCo$_2$(CO)$_9$ (*1*)	
Distance					
P1—C11	1.82(2)	Co11—Fe1	2.498(4)	Co31—Fe3	2.512(4)
P2—C16	1.84(2)	Co12—Fe1	2.519(4)	Co32—Fe3	2.512(4)
Co2—Fe1	2.584(4)	Co11—C1	1.88(2)	Co31—C3	1.85(2)
Co1—P1	2.208(6)	Co12—C1	1.87(2)3	Co32—C3	1.85(2)
Co2—P2	2.271(7)	Fe1—C1	1.94(2)	Fe3—C3	1.93(2)
Fe1—C2	2.22(2)	Fe1—C10	2.63(3)	Fe3—C30	2.54(3)
Fe1—C1	1.97(2)	C1—C10	1.31(4)	C3—C30	1.39(4)
Co1—C1	1.92(2)	Co11—C11	1.73(3)	Co31—C31	1.74(2)
Co2—C1	1.88(2)	Co11—C12	1.81(2)	Co31—C32	1.78(2)
Co1—C3	1.76(2)	Co11—C13	1.74(2)	Co31—C33	1.72(3)
Co1—C4	1.71(2)	Co12—C14	1.76(2)	Co32—C34	1.69(2)
Co2—C5	1.84(2)	Co12—C15	1.80(2)	Co32—C35	1.80(3)
Co2—C6	1.76(2)	Co12—C16	1.76(2)	Co32—C36	1.70(2)
Fe1—C7	1.82(2)	Fe1—C17	1.77(2)	Fe3—C37	1.76(2)
Fe1—C8	1.74(2)	Fe1—C18	1.79(3)	Fe3—C38	1.73(2)
Fe1—C9	1.80(2)	Fe1—C19	1.74(3)	Fe3—C39	1.76(2)
Fe2—C11	2.04(2)	C10—C51	1.50(3)	C30—C71	1.51(3)
Fe2—C12	2.10(2)	C11—O11	1.18(3)	C31—O31	1.14(3)
Fe2—C13	2.08(3)	C12—O12	1.15(3)	C32—O32	1.14(3)
Fe2—C14	2.10(3)	C13—O13	1.15(3)	C33—O33	1.20(3)
Fe2—C15	2.10(2)	C14—O14	1.16(2)	C34—O34	1.18(3)
Fe2—C16	2.00(2)	C15—O15	1.18(3)	C35—O35	1.15(3)
Fe2—C17	2.04(2)	C16—O16	1.16(2)	C36—O36	1.13(3)
Fe2—C18	2.07(2)	C17—O17	1.15(3)	C37—O37	1.17(4)
Fe2—C19	2.07(2)	C18—O18	1.14(2)	C38—O38	1.19(3)
Fe2—C20	2.02(2)	C19—O19	1.14(4)	C39—O39	1.21(3)
P1—C31	1.85(2)	Molecule 2		Molecule 4	
P1—C41	1.86(2)	Co21—Co22	2.492(4)	Co41—Co42	2.497(4)
P2—C51	1.86(2)	Co21—Fe2	2.531(4)	Co41—Fe4	2.524(4)
P2—C61	1.83(2)	Co22—Fe2	2.514(4)	Co42—Fe4	2.519(4)
C2—C21	1.45(3)	Co21—C2	1.90(2)	Co41—C4	1.91(3)

TABLE III (*Continued*)

Compound: (μ_3-H(Ph)C=C}FeCo$_2$(CO)$_7$dppfe (*2*)				(μ_3-H(Ph)C=C}FeCo$_2$(CO)$_9$ (*1*)	
Distance					
C2—H1	1.1(1)	Co22—C2	1.90(2)	Co42—C4	1.84(2)
C3—O3	1.17(3)	Fe2—C2	1.96(2)	Fe4—C4	1.95(2)
C4—O4	1.19(2)	Fe2—C20	2.38(2)	Fe4—C40	2.36(2)
C5—O5	1.13(2)	C2—C20	1.33(3)	C4—C40	1.34(3)
C6—O6	1.19(2)	Co21—C21	1.75(2)	Co41—C41	1.74(2)
C7—O7	1.14(3)	Co21—C22	1.81(3)	Co41—C42	1.78(3)
C8—O8	1.18(3)	Co21—C23	1.73(3)	Co41—C43	1.72(3)
C9—O9	1.13(3)	Co22—C24	1.70(2)	Co42—C44	1.74(2)
		Co22—C25	1.77(2)	Co42—C45	1.77(2)
		Co22—C26	1.76(3)	Co42—C46	1.71(3)
		Fe2—C27	1.76(3)	Fe4—C47	1.78(2)
		Fe2—C28	1.74(2)	Fe4—C48	1.76(2)
		Fe2—C29	1.76(2)	Fe4—C49	1.75(2)
		C20—C61	1.53(3)	C40—C81	1.56(3)
		C21—O21	1.16(3)	C41—O41	1.16(2)
		C22—O22	1.12(4)	C42—O42	1.18(4)
		C23—O23	1.18(3)	C43—O43	1.18(3)
		C24—O24	1.20(2)	C44—O44	1.20(3)
		C25—O25	1.12(3)	C45—O45	1.15(4)
		C26—O26	1.20(3)	C46—O46	1.15(3)
		C27—O27	1.16(3)	C47—O47	1.13(3)
		C28—O28	1.14(3)	C48—O48	1.17(3)
		C29—O29	1.15(3)	C49—O49	1.16(2)
Angle					
Co1—Co2—Fe1	59.8(1)	Molecule 1		Molecule 3	
Co2—Fe1—Co1	59.2(1)	Co11—Fe1—Co12	59.1(1)	Co31—Fe3—Co32	58.8(1)
Fe1—Co1—Co2	61.0(1)	Co11—Co12—Fe1	60.0(1)	Co31—Co32—Fe3	60.6(1)
P1—Co1—Co2	124.4(2)	Co12—Co11—Fe1	60.9(1)	Co32—Co31—Fe3	60.6(1)
P1—Co1—Fe1	135.2(2)	C1—Co11—Co12	48.6(7)	C3—Co31—Co32	48.3(6)
P2—Co2—Co1	113.8(2)	C1—Co12—Co11	48.9(6)	C3—Co32—Co31	48.2(5)

TABLE III (*Continued*)

Compound: (μ_3-H(Ph)C=C}FeCo$_2$(CO)$_7$dppfe (*2*)				(μ_3-H(Ph)C=C}FeCo$_2$(CO)$_9$ (*1*)	
Angle					
P2—Co2—Fe1	155.4(2)	C1—Fe1—Co11	48.1(6)	C3—Fe3—Co31	49.8(6)
Co1—C1—Co2	83.8(8)	C1—Fe1—Co12	47.4(7)	C3—Fe3—Co32	47.1(6)
Fe1—C1—Co1	82.1(8)	Co11—C1—Co12	82.5(9)	Co31—C3—Co32	83.5(8)
Fe1—C1—Co2	84.2(7)	Co11—C1—Fe1	81.6(9)	Co31—C3—Fe3	83.1(8)
C2—C1—Co1	133(1)	Co12—C1—Fe1	82.7(9)	Co32—C3—Fe3	83.1(8)
C2—C1—Co2	137(1)	C10—C1—Co11	138(2)	C30—C3—Co31	130(2)
C2—C1—Fe1	80(1)	C10—C1—Co12	139(2)	C30—C3—Co32	146(1)
P1—Co1—C3	102.3(8)	C10—C1—Fe1	106(2)	C30—C3—Fe3	98(2)
P1—Co1—C4	92.4(7)	C1—C10—C51	133(2)	C3—C30—C71	129(2)
P2—Co2—C5	99.0(8)	C1—Co11—C11	101(1)	C3—Co31—C31	101(1)
P2—Co2—C6	94.8(7)	C1—Co11—C12	146(1)	C3—Co31—C32	147.4(9)
P1—Co1—C1	97.7(6)	C1—Co11—C13	102.2(9)	C3—Co31—C33	99(1)
P2—Co2—C1	107.4(6)	C1—Co12—C14	98(1)	C3—Co32—C34	99(1)
C1—Co1—C3	137.0(8)	C1—Co12—C15	140(1)	C3—Co32—C35	142.9(9)
C1—Co1—C4	116(1)	C1—Co12—C16	111(1)	C3—Co32—C36	111(1)
C1—Co2—C5	143.3(8)	C1—Fe1—C17	110.4(9)	C3—Fe3—C37	132(1)
C1—Co2—C6	106.3(9)	C1—Fe1—C18	136(1)	C3—Fe3—C38	112(1)
C1—Fe1—C7	116.9(9)	C1—Fe1—C19	109(1)	C3—Fe3—C39	113.6(9)
C1—Fe1—C8	114(1)	Co12—Co11—C11	147.9(8)	Co32—Co31—C31	147.5(7)
C1—Fe1—C9	129(1)	Co12—Co11—C12	102.9(7)	Co32—Co31—C32	103.4(7)
Co2—Co1—C3	89.5(6)	Co12—Co11—C13	96.8(7)	Co32—Co31—C33	96.9(8)
Co2—Co1—C4	138.8(8)	Co11—Co12—C14	100.4(7)	Co31—Co32—C34	101.8(7)
Fe1—Co1—C3	122.5(8)	Co11—Co12—C15	93.6(7)	Co31—Co32—C35	96.8(7)
Fe1—Co1—C4	80.2(8)	Co11—Co12—C16	154.6(9)	Co31—Co32—C36	152(1)
Co1—Co2—C5	97.0(6)	C17—Fe1—Co11	155.9(8)	C37—Fe3—Co31	93.3(7)
Co1—Co2—C6	145.9(6)	C17—Fe1—Co12	99.2(8)	C37—Fe3—Co32	93.0(8)
Fe1—Co2—C5	105.3(7)	C18—Fe1—Co11	93.4(8)	C38—Fe3—Co31	156.6(8)
Fe1—Co2—C6	86.5(6)	C18—Fe1—Co12	98(1)	C38—Fe3—Co32	100.5(8)
Co1—Fe1—C7	161.3(7)	C19—Fe1—Co11	102.5(7)	C39—Fe3—Co31	104.0(6)
Co1—Fe1—C8	105.0(9)	C19—Fe1—Co12	155.6(8)	C39—Fe3—Co32	159.5(7)
Co1—Fe1—C9	87.9(9)	Molecule 2		Molecule 4	

TABLE III (*Continued*)

Compound: $(\mu_3$-H(Ph)C=C}FeCo$_2$(CO)$_7$dppfe (*2*)				$(\mu_3$-H(Ph)C=C}FeCo$_2$(CO)$_9$ (*1*)	
Angle					
Co2—Fe1—C7	102.6(6)	Co21—Fe2—Co22	59.2(1)	Co41—Fe4—Co42	59.4(1)
Co2—Fe1—C8	160.6(9)	Co21—Co22—Fe2	60.7(1)	Co41—Co42—Fe4	60.4(1)
Co2—Fe1—C9	91.3(8)	Co22—Co21—Fe2	60.0(1)	Co42—Co41—Fe4	60.2(1)
		C2—Co21—Co22	49.1(6)	C4—Co41—Co42	47.0(5)
		C2—Co22—Co21	48.9(6)	C4—Co42—Co41	49.5(6)
		C2—Fe2—Co21	47.9(6)	C4—Fe4—Co41	48.6(6)
		C2—Fe2—Co22	48.4(6)	C4—Fe4—Co42	46.5(5)
		Co21—C2—Co22	82.0(8)	Co41—C4—Co42	83.4(7)
		Co21—C2—Fe1	82.0(8)	Co41—C4—Fe4	81.6(8)
		Co22—C2—Fe1	81.2(8)	Co42—C4—Fe4	83.3(8)
		C20—C2—Co21	142(2)	C40—C4—Co41	129(1)
		C20—C2—Co22	133(2)	C40—C4—Co42	145(2)
		C20—C2—Fe2	91(1)	C40—C4—Fe4	90(2)
		C2—C20—C61	128(2)	C4—C40—C81	123(2)
		C2—Co21—C21	109(1)	C4—Co41—C41	105.0(9)
		C2—Co21—C22	140(1)	C4—Co41—C42	146(1)
		C2—Co21—C23	102(1)	C4—Co41—C43	98(1)
		C2—Co22—C24	102(1)	C4—Co42—C44	142(1)
		C2—Co22—C25	98.8(9)	C4—Co42—C45	107.2(9)
		C2—Co22—C26	146(1)	C4—Co42—C46	100(1)
		C2—Fe2—C27	135.6(9)	C4—Fe4—C47	132.2(9)
		C2—Fe2—C28	111.4(9)	C4—Fe4—C48	111.0(9)
		C2—Fe2—C29	112.6(9)	C4—Fe4—C49	112.7(9)
		Co22—Co21—C21	153.9(8)	Co42—Co41—C41	149.7(8)
		Co22—Co21—C22	95(1)	Co42—Co41—C42	102.3(8)
		Co22—Co21—C23	100(1)	Co42—Co41—C43	97.9(8)
		Co21—Co22—C24	98.6(8)	Co41—Co42—C44	95.5(8)
		Co21—Co22—C25	146.8(6)	Co41—Co42—C45	152.1(6)
		Co21—Co22—C26	103.6(9)	Co41—Co42—C46	100(1)
		C27—Fe2—Co21	97.1(7)	C47—Fe4—Co41	92.2(8)
		C27—Fe2—Co22	92.8(8)	C47—Fe4—Co42	93.4(7)

TABLE III (*Continued*)

	Compound: $(\mu_3\text{-H(Ph)C}{=}\text{C}\}\text{FeCo}_2(\text{CO})_7\text{dppfe}$ (*2*)		$(\mu_3\text{-H(Ph)C}{=}\text{C}\}\text{FeCo}_2(\text{CO})_9$ (*1*)	
Angle				
	C28—Fe2—Co21	158.1(7)	C48—Fe4—Co41	157.3(7)
	C28—Fe2—Co22	102.9(7)	C48—Fe4—Co42	100.1(6)
	C29—Fe2—Co21	98.8(7)	C49—Fe4—Co41	101.0(8)
	C29—Fe2—Co22	156.8(6)	C49—Fe4—Co42	157.3(8)

TABLE IV Voltammetric data[a]

Compound	*Reduction*			*Oxidation*		
				1st oxidation	*2nd oxidation*	*3rd oxidation*
	E_{pc}[b]	E_{pa}[c]	$E_{1/2}$[d]	E_{pa}[c]	E_{pa}[c]	E_{pa}[c]
$\{\mu_3\text{-H(Ph)C}{=}\text{C}\}\text{FeCo}_2(\text{CO})_9$ (1)	−1.07	−0.89	−0.98	1.16	1.36	
$\{\mu_3\text{-H(Ph)C}{=}\text{C}\}\text{FeCo}_2(\text{CO})_7\text{dppfe}$ (2)	−1.49	−0.91	−1.20	0.47	1.03	1.35

[a] a platinum electrode (Ag/Ag^+ standard) with 0.1M TBAP at 25°C in 200 mV scan rate. [b] E_{pc} = cathodic peak potential (V). [c] E_{pa} = anodic peak potential (V). [d] $E_{1/2}$ = half-wave potential (V).

Electrochemical Measurements

Cyclic voltammetry was done at 25°C with a BAS CV-50W electrochemical analyzer equipped with a platinum electrode for the working electrode and a platinum coil for the auxiliary electrode. A $Ag/AgNO_3$ (0.01M) electrode was employed as the reference electrode with 0.1M $n\text{-}Bu_4NClO_4$ (TBAP) in CH_2Cl_2 ($1M = 1\ moldm^{-3}$). Approximately a 10^{-3} M solution for each sample was prepared in CH_2Cl_2 which contained 0.1M TBAP as a supporting electrolyte. A sweep rate of 200 mV/s was generally used for CV. All of the manipulations were made under an argon atmosphere.

The electrochemical data are given in Table IV.

RESULTS AND DISCUSSION

Single crystal x-ray analysis has confirmed that the product of the thermal reaction between dppfe and **1** is $\{\mu_3\text{-}H(Ph)C{=\!=}C\}FeCo_2(CO)_7(\mu\text{-dppfe})$(**2**) which is apparently composed of one cluster unit and in which dppfe bridges two cobalt atoms (Figure 1); two 8-line peaks in the ^{31}P NMR at -50 °C substantiate the coordination of dppfe to two cobalt atoms, not to cobalt and iron atoms. X-ray analysis has also unraveled the structural feature, that is, dppfe replaces two equatorial carbonyls of two cobalt atoms (Figure 2: the molecular structure of the parent **1**). Thus dppfe occupies the structurally crowded space. The result is a clear contrast to the thermal reaction between $RCCo_3(CO)_9$ ($R = CH_3$ and C_6H_5) and dppfe[3, 8] where dppfe replaces two axial carbonyls and resides on the sterically less crowded opposite site of the Co_3 plane with respect to the apical substituent R, although a similar type of product $RCCo_3(CO)_7(\mu\text{-dppfe})$ is obtained. As a heuristic argument, it should be pertinent to note that dppm (dppm = bis(diphenylphosphino)methane), which is less bulky and less electron-donating[5] than dppfe, replaces two equatorial carbonyls in the thermal reaction with $CH_3CCo_3(CO)_9$.[9] We have examined computer visualization analysis of the π electrons of the phenyl groups using the CAChe program.[10] As is shown in Figure 3, the π electrons of the apical phenyl group are in close contact with those of one of the phenyl groups in dppfe. We believe that the tenable explanation for this crowded arrangement of dppfe rests on the π-π interaction between these phenyl groups. We have attempted to get insight into why dppfe coordinates to cobalt atoms preferentially. E.H. calculation based on the molecular parameters obtained from single crystal X-ray analysis of **1** has shown that the net positive atomic charges on two cobalt atoms are greater than that on iron atom in **1**. Presumably dppfe prefers more positive cobalt atoms to the less positive iron atom.

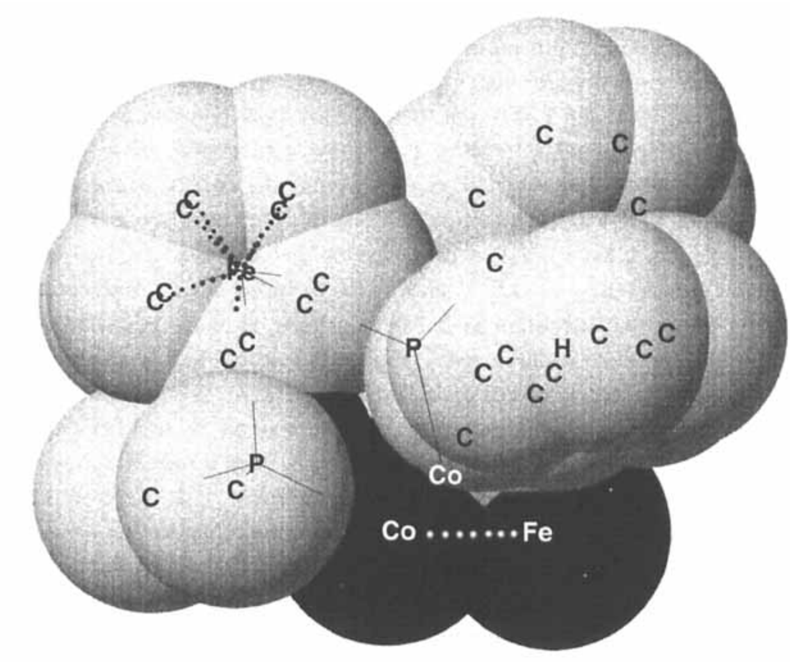

FIGURE 3 Space-filling representation of the interaction between the phenyl group of the apical C=C(Ph) group and one of the phenyl groups in dppfe.

Table III lists important bond lengths for **2** and **1**. The Co—Co and Co—Fe lengths in **2** are significantly elongated compared with those of **1**, while the Fe—C_1 and Co_1—C_1 and Co_2—C_1 bond lengths of **2** are close to those of **1**. However, the Fe—C_2 distance of **2** is far shorter than that of **1**; the apical C=C(Ph) group in **2** is pushed back to the proximity of the $FeCo_2$ core. This approach should increase the π electron donation from the apical C=CH(Ph) group to Fe, thus reinforcing the interaction between Fe and the C=C group.[7] Indeed, the C=C bond length of the apical C=CH(Ph) group in **2** (1.40(3) Å is longer than those in **1** (1.31(4)–1.39(4) Å) and the finding is consonant with the increased π electron donation from this group to Fe. Thus, increased π donation from the apical C=CH(Ph) group should be another origin of the crowded arrangement of the dppfe group in the equatorial positions.[11] The P–Co bond lengths of **2** are 2.208(6) and 2.271(7) Å, which are significantly shorter than those of $CH_3CCo_3(CO)_7$dppfe (2.297(2)–2.314(2) Å)[3] and of $C_6H_5CCo_3$ $(CO)_7$dppfe (2.310(3)–2331(2) Å)[8] but are close to that of $[CH_3CCo_3(CO)_8]_2$(μ-dppfe) (2.240(1) Å).[6] M-CO and C-O bond lengths of **2** are close to those of **1**. Figure 4 shows cyclic voltammograms for **2** and **1**. The most striking feature in the CV of **2** is that an irreversible peak is observed at

E_{pa} = 0.48 V which is absent for **1**. This peak is assignable to the oxidation of Fe in dppfe according to our previous CV study for a series of dppfe complexes with manganese carbonyl derivatives.[5] There are two other irreversible oxidation peaks at E_{pa} = 1.03 V and 1.35 V for **2** which correspond to irreversible oxidation peaks at E_p = 1.16 V and 1.34 V for **1**. **1** shows a reversible reduction peak at $E_{1/2}$ = −1.0 V, while **2** shows a significantly cathodic shifted irreversible peak at $E_{1/2}$ = −1.42 V. For a series of phosphine-substituted homonuclear trimetallic $RCCo_3(CO)_{9-x}L_x$ clusters, it has been shown that the cluster core reduction takes place around $E_{1/2}$ = −1.0 V and shifts to more negative potential with increasing phosphine substituents. It has also been demonstrated that a *quasi*-reversible cluster-core oxidation peak appears at $E_{1/2}$ = 0.85 V in the case of $FcCCo_3(CO)_7[P(OMe)_3]_2$ and/or of $RCCo_3(CO)_7(PR_3)_2$; first oxidation process occurs on Fe of the apical Fc group at $E_{1/2}$ = 0.50 V for $FcCCo_3(CO)_7[P(OMe)_3]_2$.[13] These redox processes have been interpreted in terms of the HOMO-LUMO term on the basis of E.H. calculations;[12–13] an electron is added to the LUMO which is of σ*(Co-Co) character in the reduction process and an electron is removed from the σ(Co-Co) HOMO in the oxidation process of $RCCo_3(CO)_7(PR_3)_2$. The facts that the cluster-core reduction becomes more difficult and the cluster core oxidation becomes easier with increasing phosphine-substituents have also been interpreted in terms that the increase of phosphine-substituents permits accumulation of electron density on the cluster-core to lead to destabilization of the LUMO and an increase in electron density on the cluster-core raises the level of the HOMO to enable easy electron removal from the HOMO because phosphines are good σ-electron donors and weak π-electron acceptors.[12–13] Therefore, we have also attempted E. H. calculation analysis of the HOMO-LUMO character for **1** and **2** by use of the CAChe program system[10] hoping to get insight into the redox processes for **1** and **2**. The calculations have shown that **2** has energetically close HOMO and next HOMO both of which have σ(M-M) character and has a LUMO which has σ*(M-M) character. **1** has similar HOMO and next HOMO with σ(M-M) character and has a LUMO with σ*(M-M) character. The results for these analyses on the HOMO and LUMO of **1** and **2** are quite similar to those of $RCCo_3(CO)_{9-x}L_x$.[12–13] In previous reports we have shown that dppfe is a strong electron donor.[2–3] Therefore, the shift of the reduction potential to more negative for **2** compared with that of **1** can be interpreted in terms of the destabilization of the LUMO because of the increase in electron density of the cluster-core. The first oxidation potential of **2** is significantly shifted to lower oxidation potential as mentioned above. The result is also interpreted in terms of an increase in electron density on the $FeCo_2$ core. The second oxidation process should originate from the HOMO. However, detailed discussion must wait for a future ESR study on the oxidation processes of **1** and **2**.

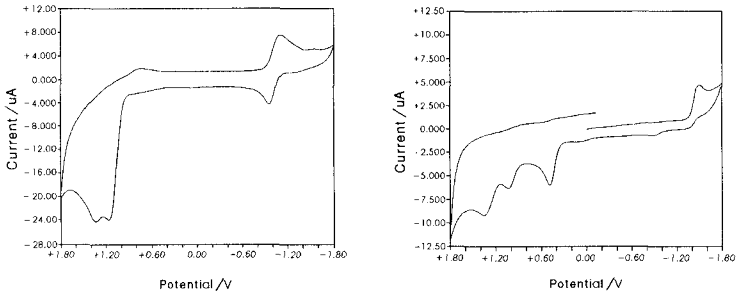

FIGURE 4 Cyclic voltammograms of **1** (left) and **2** (right) in CH_2Cl_2 at 25°C; 200 mV/s, Pt plate (working electrode), Ag/Ag^+ in CH_3CN (reference electrode).

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[11] The angle between the apical phenyl group and the basal $FeCo_2$ plane of **2**, 34.28° is not decreased so much as to compared with those of **1**, 36.49–38.02°. Therefore, π-π interaction between the apical phenyl group and the basal $FeCo_2$ plane for **2**, if any, is not increased so much as compared with **1**.

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