Metal–Nitroxyl Interactions. 8. Exchange Interactions in a Spin-Labeled Copper Complex (3-(N-(3-2,2,5,5-Tetramethylpyrroline-1-oxyl)amido)-4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)copper(II)

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Abstract: Resolved electron–electron coupling is observed in the room temperature solution EPR spectra of the spin-labeled copper complex (3-(N-(3-2,2,5,5-tetramethylpyrroline-1-oxyl)amido)-4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)-copper(II). Values of the coupling constant at room temperature vary with solvent (toluene, CH_2Cl_2, THF, 1:1 THF–CH_2Cl_2, $CHCl_3$, pyridine, Me_2SO, 1:1 toluene–acetone, and 10:1 toluene–THF), ranging from 475 G (0.0454 cm^{-1}) in THF to 520 G (0.0496 cm^{-1}) in Me_2SO. The coupling constant is also temperature dependent with values changing from 525 G (0.0501 cm^{-1}) at -20 °C to 472 G (0.0451 cm^{-1}) at 119 °C in toluene solution.

Introduction

The widespread use of the spin label or spin probe technique[2] in the study of biomolecules has led to numerous examples of the interaction of the nitroxyl electron with unpaired electrons of paramagnetic metals.[3] We are investigating a wide range of discrete transition metal complexes containing nitroxyl radicals to elucidate the nature and magnitude of the electron–electron interaction as evidenced in the EPR spectra. We have recently reported resolved electron–electron spin–spin coupling in the EPR spectra of a spin-labeled copper porphyrin,[4] of spin-labeled copper salicylaldimines,[5] and of complexes of bis(hexafluoroacetylacetonato)copper(II) with nitroxyl-containing ligands which coordinate via a pyridine nitrogen.[6] In this paper we report the preparation and EPR study of a new spin-labeled copper complex, I, derived from Cu(baen).

I, R = [structure]

II, R = Me
III, R = Ph
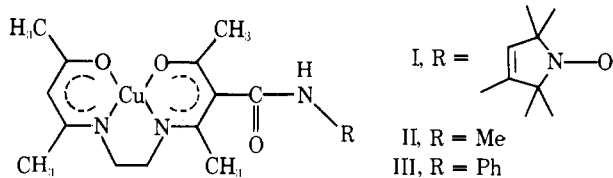
Experimental Section

Physical Measurements. All spectra were obtained in dry, purified solvents. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer 337 grating spectrometer. Visible spectra were obtained in CH_2Cl_2, THF, and pyridine solutions on a Beckman Acta V spectrometer; 1.0–3.0 × 10^{-3} M solutions were used in 1-cm, 1-mm, and 0.1-mm path length cells to avoid using highly diluted solutions since the EPR spectra indicated a larger percent decomposition at lower concentrations. Data are given below with wavelengths in nanometers and log ε in parentheses. Magnetic susceptibilities were measured on a Bruker Faraday balance with 1-μg sensitivity using $HgCo(SCN)_4$[7] and $[Ni(en)_3]S_2O_3$[8] as calibrants. Values of μ_{eff} in Bohr magnetons are given below with the diamagnetic correction[9a] (χ^{dia}) used in the calculations. A temperature-independent paramagnetism (TIP) of 60 × 10^{-6} was assumed for copper(II). This assumption is common, but, in the few cases in which experimental estimates have been made, the TIP for copper(II) ranges from zero to 168 × 10^{-6}.[10] Thus the uncertainty in the correction may be about as large as the correction. Until temperature-dependent magnetic susceptibility data are available for these compounds the significance of the differences between the room temperature susceptibilities and the values expected for magnetically dilute systems cannot be assessed. EPR spectra were obtained on a Varian E-9 spectrometer using an E-231 cavity containing the quartz Dewar of the E-257 variable-temperature accessory. Temperatures were measured with a copper–constantan thermocouple

inserted in the Dewar. The spectrometer is interfaced to a Varian 620/L-100 computer permitting data manipulation with the CLASS language.[11] Spectra were run on 1.5 × 10^{-3} to 1.0 × 10^{-2} M solutions at power levels below saturation and modulation amplitudes which did not cause line broadening. The relatively high concentrations were needed to obtain reasonable signal to noise levels for the "outer lines" in the spectra of the spin-spin coupled systems (see below). Since the line shapes of the "center lines" and positions of the "outer lines" were independent of concentration from 5.0 to 10^{-4} to 1.0 × 10^{-2} M in THF and CH_2Cl_2, spectra in other solvents were routinely run at concentrations of 5.0 × 10^{-3} to 1.0 × 10^{-2} M. The g values were measured by means of the "marker" mode of the E-272B field-frequency lock, which puts a mark on the spectrum at the zero-crossing point of the derivative spectrum of DPPH. The calibration of the field difference between DPPH in the cavity and DPPH in the E-272B accessory was reproducible to within ±0.05 G on different days. All coupling constants are given in gauss (1 G = 0.1 mT).

Preparation of Compounds. (3-(N-3-2,2,5,5-Tetramethylpyrroline-1-oxyl)amido)-4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)copper(II) (I). The compound was prepared by the method reported for II[12] using 3-isocyanato-2,2,5,5-tetramethylpyrroline-1-oxyl:[5] yield 69%; IR ν_{NH} 3280, ν_{CO}(amide) 1655, ν_{CO} 1590, ν_{CN} 1510; μ_{eff} = 2.47 (measured at 27 °C, χ^{dia} = -218 × 10^{-6}); visible spectrum (CH_2Cl_2 solution) 545 nm (log ε 2.36), 311 (4.35), 278 (4.22), 234 (4.40); (THF solution) 547 (2.41), 313 (4.25), 278 (4.12), 233 (4.32); (pyridine solution) 553 (2.33). Anal. Calcd for $C_{21}H_{31}N_4O_4Cu$: C, 54.00; H, 6.69; N, 12.00; Cu, 13.60. Found: C, 53.86; H, 6.65; N, 11.76; Cu, 13.43.

(3-(N-Methylamido)-4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)copper(II) (II). The compound was prepared and characterized as reported by Howells et al.:[12] μ_{eff} = 1.81 (measured at 27 °C, χ^{dia} = -88.6 × 10^{-6}); visible spectrum (CH_2Cl_2 solution) 544 nm (log ε 2.34), 311 (4.36), 278 (4.07), 227 (4.20); (THF solution) 548 (2.38), 311 (4.33), 278 (4.03), 227 (4.17); (pyridine solution) 553 (2.31).

(3-(N-Phenylamido)-4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)copper(II) (III). The compound was prepared and characterized as reported by Howells et al.:[12] μ_{eff} = 1.78 (measured at 27 °C, χ^{dia} = -182.1 × 10^{-6}); visible spectrum (CH_2Cl_2 solution) 544 nm (log ε 2.38), 311 (4.38), 276 (4.27), 243 (4.43); (pyridine solution) 553 (2.34).

Computer Simulations. The EPR spectra of complexes I–III were simulated using the computer program CUNO, which has been described in detail.[13] The simulations of the EPR spectra of II and III provided values of the copper hyperfine coupling constant, $\langle a \rangle_{Cu}$, the nitrogen hyperfine coupling constant, $\langle a \rangle_{N}$, and the g value of the copper electron as summarized in Table I. Line widths were assumed to vary with copper nuclear spin as $A + Bm_1 + Cm_1^2$.[14] All lines in the spectra of II and III were assumed to have a Lorentzian line shape. The coupling constants and g values obtained for II and III and the values for free nitroxyl radicals (g = 2.0059, $\langle a \rangle'_{N}$ = 14.2 ± 0.2 de-

Table I. EPR Parameters for Copper Complexes with Diamagnetic Ligands

compd	solvent	$g_{iso}{}^a$	$\langle a \rangle_{Cu},{}^b$ G	$\langle a \rangle_N,{}^c$ G	A^d	B^d	C^d
II	toluene	2.0922	87.2	14.5	16.8	5.7	1.2
II	CH₂Cl₂	2.0922	87.8	14.5	16.8	5.7	1.2
III	CH₂Cl₂	2.0926	87.8	14.5	16.2	6.5	1.4
II	10:1 toluene-THF	2.0920	87.0	14.5	17.2	6.2	1.3
II	1:1 CH₂Cl₂–THF	2.0924	86.8	14.5	17.0	6.3	1.3
III	1:1 CH₂Cl₂–THF	2.0927	86.8	14.5	16.7	7.1	1.4
II	THF	2.0934	86.4	14.5	17.3	5.8	1.2
II	pyridine	2.0972	82.3	14.3	19.9	10.4	2.2
III	pyridine	2.0968	82.0	14.2	21.0	11.5	2.2
II	Me₂SO	2.0912	86.0	14.5	29.8	19.9	3.7
III	Me₂SO	2.0912	85.0	14.3	32.4	22.2	4.2

^{a} Relative to DPPH (2.0036). Uncertainty ±0.0007. ^{b} Uncertainty ±0.2. Value given is for ^{63}Cu. Value for ^{65}Cu is 1.07 × the value given. ^{c} Uncertainty ±0.1. ^{d} A, B, C are line width parameters; see text. Values given are for 100% Lorentzian lines.

pending on solvent) were used as starting parameters in the simulation of the EPR spectra of I. The value of J was chosen to fit the positions of the "outer" lines. $\langle a \rangle_{Cu}$ was adjusted to optimize the spacing of the low-field ("copper outer") and center lines and was found to be the same as $\langle a \rangle_{Cu}$ in the analogous complexes, II and III, in the same solvent. Values of $\langle a \rangle_N$ and $\langle a \rangle_N'$ in I were assumed to be the same as in II (or III) and free nitroxyl, respectively. Simulated spectra of I were relatively insensitive to the fraction of Lorentzian and Gaussian line shapes. A mixture of 75% Lorentzian and 25% Gaussian was found to be optimum for the high-field portion of the center lines of the spectra in CH₂Cl₂ and 1:1 THF:CH₂Cl₂ solutions. To facilitate line-width comparisons between solvents it was decided to use the same contributions of Lorentzian and Gaussian line shapes for all solvents. The assumption was also made that all transitions had the same line shape. Line widths for both "copper" and "nitroxyl" lines were assumed to vary with copper nuclear spin as $A + Bm_1 + Cm_1^2$ [14] where m_1 refers to the copper nuclear spin state for each individual AB pattern.[13] Both ^{63}Cu and ^{65}Cu were included in the calculation.

Results and Discussion

The spin-labeled copper complex, I, was prepared by the reaction of 3-isocyanato-2,2,5,5-tetramethylpyrroline-1-oxyl with Cu(baen) analogous to the preparation of II and III reported by Howells et al.[12] The IR spectrum of the product includes CO and NH stretches characteristic of substituted amides. The compounds are stable in the solid phase when stored in a desiccator but decompose slowly in solution.

Magnetic Susceptibility. The solid-state magnetic moments of the copper complexes with diamagnetic ligands, II and III, are 1.81 and 1.78 μ_B, respectively, which is reasonable for Cu(II) with a small orbital contribution.[9b] The solid-state magnetic moment for the spin-labeled copper complex, I, is 2.47 μ_B, which agrees well with the values reported recently for spin-labeled copper salicylaldimines.[5] Since a spin-only value of $\sqrt{2} \times 1.73$ or 2.44 μ_B would be expected for two independent electrons, assuming no orbital contribution, the magnetic susceptibilities of the spin-labeled copper complexes are consistent with very small ($<kT$) interaction between the copper and nitroxyl electrons in the solid phase. Detailed interpretation of the solid-state susceptibilities must await variable-temperature data.

Electronic Spectra. The close similarities between the visible spectra of the spin-labeled copper complex, I, and the spectra of the copper complexes with diamagnetic ligands, II and III, suggests that the electronic structure of the copper complexes is not strongly perturbed by the spin labeling.

The effect of solvent on the d–d band was examined for CH₂Cl₂, THF, and pyridine solutions of I and II and for CH₂Cl₂ and pyridine solutions of III. (III is only sparingly soluble in THF.) For both I and II there is a small decrease in the energy of the d–d transition on changing from CH₂Cl₂ to THF and a considerably larger decrease on changing from THF to pyridine. For III, also, the energy of the d–d band is lower in pyridine than in CH₂Cl₂. The shift of the d–d band

to lower energies along the series CH₂Cl₂ > THF > pyridine is consistent with increasing strength of donor interaction in a fifth coordination site.[15]

EPR Spectra. The EPR spectra of the copper complexes with diamagnetic ligands exhibit the typical four-line pattern expected for coupling the copper nucleus ($I = \frac{3}{2}$) with nitrogen superhyperfine coupling clearly resolved on the high-field peak ($m_1 = -\frac{3}{2}$) and partially resolved on the $m_1 = -\frac{1}{2}$ peak. Line width and coupling parameters obtained from the computer simulations of the spectra of II and III in various solvents are given in Table I. Coupling to other nuclei in the molecule may be present, but is not resolved in the spectra, so it is treated only as line broadening in the simulations. In each case where values for II and III were obtained in the same solvent, the results for the coupling constants and g value are similar, indicating that the amide substituent has little influence on the electronic structure of the copper ion. The values obtained for II and III are also similar to those obtained for a single crystal of Cu(baen).[16] Using the equations $g_{iso} = \frac{1}{3}(g_x + g_y + g_z)$ and $\langle a \rangle = \frac{1}{3}(A_x + A_y + A_z)$ the single-crystal results yield $g = 2.0927$, $\langle a \rangle_{Cu} = 87.4$, and $\langle a \rangle_N = 14.2$.[16] The close resemblance between the three sets of values suggests that similar values would be expected for the spin-labeled complex, I, in the absence of electron–electron coupling.

The influence of solvent on the EPR parameter is clearly indicated by the data in Table I. As the donor ability of the solvent increases the value of $\langle a \rangle_{Cu}$ decreases and g increases. The g values in Me₂SO, however, do not follow this pattern. The decreases in $\langle a \rangle_{Cu}$ and increases in g are consistent with the general pattern of increasing $g_\parallel$ and decreasing $A_\parallel$ observed in frozen solutions of copper complexes as the strength of interaction with a fifth ligand increases.[15,17]

The EPR spectra of the spin-labeled complex, I, are markedly different from the spectra of the related copper complexes with diamagnetic ligands, II and III. Spectra of I in CHCl₃ solution are given in Figure 1. An apparent four-line pattern is observed centered at about 3150 G. However, the line shape is not similar to the spectra of II or III and the apparent copper hyperfine (~55 G) is substantially reduced from the copper hyperfine in II or III (~87 G). When the spectrometer gain and modulation amplitude are increased to give an amplification 100 times greater than that used to record the center portion of the spectrum, weak "outer lines" are observed at ~2600 and 3650 G as indicated in Figure 1. The positions of these "outer lines" indicate that the electron–electron coupling constant in complex I is about 500 G (0.0478 cm⁻¹) and that the pattern can be interpreted as an ABMX spin coupled system. Simulated spectra were obtained using the computer program CUNO,[13] and are included in Figure 1. As shown in the figure the calculated and observed line shapes are in good agreement. The relative intensities of the "inner" and "outer" lines in the calculated spectra are also in good agreement with
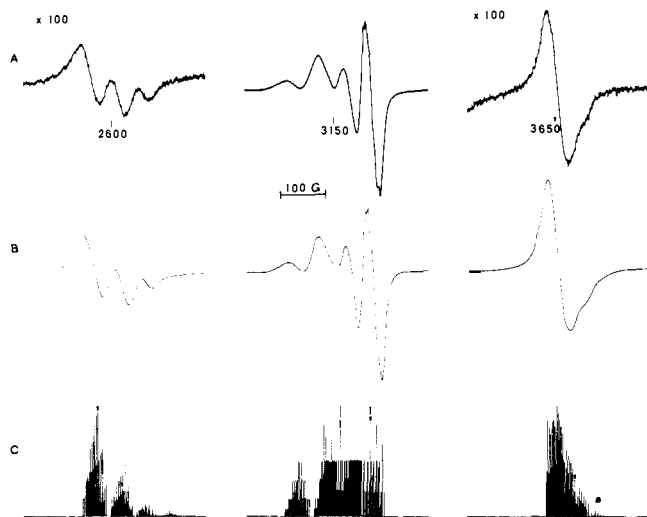
Figure 1. X-Band (9.10 GHz) EPR spectra of I in $CHCl_3$ solution and computer simulations: (A) observed spectra, 400-G scans, 100 G/min scan rate, 30 mW, center lines 0.20 G modulation amplitude, outer lines product of gain and modulation amplitude $100\times$ greater than for center lines; (B) simulated spectra as described in text; (C) stick plot of line positions and intensities.

Table II. Solvent Dependence of the Electron–Electron Coupling Constant, J

solvent	J, G^a	J, cm^{-1} ^{a}
THF	475.	0.0454
1:1 THF–CH_2Cl_2	498.	0.0476
1:1 toluene–acetone	498.	0.0476
pyridine	500.	0.0478
toluene	505.	0.0482
10:1 toluene–THF	505.	0.0482
CH_2Cl_2	505.	0.0482
$CHCl_3$	510.	0.0487
Me_2SO	520.	0.0496

^{a} Obtained by computer simulation. Uncertainty ± 2 G, ± 0.0002 cm^{-1}.

the experimental spectra. Similar spectra were obtained in a range of solvents, though with some variation in the magnitude of the electron–electron coupling constant, J, and changes in line-width parameters. The observed coupling constants as a function of solvent are listed in Table II. The fact that J increases in the order THF $<$ pyridine $<$ CH_2Cl_2 whereas the energy of the d–d transitions observed in the electronic spectra increases in the order pyridine $<$ THF $<$ CH_2Cl_2 indicates that J does not correlate with the energy of the d–d transitions. Further, the value of J does not appear to correlate with any of the commonly cited solvent properties.

The magnitude of J has also been found to be markedly temperature dependent as indicated by the plots in Figure 2. In toluene solution J varies from 525 G (0.0501 cm^{-1}) at -20 °C to 472 G (0.0451) at 119 °C and in 10:1 toluene–THF J varies from 537 G (0.0512 cm^{-1}) at -38 °C to 489 G (0.0467 cm^{-1}) at 57 °C. In addition, in the low-temperature spectra in toluene solution there is evidence for a small amount of a second species with $J \sim 3000$ G (0.315 cm^{-1}). The nature of this species will be discussed later.

EPR microwave power saturation studies also provide evidence of the metal–nitroxyl interactions. In the absence of saturation effects, a plot of signal amplitude vs. the square root of the microwave power, $P^{1/2}$, is linear. Linear plots of amplitude vs. $P^{1/2}$ were obtained for the copper complexes with diamagnetic ligands, II and III, with power settings up to 200 mW. However, plots of amplitude vs. $P^{1/2}$ for nitroxyl radicals exhibit nonlinear behavior above 1–2 mW. In the EPR spectra
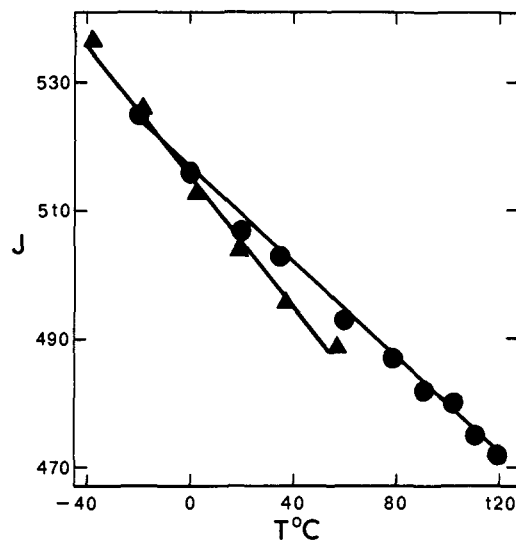

Figure 2. Temperature dependence of the electron–electron coupling constant observed in the EPR spectra of I: ●, toluene solution; ▲, 10:1 toluene–THF solution.

of the spin-labeled copper complex, I, linear plots of amplitude vs. $P^{1/2}$ were observed for both sets of "outer lines" as well as for the center lines with power settings up to 200 mW. Clearly the electron–electron coupling has a large impact on the relaxation behavior of the "nitroxyl electron". There is no evidence of Cu–Cu interactions in the solution EPR spectra of complexes I, II, or III.

Comparison with Prior Results. The room temperature values of J (475–520 G, 0.0454–0.0496 cm^{-1}) in the spin-labeled copper complex, I, are substantially larger than the values we have previously reported for other spin-labeled copper complexes—copper salicylaldimines, 4.8–11.8 G (0.000 46–0.001 13 cm^{-1});[5] copper porphyrin, 77–92 G (0.0072–0.0086 cm^{-1});[4] copper (hexafluoroacetylacetonate) adduct, 45 G (0.0044 cm^{-1}).[6]

We have previously noted that electron–electron coupling constants are solvent dependent.[4,5] However, the patterns observed for J as a function of solvent appear to differ from one compound to another.[4,5] It seems likely that the effect of solvent on J includes conformational influences as well as subtle changes in energy levels of states involved in the exchange which vary from one compound–solvent pair to another. The difficulties in interpreting solvent effects on electron–electron coupling have also been noted in dinitroxides.[18]

Changes in J with temperature have also been observed in dinitroxides[18] and in spin-labeled salicylaldimines.[19] For some systems, including I, J decreases as temperature increases[18] whereas in others J increases as temperature increases.[18,19] The relative impact of conformational changes and changes in solvation as a function of temperature cannot be readily separated on the basis of the limited data currently available.

References and Notes

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Metal Complexes of Fluorophosphines. 9. Structure of a Novel Complex from Benzalacetonetricarbonyliron and Methylaminobis(difluorophosphine)[1,2]

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Abstract: Reaction of $(C_6H_5CH=CHCOCH_3)Fe(CO)_3$ with $CH_3N(PF_2)_2$ in boiling hexane gives yellow $[C_6H_5CH=CHC(CH_3)=C(POF_2)N(CH_3)PF_2]Fe(CO)(PF_2)_2NCH_3$. X-ray diffraction analysis of this complex indicates an unexpected structure containing a novel chelating ligand bonding to iron through both tetrahapto-1,3-diene and aminodifluorophosphine units. The formation of this complex can be rationalized by a scheme involving an intramolecular Wittig-type reaction as a key step.

Introduction

Previous papers from this laboratory have described a variety of iron carbonyl complexes of the potentially bidentate ligand $CH_3N(PF_2)_2$ including $CH_3N(PF_2)_2[Fe(CO)_4]_2$,[3,4] $CH_3N(PF_2)_2Fe_2(CO)_7$,[3,4] $[CH_3N(PF_2)_2Fe(CO)_3]_2$,[3,4] $[CH_3N(PF_2)_2]_2Fe_2(CO)_5$,[3,4] $[CH_3N(PF_2)_2]_2FeCO$,[4] and $[CH_3N(PF_2)_2]_4Fe_2CO$.[5] An obvious gap in this chemistry is the mononuclear complex $CH_3N(PF_2)_2Fe(CO)_3$ derived from $Fe(CO)_5$ by substitution of a single pair of its CO groups with the bidentate $CH_3N(PF_2)_2$ ligand. In an attempt to fill this gap the reaction of benzalacetonetricarbonyliron with $CH_3N(PF_2)_2$ was investigated hoping to effect the following reaction:

$$(C_6H_5CH=CHCOCH_3)Fe(CO)_3 + CH_3N(PF_2)_2$$
$$\rightarrow CH_3N(PF_2)_2Fe(CO)_3 + C_6H_5CH=CHCOCH_3 \quad (1)$$
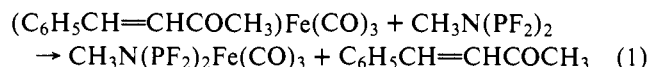
However, preliminary investigation of the resulting product indicated retention of the benzalacetone ligand and suggested the unexpected formulation $(C_6H_5CH=CHCOCH_3)-Fe(CO)[(PF_2)_2NCH_3]_2$. An X-ray crystal structure of this complex, however, revealed that this suggested structure was incorrect and instead indicated structure I containing a chelating ligand with both tetrahapto-1,3'-diene and aminodifluorophosphine as donor units. This paper describes the details of this work.

Experimental Section

Reaction of Benzalacetonetricarbonyliron with $CH_3N(PF_2)_2$. A mixture of 3.0 g (10.5 mmol) of $(C_6H_5CH=CHCOCH_3)Fe(CO)_3$,[6,7] 5.0 g (30 mmol) of $CH_3N(PF_2)_2$,[4,8] and 150 mL of hexane was boiled for 3 h under reflux in a nitrogen atmosphere. The reaction mixture turned yellow and a yellow powder precipitated. The hot reaction mixture was filtered and the precipitate washed with hexane. Cooling

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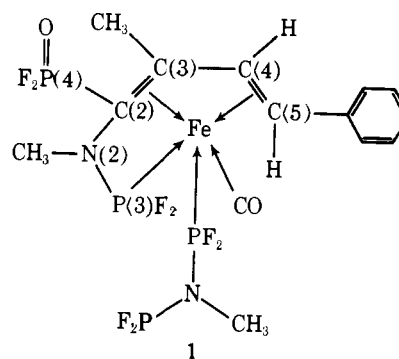
the hexane solution at 0 °C precipitated 0.7 g (11.6% yield) of yellow crystals. The analytical sample, mp 142–144 °C, was purified by further crystallization from hexane. This product decomposed upon attempted chromatography on a Florisil column. The infrared spectrum suggested the presence of additional material in both the residue from the original hexane washing and in the filtrate from the original hexane crystallization but pure product could not readily be isolated from these fractions.

Anal. Calcd for $C_{13}H_{16}F_8FeN_2O_2P_4$ (i.e., $(C_6H_5CH=CHCOCH_3)Fe(CO)[(PF_2)_2NCH_3]_2$): C, 27.6; H, 2.8; F, 27.0; N, 5.0; P, 22.0; mol wt, 564. Calcd for $C_{14}H_{16}F_8FeN_2O_2P_4$ (i.e., $[C_6H_5CH=CHC(CH_3)=C[P(O)F_2]N(CH_3)PF_2]Fe(CO)-(PF_2)_2NCH_3$): C, 29.2; H, 2.8; F, 26.4; N, 4.9; P, 21.5; mol wt, 576. Found: C, 28.8; H, 2.9; F, 24.9; N, 4.9; P, 20.4; mol wt, 600 in benzene.

Infrared spectrum in KBr: 1975 (s), 1932 (w), 1490 (w), 1447 (w), 1381 (vw), 1316 (m), 1244 (w), 1192 (w), 1071 (s), 1048 (vw), 1033 (vw), 997 (vw), 974 (m), 910 (s), 882 (s), 858 (s), 835 (s), 822 (s), 808 (s), 778 (s), 760 (m), 697 (m), 682 (m), 642 (m), 595 (m), 556 (s), 533 (m), 510 (m), 485 (m) cm⁻¹.

¹H NMR spectrum in $CDCl_3$: τ 2.69 (singlet, 5 H, C_6H_5), 4.15 (broad triplet, $J \approx 9$ Hz, 1 H, CH), 5.6 (broad, 1 H, CH), 7.15 (doublet, $J = 11$ Hz, 3 H, CH_3), and 7.43 (singlet, 6 H, 2 CH_3).