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(Fluoroalkyl)phosphine Coordination Chemistry: Synthesis and Structure of $\{[\mu,\eta^1,\eta^6\text{-}(C_6H_5)P(C_2F_5)_2]Cr(CO)_2\}_2$

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Introduction

Tertiary phosphine ligands are ubiquitous to modern transition metal coordination chemistry.[1,2] The range of both steric and electronic R_3P coordination properties is quite broad and is effectively limited only by the availability of synthetic procedures for introducing appropriate R groups. We have a longstanding interest in the synthesis and coordination properties of perfluoroalkyl-substituted phosphine ligands, $(R_f)_nR_{3-n}P$.[3−5] These phosphines exhibit a unique combination of properties: strong π-acceptor ability and steric influence, as well as chemical inertness and solubility in fluorous media afforded by the perfluoroalkyl substituents. Although early reports had established synthetic routes to trifluoromethyl-substituted phosphines such as $(CF_3)_3P$,[6] $(CF_3)_nP(R)_{3-n}$ (R = H, halide, alkyl, Ph, Et_2N),[6,7] and $(CF_3)_2PCR_2CR_2P(CF_3)_2$ (R = H, F),[8] as well as some higher perfluoroalkyl congeners,[9] the practical difficulties inherent in these procedures have limited the development of this class of compounds. More recent reports by Cavell,[10] Field,[11] and Lagow[12] have extended the range of perfluoroalkylated phosphines available, but the synthetic procedures utilized are still nontrivial.

A number of years ago, we reported the convenient synthesis of the perfluoroethyl-substituted chelate $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe).[3] This synthesis exploits the enhanced stability of C_2F_5Li under conditions where phosphine alkylation is practical, and it routinely affords reasonable quantities (>50 g) of dfepe in high yield in a one-pot procedure. The fundamental coordination properties of the dfepe chelate have been detailed in a wide range of systems. However, we have recently become interested in the coordination properties of related monodentate (fluoroalkyl)phosphine systems, which should offer both enhanced ligand labilities and the additional possibility of alternative π-acceptor coordination geometries which are not restricted by chelation. To this end, we report here the synthesis of a series of alkyl-substituted derivatives $(C_2F_5)_2P(R)$ (R = C_2F_5, Me, Ph, *t*-Bu, Et_2N) and $(R_3P)M(CO)_5$ (M = Cr, Mo) substitution complexes which provide general electronic comparisons with other phosphine ligands. In the case of $(C_2F_5)_2P(Ph)$ substitution with $Cr(CO)_6$, an unusual dimeric species $\{[\mu,\eta^1,\eta^6\text{-}(C_6H_5)P(C_2F_5)_2]Cr(CO)_2\}_2$ was also isolated and has been crystallographically characterized.

Experimental Section

General Procedures. All manipulations were conducted under N_2 using high-vacuum, Schlenk, and glovebox techniques. All reactions were carried out under an ambient pressure of approximately 590 Torr (elevation ~2195 m). All solvents were dried over sodium benzophenone ketyl and stored under vacuum. Deuterated solvents were dried over activated 3 Å molecular sieves. CF_3CF_2Cl (PCR, Inc.) and the dichlorides $(Me)PCl_2$, $(t\text{-}Bu)PCl_2$, and $(Ph)PCl_2$ (Strem) were used as received. $(NEt_2)PCl_2$ was prepared according to an established literature procedure.[13] Elemental analyses were performed by Desert Analytics. Infrared spectra were obtained on a Perkin-Elmer 1600 FTIR instrument as Nujol mulls, unless otherwise noted. NMR spectra were recorded with a JEOL GSX-270 or a Bruker Avance-400 instrument. ^{31}P NMR spectra were referenced to an 85% H_3PO_4 external standard. ^{19}F NMR spectra were referenced to either CCl_3F (0 ppm) or CF_3CO_2Et (−75.32 ppm) as external standards.

Bis(pentafluoroethyl)phenylphosphine (1). To a 250 mL two-necked flask under an atmosphere of nitrogen was added 56 mL of *n*-BuLi (2.5 M in hexanes, 140 mmol). The hexanes were removed under vacuum, and the *n*-BuLi was taken up in 125 mL of diethyl ether. After cooling to −90 °C (N_2(l)/toluene bath), 16 mL of C_2F_5Cl (bp −34 °C, density 1.88 g/mL, 195 mmol) maintained at −78 °C was slowly vacuum transferred into the well-stirred *n*-BuLi/ether solution so as to maintain the reaction temperature below −80 °C. Upon completion of the transfer the solution temperature was maintained at −85 °C and stirred for an additional 60 min. At this point a 7.60 mL aliquot of $(Ph)PCl_2$ (10.02 g, 56 mmol) was slowly added via syringe under a nitrogen counterflow to the solution while the bath temperature was maintained below −80 °C. After an additional 15 min of stirring, the reaction mixture was allowed to slowly warm to room temperature and the volatile components (ether, butyl chloride) were removed by distillation at atmospheric pressure. The pressure was reduced to 100 Torr, and 17.20 g (10.7 mL, *d* = 1.61 g/mL, 89%) of product was collected between 100 and 106 °C. Anal. Calcd for $C_{10}H_5F_{10}P$: C, 34.70; H, 1.46. Found: C, 34.69; H, 1.46. IR (neat, KCl, cm^{-1}): 3073 (m), 1440 (sh), 1298 (vs), 1215 (vs), 1137 (vs), 948 (s), 750 (sh), 693 (sh), 624 (m). ^1H NMR (benzene-d_6, 400.13 MHz , 22 °C): δ 7.56 (t, $^3J_{HH}$ = 18 Hz, 2H; ortho C_6H_5), 7.03 (t, $^3J_{HH}$ = 14 Hz, 1H; para C_6H_5), 6.91 (t, $^3J_{HH}$ = 16 Hz, 2H; meta C_6H_5). ^{19}F NMR (benzene-d_6, 376.05 MHz, 22 °C): δ −79.63 (d, $^3J_{PF}$ = 18 Hz, 6F; CF_2CF_3), −108.7, −108.9 (AB portion of ABX spin system , $^2J_{FF}$ ~ 300 Hz, $^2J_{PF}$(A) = 63 Hz, $^2J_{PF}$(B) = 35 Hz, 4F; CF_2CF_3). ^{31}P NMR (benzene-d_6, 161.70 MHz, 22 °C): δ 3.5 (m).

Bis(pentafluoroethyl)methylphosphine (2). The synthesis of **2** follows the procedure described for **1** using 6.55 g (56 mmol) of $(Me)PCl_2$ as the limiting reagent, except that 125 mL of *n*-butyl ether was used as the solvent. Atmospheric distillation and collection of the lower boiling fraction of the final product mixture up to 70 °C yielded **2** as an approximately 1:1 mixture with butyl chloride (phosphine yield ~ 70%). This phosphine solution was used for further reactions without further purification. ^1H NMR (benzene-d_6, 400.13 MHz, 22 °C): δ 0.91 (d, $^2J_{PH}$ = 6.5 Hz; PCH_3). ^{19}F NMR (benzene-d_6, 376.50 MHz, 22 °C): δ −79.92 (d, $^3J_{PF}$ = 15 Hz, 6F; CF_2CF_3), −112.8 (AB portion of ABX spin system, δ(A) = δ(B), $^2J_{PF}$(av) = 52 Hz, 4F; CF_2CF_3). ^{31}P NMR (benzene-d_6, 161.70 MHz, 22 °C): δ 1.8 (m).

Bis(pentafluoroethyl)-*tert*-butylphosphine (3). The procedure for this compound is analogous to that for **1** with the following modifications: To 63 mL of *n*-BuLi (2.5 M in hexanes, 158 mmol) in 100 mL

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of diethyl ether was added 18.2 mL of C_2F_5Cl (221 mmol); 10.0 g (63 mmol) of (*t*-Bu)PCl_2 in 10 mL of ether was added dropwise to this reaction mixture over the course of 20 min, and the solution was allowed to warm to ambient temperature; 18.3 g (92.1%) of $(C_2F_5)_2P$(*t*-Bu) was isolated as a colorless liquid by distillation between 92 and 98 °C at 200 Torr. Anal. Calcd for $C_8H_9F_{10}P$: C, 29.46; H, 2.76. Found: C, 29.36; H, 2.65. IR (neat, KCl, cm^{-1}): 1481 (m), 1377 (m), 1303 (vs), 1215 (vs), 1146 (vs), 1016 (w), 944 (m) 872 (w), 810 (w), 747 (sh). ^1H NMR (benzene-d_6, 400.13 MHz, 22 °C): δ 1.03 (d, $^3J_{PH} = 15$ Hz; $C(CH_3)_3$). ^{19}F NMR (benzene-d_6, 376.05 MHz, 22 °C): δ -80.80 (d, $^3J_{PF} = 9$ Hz, 6F; CF_2CF_3), -104.8 , -108.1 (AB portion of ABX system , $^2J_{FF} = 308$ Hz, $^2J_{PF}(A) = 38$ Hz ($^2J_{PF}(B)$ unresolved), 4F; CF_2CF_3). ^{31}P NMR (benzene-d_6, 161.70 MHz, 22 °C): δ 35.6 (m).

Bis(pentafluoroethyl)(diethylamino)phosphine (4). The procedure for **4** is analogous to that described for **1**, based on 8.27 mL of $(NEt_2)PCl_2$ (56 mmol) as the limiting reagent. Distillation between 54 and 55 °C at 22 Torr yielded 17.01 g (89.4%) of pure $(C_2F_5)_2P(NEt_2)$. Anal. Calcd for $C_8H_{10}F_{10}NP$: C, 28.19; H, 2.95. Found: C, 28.14; H, 2.88. IR (neat, KCl cm^{-1}): 2981 (s), 2948 (m), 2885 (m), 1471 (m), 1388 (s), 1297 (vs), 1209 (vs), 1165 (w), 1137 (s), 1118 (s), 1060 (w), 1032 (s), 944 (vs), 798 (m), 746 (s). ^1H NMR (benzene-d_6, 399.65 MHz, 22 °C): δ 2.98 (br s, 2H; CH_2CH_3), 2.67 (br s, 2H; CH_2CH_3), 0.74 (t, $^3J_{HH} = 7$ Hz, 6H; NCH_2CH_3). ^{19}F NMR (benzene-d_6, 376.05 MHz, 22 °C): δ -79.9 (d, $^3J_{PF} = 19$ Hz, 6F; CF_2CF_3), -113.7, -114.2 (AB portion of ABX system , $^2J_{FF} = 312$ Hz, $^2J_{PF}(A) = 77$ Hz, $^2J_{PF}(B) = 27$ Hz, 4F; CF_2CF_3). ^{31}P NMR (benzene-d_6, 161.70 MHz, 22 °C): δ 46.9 (m).

Tris(pentafluoroethyl)phosphine (5). The procedure for this compound is analogous to that for **1** with the following modifications: To 0.48 mol of *n*-BuLi in 650 mL of diethyl ether was added 42 mL of C_2F_5Cl (0.51 mol) at a temperature maintained between -80 and -90 °C. PCl_3 (21.2 g, 0.155 mol) was added dropwise to this reaction mixture over the course of 20 min, and the solution was then allowed to slowly warm to ambient temperature. Isolation of product was difficult due to formation of a binary azeotrope with diethyl ether: After *ca*. 300 mL of ether was removed under vacuum, the remaining volatiles were transferred to a 500 mL flask and the solution was cooled to -78 °C. At this temperature $(C_2F_5)_3P$ crystallized from solution and the supernatant was removed via cannula. Distillation of the crude phosphine product at 70−72 °C at 590 Torr yielded 25 g of **5** (41%) which contained a small amount (<5%) of residual ether. IR (neat, cm^{-1}): 1301 (s), 1230 (sh), 1158 (s), 1101 (s), 946 (s), 748 (m), 628 (m). NMR data obtained for **5** are in agreement with data reported previously by Lagow.[12]

$[(C_2F_5)_2P(Ph)]Mo(CO)_5$ (6). To a solution of 0.300 g of $Mo(CO)_6$ (1.14 mmol) in 10 mL of octane was added 0.865 g (2.51 mmol) of $(C_2F_5)_2P(Ph)$. After refluxing for 8 h, the reaction mixture was transferred to a filtration assembly. The volatiles were removed, and the residue was extracted with petroleum ether. Reduction of the filtrate volume to *ca*. 3 mL and cooling to -78 °C afforded 0.360 g (54%) of **6** as a light brown solid. Anal. Calcd for $C_{15}H_5F_{10}MoO_5P$: C, 30.95; H, 0.87. Found: C, 30.84; H, 0.93. IR (cm^{-1}): 2089 (s), 2012 (w), 1974 (vs, br), 1219 (s), 1136 (s), 1086 (m), 1014 (w), 961 (w), 947 (m). ^1H NMR (benzene-d_6, 270.05 MHz, 22 °C): δ 7.91 (t, $^3J_{HH} = 18$ Hz, 2H; ortho C_6H_5), 6.88 (m, 3H; meta, para C_6H_5). ^{31}P NMR (benzene-d_6, 109.25 MHz, 22 °C): δ 56.7 (m).

$[(C_2F_5)_2P(NEt_2)]Mo(CO)_5$ (7). A mixture of $Mo(CO)_6$ (0.200 g, 0.752 mmol) and $(C_2F_5)_2P(NEt_2)$ (0.280 g, 0.821 mmol) in 10 mL of octane was heated to reflux for 4 h. Removal of the volatiles and precipitation of the residue from *ca*. 3 mL of petroleum ether at -78 °C afforded 0.100 g (23%) of **7** as an off-white solid. Anal. Calcd for $C_{13}H_{10}F_{10}MoNO_5P$: C, 27.06; H, 1.75. Found: C, 26.51; H, 1.40. IR (cm^{-1}): 2088 (m), 2009 (w), 1978 (m), 1970 (vs), 1286 (w), 1220 (m) 1125 (w), 1022 (w), 945 (w), 804 (w). ^1H NMR (benzene-d_6, 400.13 MHz, 22 °C): δ 3.02 (m, 4H; NCH_2CH_3), 0.67 (t, $^3J_{HH} = 7$ Hz), 6H; NCH_2CH_3). ^{19}F NMR (benzene-d_6, 376.50 MHz, 22 °C): δ -80.5 (s, 6F; PCF_2CF_3), -111.2 to -117.2 (m, 4F; PCF_2CF_3). ^{31}P NMR (benzene-d_6, 161.98 MHz, 22 °C): δ 100.0 (t, $^2J_{PF} = 186$ Hz).

$[(C_2F_5)_2P(Me)]Mo(CO)_5$ (8). A solution of 0.200 g of $Mo(CO)_6$ (0.200 g, 0.752 mmol) and 1.1 mL of a 1:1 $MeP(C_2F_5)_2$/BuCl mixture in 10 mL of petroleum ether was warmed to 120 °C in a sealed glass vessel for 90 min. After cooling to ambient temperature, the solution was transferred to a filtration assembly. Cooling the solution to -78 °C precipitated 0.142 g (36%) of **8** as a sublimable white solid. Anal. Calcd for $C_{10}H_3F_{10}MoO_5P$: C, 23.10; H, 0.58. Found: C, 22.81; H, 0.41. IR (cm^{-1}): 2090 (m), 2013 (w), 1987 (vs), 1969 (s), 1302 (m), 1227 (m), 1105 (m), 1012 (m), 880 (w). ^1H NMR (acetone-d_6, 400.13 MHz, 22 °C): δ 2.39 (s, br). ^{19}F NMR (acetone-d_6, 376.50 MHz, 22 °C): δ -76.8 (s, 6F; PCF_2CF_3), -109.1 to -112.2 (m, 4F; PCF_2CF_3). ^{31}P NMR (acetone-d_6, 161.98 MHz, 22 °C): δ 73.7 (m).

Table 1. Crystallographic Data for $\{[\mu,\eta^1,\eta^6\text{-}(C_6H_5)P(C_2F_5)_2]Cr(CO)_2\}_2$ (**10**)

chem formula	$C_{24}H_{10}Cr_2F_{20}O_4P_2$
formula wt	908.26
space group	$P\bar{1}$ (No. 2)
a (Å)	7.9891(3)
b (Å)	9.7673(4)
c (Å)	10.5833(4)
α (deg)	73.264(1)
β (deg)	69.896(1)
γ (deg)	73.134(1)
V ($Å^3$)	725.70(5)
Z	1
T (°C)	−80
ρ_{calc} (g cm^{-3})	2.078
R_1 (all data)[a]	0.0404

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$.

$[(C_2F_5)_2P(C_6H_5)]Cr(CO)_5$ (9). A mixture of $Cr(CO)_6$ (0.300 g, 1.36 mmol) and $(C_2F_5)_2P(Ph)$ (0.944 g, 2.73 mmol) in 25 mL of heptane was refluxed under nitrogen for 48 h, at which time $Cr(CO)_6$ ceased to sublime from the solution. The volatiles were removed by vacuum, and the residual material was taken up in 15 mL of petroleum ether and filtered. The solvent volume was reduced to approximately 3 mL, and cooling to -78 °C afforded 0.185 g (25%) of **9** as a bright yellow solid. Anal. Calcd for $C_{15}H_5CrF_{10}O_5P$: C, 33.48; H, 0.94. Found: C, 33.79; H, 1.03. IR (CH_2Cl_2 solution, cm^{-1}): 2082 (w), 1991 (m), 1964 (vs), 1924 (vs), 1314 (m), 1212 (s), 1136 (vs), 1086 (sh), 1012 (s), 947 (sh), 811 (m). ^1H NMR (270.05 MHz, benzene-d_6, 25 °C): δ 7.84 (t, $^3J_{HH} = 16$ Hz, 2H; ortho C_6H_5), 6.86 (m, 3H; meta, para C_6H_5). ^{31}P NMR (benzene-d_6, 109.25 MHz, 25 °C): δ 98.3 (m).

$\{[\mu,\eta^1,\eta^6\text{-}(C_6H_5)P(C_2F_5)_2]Cr(CO)_2\}_2$ (10). A solution of **9** (0.100 g) in octane was refluxed for 48 h. The solvent was removed, and the residue was taken up in 10 mL of petroleum ether and filtered. Reduction of the filtrate to 2 mL and cooling to -78 °C yielded 0.050 g (35%) of **10** as an oily solid contaminated by traces of unreacted **9**. IR (CH_2Cl_2 solution, cm^{-1}): 1935 (s), 1907 (s), 1311, (vs), 1294 (vs), 1209 (vs), 1173 (s), 1107 (s), 1088 (s), 1075 (s), 966 (m). ^1H NMR (270.05 MHz, benzene-d_6, 25 °C): δ 4.84 (t, $^3J_{HH} = 13$ Hz, 2H; ortho C_6H_5), 4.42 (t, $^3J_{HH} = 12$ Hz, 1H; para C_6H_5), 3.90 (t, $^3J_{HH} = 12$ Hz, 2H; meta C_6H_5). ^{19}F NMR (benzene-d_6, 376.50 MHz, 22 °C): δ -78.8 (d, $^3J_{PF} = 13$ Hz, 6F; PCF_2CF_3), -105.3 to -108.3 (m, 4F; PCF_2CF_3). ^{31}P NMR (benzene-d_6, 109.25 MHz, 25 °C): δ 11.2 (m).

Crystal Structure of $\{[\mu,\eta^1,\eta^6\text{-}(C_6H_5)P(C_2F_5)_2]Cr(CO)_2\}_2$ (10). Recrystallization of the crude product mixture of **9** and **10** from benzene gave orange crystals of **10**. A crystal of suitable size was mounted on a glass fiber using grease. Data were collected using a Siemens SMART CCD diffractometer using monochromatic molybdenum radiation and an LT-2 low-temperature apparatus operating at 193 K. A summary of crystal data is presented in Table 1. Cell parameters were obtained from a least-squares fit to the angular coordinates of 51 reflections of a series of oscillation frames. Data were measured using *ω* scans of 0.3°/frame for 30 s. The first 50 frames were re-collected at the end of data collection to monitor for decay. The data that were collected (9599 total reflections, 3322 unique, $R_{int} = 0.0182$) were corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS. The structure was solved (SHELXTL 5.0) by direct methods and standard difference Fourier techniques.[14] The maximum and minimum residual electron densities were 0.509 and -0.503 $Å^3$. Selected metrical parameters for **10** are presented in Table 2.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\{[\mu,\eta^1,\eta^6\text{-}(C_6H_5)P(C_2F_5)_2]Cr(CO)_2\}_2$ (**10**)

Cr(1)−P(1)	2.2385(6)	Cr(1)−C(1)	1.842(3)
Cr(1)−C(2)	1.847(3)	Cr(1)−C(3)	2.222(2)
Cr(1)−C(4)	2.193(2)	Cr(1)−C(5)	2.226(2)
Cr(1)−C(6)	2.201(2)	Cr(1)−C(7)	2.202(2)
Cr(1)−C(8)	2.187(2)	C(1)−O(1)	1.153(3)
C(2)−O(2)	1.150(3)		
P(1)−Cr(1)−C(1)	90.95(8)	P(1)−Cr(1)−C(2)	91.42(8)
C(1)−Cr(1)−C(2)	88.66(12)	Ct−Cr(1)−P(1)[a]	128.9
Ct−Cr(1)−C(1)	122.0	Ct−Cr(1)−C(2)	123.8

[a] Ct = ring centroid.

Results and Discussion

Prior results from our laboratory have shown that C_2F_5Li may be conveniently generated *in situ* at −90 °C and used for the efficient fluoroalkylation of P−Cl bonds.[3] Following the procedure developed for the (fluoroalkyl)phosphine chelate dfepe, the controlled addition of $RPCl_2$ precursors (R = Ph, *t*-Bu, NEt_2) to ethereal solutions of C_2F_5Li maintained between −90 and −85 °C gave excellent (>85%) isolated yields of $(C_2F_5)_2PR$, which were isolated by vacuum distillation as colorless liquids (eq 1). In the case of R = Me, the product phosphine and the butyl chloride side product codistill and $(C_2F_5)_2P(Me)$ was obtained as an approximately 1:1 phosphine/BuCl mixture. This mixture was used in reactions without further purification. The perfluorinated phosphine $(C_2F_5)_3P$ (**5**) forms an azeotrope with the diethyl ether solvent, but may be selectively crystallized out of solution at −78 °C, redistilled, and isolated in reasonably pure form.

$$C_2F_5Cl \xrightarrow[-78\ °C,\ Et_2O]{n\text{-BuLi}} [C_2F_5Li]_n \xrightarrow{(R)PCl_2} (C_2F_5)_2P(R) \qquad (1)$$

R = Ph (**1**)
Me (**2**)
^{t}Bu (**3**)
NEt_2 (**4**)
C_2F_5 (**5**)

The spectroscopy for all $(CF_3CF_2)_2P(R)$ phosphines is straightforward. ^{19}F and $\{^1H\}^{31}P$ NMR spectra are described by $A_2B_2M_6X$ spin systems with $^3J_{FF} \sim 0$ between the diastereotopic A_2B_2 CF_2 and M_6 CF_3 spin systems. ^{19}F resonances for the CF_3 groups generally appear as simple doublets due to $^3J_{PF}$ and are 20−30 ppm downfield from the CF_2 region. The appearance of the CF_2 portion of the spectra ranges between a classic eight-line pattern due to the AB portion of an ABX spin system found for **3** to a deceptively simple doublet ($\delta(A) \sim \delta(B)$) observed for **2**. Consistent with ^{19}F NMR data, the ^{31}P NMR spectra for all $(C_2F_5)_2P(R)$ compounds show extensive fluorine coupling.

A wide range of $(R_3P)_nM(CO)_{6-n}$ derivatives have been reported which serve as useful benchmarks for relative phosphine donor comparisons. Accordingly, the substitution chemistry of **1**−**5** with the hexacarbonyls $M(CO)_6$ (M = Cr, Mo) was examined in order to compare their electronic properties with those of other phosphine ligands. Direct thermal substitution of $Mo(CO)_6$ with ligands **1**, **2**, and **4** in refluxing octane yielded the corresponding pentacarbonyl complexes, $[(C_2F_5)_2P(R)]Mo(CO)_5$ (R = Ph (**6**), NEt_2 (**7**), Me (**8**)) (eq 2). In contrast, no pentacarbonyl derivative was obtained from the thermolysis of $Mo(CO)_6$ with the more sterically encumbering $(C_2F_5)_2P(t\text{-}Bu)$ ligand or totally perfluorinated $(CF_3CF_2)_3P$ ligand under more forcing conditions up to the decomposition point of the hexacarbonyl. Ligand substitution with **3** or **5** under photolytic conditions was not attempted. Unlike donor phosphine systems, which can readily form di- and trisubstitution products, further treatment of the pentacarbonyls **6**, **7**, and **8** with excess phosphine did not yield detectable amounts of multiple substitution products. This observation is counter to the increased CO lability expected for these electron-poor pentacarbonyls, but may be due to a decreased trapping efficiency for a transient 16-electron $(R_3P)Mo(CO)_4$ intermediate by these poorly donating sterically demanding $(C_2F_5)_2P(R)$ ligands.

$$Mo(CO)_6 + (C_2F_5)_2P(R) \xrightarrow[\text{octane}]{\Delta} [(C_2F_5)_2P(R)]Mo(CO)_5 + CO \qquad (2)$$

R = Ph (**6**)
NEt_2 (**7**)
Me (**8**)

Compounds **6**−**8** were characterized by NMR, IR, and elemental analysis. As observed previously for dfepe systems, complexation of $(C_2F_5)_2P(R)$ ligands generally results in a downfield ^{31}P NMR shift of over 50 ppm. This shift is comparable to values reported for PF_3 as well as alkyl- and arylphosphine ligands.[15] IR spectra of these complexes are consistent with monosubstitution. For local metal C_{4v} symmetry, three IR bands ($A_1^{(2)}$, E, $A_1^{(1)}$) are anticipated. In complexes **6**−**8** the E and $A_1^{(1)}$ bands are nearly degenerate in energy and additional weak bands at ∼2000 cm^{-1} are observed, which are attributed to the reduced axial symmetry of the phosphine ligands.[16] A comparison of $A_1^{(2)}$ CO stretching modes for a number of $(L)Mo(CO)_5$ phosphine systems is instructive. The essentially identical values of $\Delta\nu(A_1^{(2)})$ found for complexes **6**−**8** (2089, 2088, and 2090 cm^{-1}, respectively) and the small difference between $\Delta\nu(A_1^{(2)})$ reported for $(CF_3)_2P(Me)$ (2094 cm^{-1}) and $(CF_3)P(Me)_2$ (2086 cm^{-1}) molybdenum pentacarbonyl derivatives[17] demonstrate that $\nu(A_1^{(2)})$ values are relatively insensitive to phosphine substituent effects and should be viewed as only a rough indicator of changes in effective metal electron density. Nevertheless, in accord with our previous dfepe studies,[3] the net donor ability of $(C_2F_5)_2P(R)$ ligands lies between that of Me_3P, Ph_3P, and $(MeO)_3P$ ($A_1^{(2)}[Mo(CO)_5(L)]$ = 2071, 2073, 2080 cm^{-1}, respectively)[15,16] and that of the strong π-acceptor ligands PF_3 (2103 cm^{-1}, hexane) and $(CF_3)_3P$ (2104 cm^{-1}, hexane).[17]

In addition to $Mo(CO)_6$ substitution chemistry, the reactivity of $Cr(CO)_6$ with $(C_2F_5)_2P(Ph)$ was also examined. Treatment of $Cr(CO)_6$ with $(C_2F_5)_2P(Ph)$ in boiling octane for 2 days resulted in the expected formation of $[(C_2F_5)_2P(Ph)]Cr(CO)_5$ **(9)**, as well as small amounts of an additional chromium species **10**. The presence of two characteristic ν(CO) bands together with a substantial upfield shift of phosphine ligand aromatic resonances suggested a π-arene dicarbonyl formulation (π-arene)$Cr(CO)_2(L)$ for this minor side product; a symmetrical dimeric structure for **10** with mutually bridging arylphosphine ligands, $\{[\mu,\eta^1,\eta^6\text{-}(C_6H_5)P(C_2F_5)_2]Cr(CO)_2\}_2$, was subsequently confirmed by X-ray crystallography (see below). The carbonyl bands for **10**, $\nu(CO)$ = 1935, 1907 cm^{-1}, are higher in energy than values reported for $\{[\mu,\eta^1,\eta^6\text{-}(C_6H_5)P(Ph)_2]Cr(CO)_2\}_2$ (1900, 1850 cm^{-1})[18] and reflect a lowering of metal electron density due to both phosphine and arene substituent effects. The

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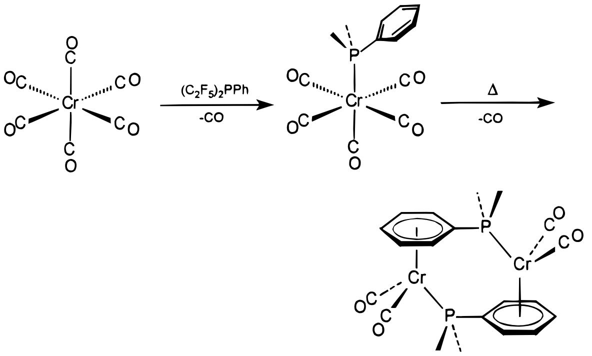
formation of **10** may be viewed formally as the dimerization product of the unsaturated 12e$^-$ moiety [$(C_2F_5)_2P(Ph)$]$Cr(CO)_2$, derived from the thermal decarbonylation of **9**. Indeed, as anticipated, the thermolysis of isolated pentacarbonyl monomer in refluxing octane leads to the formation of **10** (eq 3). An additional synthetic pathway involving the initial formation of [η^6-$(C_6H_5)P(C_2F_5)_2$]$Cr(CO)_3$ followed by intermolecular phosphine substitution is also reasonable and has been reported for the photochemically induced dimerization of [η^6-$(C_6H_5)P(Ph)_2$]-$Cr(CO)_3$ to form {[μ,η^1,η^6-$(C_6H_5)P(Ph)_2$]$Cr(CO)_2$}$_2$.[18]



(3)

Recrystallization of the product mixture of **9** and **10** from warm benzene produced crystals suitable for X-ray analysis. Selected metrical parameters are given in Table 2. As shown in Figure 1, **10** consists of two (($C_2F_5)_2P(Ph)$)$Cr(CO)_2$ moieties mutually bridged by η^1,η^6-$(C_6H_5)P(C_2F_5)_2$ arylphosphine ligands. An analogous structure has been reported for {[μ,η^1,η^6-$(C_6H_5)P$-$(Ph)_2$]$Cr(CO)_2$}$_2$.[19] As noted previously for the Ph_3P analogue, the chromium units are crystallographically related by a center of inversion with no apparent metal−metal interactions (Cr−Cr = 4.577 Å). Cr−C(arene) bond distances average 2.205 Å, comparable to the average value of 2.19 Å reported for {[μ,η^1,η^6-$(C_6H_5)PPh_2$]$Cr(CO)_2$}$_2$. Negligible deviations from arene ring planarity (0.010 Å av) and only a slight tilt of the C(3)−P(1) bond vector away from the ring plane (2.5°) indicate that there is very little strain in this dimeric bridged structure.

The convenient synthesis of $(C_2F_5)_2P(R)$ compounds and simple group VI derivatives establishes a new series of phosphine acceptor ligands for study. Given the wide range of (R)PCl_2 precursors available, essentially any ligand of this type with tunable steric properties can be readily prepared and applied to systems where a substantial reduction in metal electron density is desired. The bridging coordination of $(C_2F_5)_2P(Ph)$ in complex **10** affords an unusual example of a bifunctional ligand combining both π-arene and acceptor phosphine ligand properties.

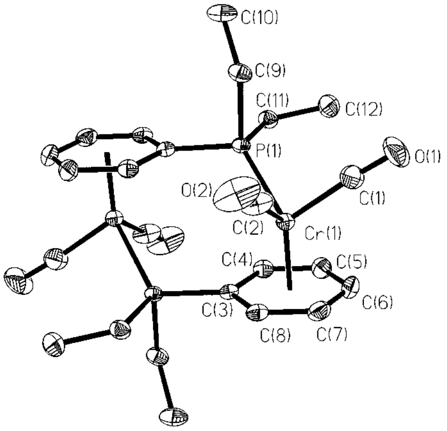


Figure 1. Molecular structure of {[μ,η^1,η^6-$(C_6H_5)P(C_2F_5)_2$]$Cr(CO)_2$}$_2$ (**10**) with atom-labeling scheme (50% probability ellipsoids; fluorine and hydrogen atoms are omitted for clarity).

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Supporting Information Available: An X-ray crystallographic file in CIF format for complex **10** is available on the Internet only. Access information is given on any current masthead page.

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