2402 *Organometallics* **2008,** *27,* 2402–2404

Synthesis, Structure, and Coordination Properties of 1,1′-Bis(bis(trifluoromethyl)phosphino)ferrocene, dfmpf

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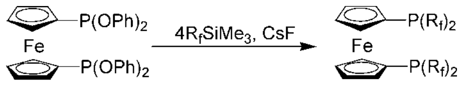
Received December 13, 2007

Summary: The new highly electron deficient ferrocenyldiphosphines [Fe{η^5-$C_5H_4P(CF_3)_2$}$_2$] (dfmpf) and [Fe{η^5-$C_5H_4P(C_2F_5)_2$}$_2$] (dfepf) were synthesized by reaction of [Fe{η^5-$C_5H_4P(OPh)_2$}$_2$] with $C_nF_{2n+1}SiMe_3$/CsF (n = 1, 2), and the structure of dfmpf was determined. The structures of the complexes (dfmpf)$PtCl_2$ and (dfepf)$PtCl_2$ indicate that both ligands offer significantly wider bite angles than $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) and that dfepf is the bulkiest chelating (perfluoroalkyl)diphosphine yet made.

Perfluoroalkyl groups confer strong π-acidity on phosphorus(III) centers, such that tris(perfluoroalkyl)phosphines can be considered as bulky mimics of the CO ligand.[1] Unlike the diatomic CO, (perfluoroalkyl)phosphines can be modified and, for example, bidentate ligands can be constructed. (Perfluoroalkyl)diphosphines, therefore, are of interest as modifiable, bidentate CO analogues.[2,3] Few applications of these diphosphines, however, have been reported to date. In the past, two issues have prevented these ligands from finding widespread use: first, convenient syntheses were not available, and second, a wider range of (perfluoroalkyl)diphosphine ligands needed to be made with differing structures and geometries and with different perfluoroalkyl substituents. We have recently communicated a more general synthesis which allows the preparation of mono- and diphosphines with a range of perfluoroalkyl groups.[4] In this report, we use this route to synthesize two new perfluoroalkyl-substituted ferrocenyldiphosphines.

There are not many (perfluoroalkyl)diphosphines known.[3,5,6] In most of these cases, coordination of these phosphines to metals has not been studied. It is really only for the ligand $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) (and to a lesser extent $(CF_3)_2PCH_2CH_2P(CF_3)_2$ (dfmpe)) that the coordination chemistry has been thoroughly examined. The body of work by the Roddick group on dfepe[2b,5,7] suggests that the chemistry of other diphosphines of differing bulk, electronic properties, and bite angles would be an area worthy of investigation. A particular point of interest is that a gap in the Tolman map for monophosphines has been identified for bulky, electron-deficient phosphines. In fact, Cundari et al. have concluded "Analysis of the most common alkyl and aryl phosphines in experimental usage suggests that the complexes are quite similar stereoelectronically. Indeed, apart from $P(CF_3)_3$, it is interesting just how similar the commonly studied phosphines are."[8] Clearly, this analysis can be extended to diphosphines, since none of the known (perfluoroalkyl)diphosphines[3,5,6] have an exceptionally large cone angle (the cone angles of two of the most commonly used (perfluoroalkyl)diphosphines have been estimated as follows: dfepe, 129°;[9] dfmpe, 120°[10]).

Scheme 1



1, $R_f = CF_3$
2, $R_f = C_2F_5$

The majority of the known (perfluoroalkyl)diphosphines are built on either a one-carbon (or heteroatom) or two-carbon backbone and consequently are ligands of modest bite angle. It is therefore of interest to synthesize a strongly electron withdrawing diphosphine of larger bite angle, since there is a scarcity of ligands with such a combination of properties. Such a ligand would electronically be the mimic of two obtuse cis CO ligands. Sterically, however, its bulk could be adjusted by modifying the perfluoroalkyl substituents.

Ferrocenyldiphosphines are an important group of chelating diphosphines that have found wide application.[11] This class of

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(10) For details of cone angle estimates, see the Supporting Information.

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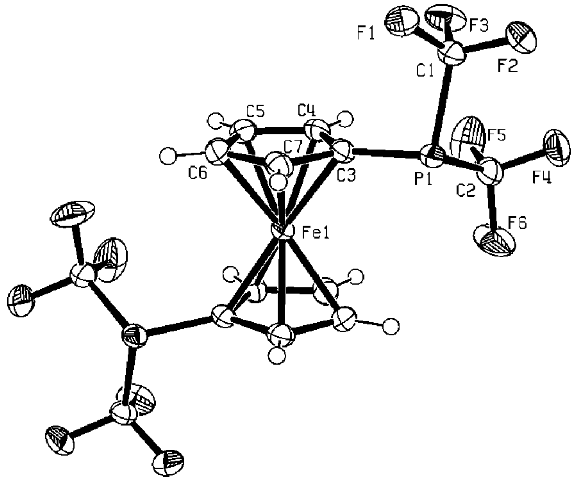
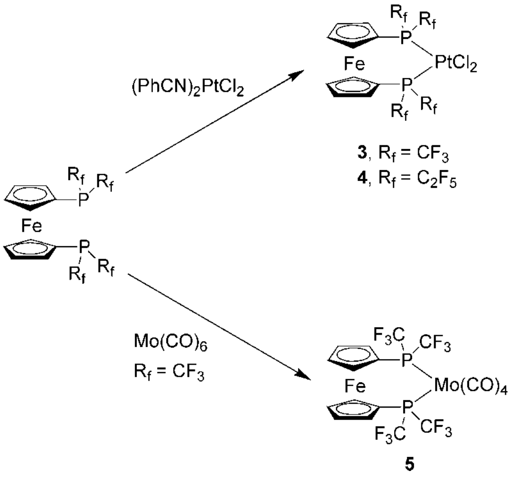


Figure 1. Solid-state structure of **1** (50% probability ellipsoids). Selected bond distances (Å) and angles (deg): P(1)−C(1), 1.885(1); P(1)−C(2), 1.877(2); P(1)−C(3), 1.790(1); C(2)−P(1)−C(1), 96.01(7); C(3)−P(1)−C(1), 98.22(6); C(3)−P(1)−C(2), 104.58(7); C(4)−C(3)−P(1), 133.3(1); C(7)−C(3)−P(1), 119.1(1).

Scheme 2



chelating ligands with a ferrocenyl backbone presents a bite angle significantly larger than those with an ethylene backbone such as dppe and dfepe. With respect to electron-withdrawing ferrocenyldiphosphine ligands, Beletskaya and co-workers have recently reported the synthesis of the (perfluoroaryl)diphosphine $[Fe\{\eta^5\text{-}C_5H_4P(C_6F_5)_2\}_2]$.[12] No perfluoroalkyl-substituted ferrocenyldiphosphines, however, have yet been made. There are known to be major differences in the properties between perfluoroalkyl-substituted and perfluoroaryl-substituted phosphines:[5,13] the former are strong π-acids, whereas it has been claimed that the latter, as exemplified by $P(C_6F_5)_3$,[1b] have no π-acidity. Considering these factors, it therefore seemed worthwhile to attempt the synthesis of previously unknown tetrakis(perfluoroalkyl)-substituted ferrocenyldiphosphine ligands and to undertake a preliminary coordination study.

We report here the synthesis of the new diphosphines $[Fe\{\eta^5\text{-}C_5H_4P(CF_3)_2\}_2]$ (abbreviated as dfmpf) and $[Fe\{\eta^5\text{-}C_5H_4P(C_2F_5)_2\}_2]$ (abbreviated as dfepf). Using the methodology we had previously developed for the synthesis of known perfluoroalkyl mono- and diphosphines,[4] dfmpf (**1**) was thus isolated in 66% yield after reaction of $[Fe\{\eta^5\text{-}C_5H_4P(OPh)_2\}_2]$ with 4 equiv of CF_3SiMe_3 and CsF in ether (Scheme 1).[14] A crystal structure of **1** was obtained (Figure 1).[15] The Fe atom lies on a 2-fold axis. The two cyclopentadienyl rings adopt an anticlinal eclipsed[11b] conformation (torsional angle of 149°), as observed for the related molecule $[Fe(\eta^5\text{-}C_5H_4PBr_2)_2]$ (154°)[16] but different from the synclinal eclipsed conformation of $[Fe(\eta^5\text{-}C_5H_4PCl_2)_2]$ (93°)[16] and the antiperiplanar staggered conformation of $[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$ (180°).[17]

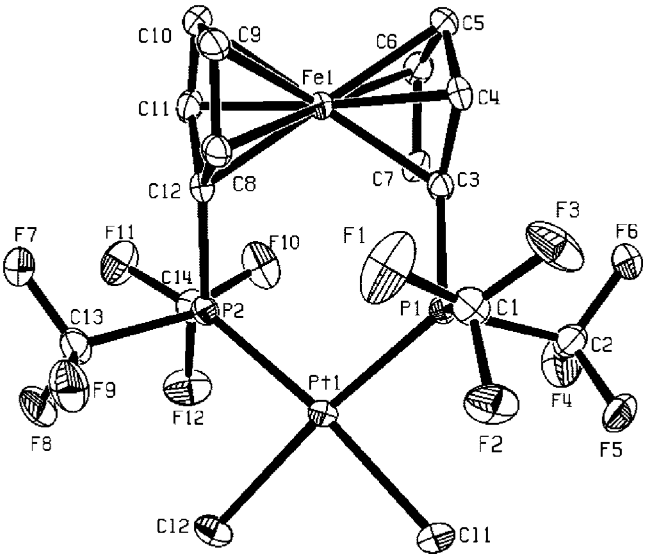


Figure 2. Solid-state structure of **3** (50% probability ellipsoids). Selected bond distances (Å) and angles (deg): Pt(1)−P(1), 2.2411(7); Pt(1)−P(2), 2.2397(7); Pt(1)−Cl(1), 2.3060(8); Pt(1)−Cl(2), 2.3112(7); P(2)−Pt(1)−P(1), 101.00(2); Cl(1)−Pt(1)−Cl(2), 87.43(3); C(1)−P(1)−C(2), 98.2(2); C(13)−P(2)−C(14), 99.3(1).

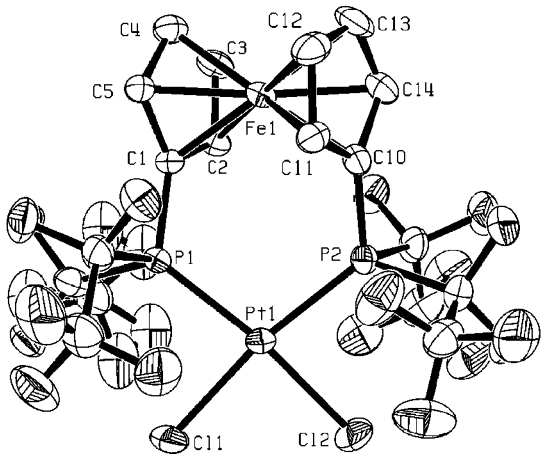


Figure 3. Solid-state structure of one of the two independent molecules of **4** (50% probability ellipsoids). Selected bond distances (Å) and angles (deg): Pt(1)−P(1), 2.239(1); Pt(1)−P(2), 2.248(1); Pt(1)−Cl(1), 2.293(1); Pt(1)−Cl(2), 2.304(1); P(2)−Pt(1)−P(1), 102.96(4); Cl(1)−Pt(1)−Cl(2), 86.75(5).

The ligand dfepf (**2**) was isolated, using the same methodology, from the reaction of $[Fe\{\eta^5\text{-}C_5H_4P(OPh)_2\}_2]$ with 4 equiv of $C_2F_5SiMe_3$ and CsF in ether with a yield of 71%. The coordination chemistry of **1** and **2** was studied. (dfmpf)$PtCl_2$ (**3**) was synthesized in 60% yield by reaction of $(PhCN)_2PtCl_2$ with **1** in CH_2Cl_2 solution (Scheme 2). An X-ray crystal structure analysis established the molecular structure of **3**, as shown in Figure 2.[18] The geometry around the metal is distorted square planar, as seen by the P−Pt−P bite angle (101.00(2)°) and the Cl−Pt−Cl angle (87.42(3)°). The cyclopentadienyl rings of the ferrocene unit are approximately synclinal staggered. From the structural data, the maximum cone angle[19] was estimated

Table 1. IR ν(CO) Bands of $Mo(CO)_4$(diphosphine) Complexes

diphosphine	abbrev	IR ν(CO) band/cm^{-1}				solvent	ref
$(CF_3)_2PCF_2CF_2P(CF_3)_2$	dfmpfe	2082	1994		1972	$CHCl_3$	3
$F_2PCH_2CH_2PF_2$	dfpe	2074	2005	1991	1973	hexane	21a
$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$	dfepe	2064	1993	1982	1955	KCl	5
$(CF_3)_2PCH_2CH_2P(CF_3)_2$	dfmpe	2063	1988		1961	$CHCl_3$	3
Fe{η^5-$C_5H_4P(CF_3)_2$}$_2$	dfmpf	2059	1998	1972	1964	hexane	this work
Fe(η^5-$C_5H_4PPh_2$)$_2$	dppf	2022	1920	1900	1880	CH_2Cl_2	21b
$Ph_2PCH_2CH_2PPh_2$	dppe	2020	1919	1907	1881	1,2-$C_2H_4Cl_2$	21c
$Et_2PCH_2CH_2PEt_2$	depe	2012	1909	1891	1873	1,2-$C_2H_4Cl_2$	21c

as 126°.[10] This means that dfmpf is a wider cone angle ligand than dfmpe and almost as wide as dfepe (129°).

(dfepf)$PtCl_2$ (**4**) was synthesized from $(PhCN)_2PtCl_2$ and dfepf. Crystals were grown from CH_2Cl_2 solution, and a crystal structure was obtained (Figure 3).[20] The geometry is distorted square planar. A difference from the structure of (dfmpf)$PtCl_2$ is that the ferrocenyl core in (dfepf)$PtCl_2$ is more twisted and the P−Pt−P bite angle increases to 102.95(4)°. The bulky pentafluoroethyl substituents are orientated approximately perpendicular to the square plane of the complex. The larger steric demands of the dfepf ligand are reflected in a larger calculated maximum estimated cone angle of 154°.[10] Ferguson et al. have pointed out that cone angles, obtained from X-ray structures, overestimate the cone angle in bulky ligands, where "cogging" of substituents occurs.[19] This is likely to be the case for dfepf, as significant voids are apparent along the *z* axis, perpendicular to the square plane of the complex, in the position where additional ligands would coordinate to give an octahedral geometry. Nevertheless, even if the 154° value is overestimated by as much as 5−10%, this still suggests that dfepf is comfortably bulkier than dfepe (129°)[9] and, consequently, constitutes the bulkiest chelating bidentate (perfluoroalkyl)diphosphine yet made. As such, it should fill a void in the Tolman map of diphosphines, exhibiting a unique combination of stereoelectronic properties; namely, it should function as a bulky, strong π-acceptor diphosphine.

(dfmpf)$Mo(CO)_4$ (**5**) was synthesized in 53% yield by reacting $Mo(CO)_6$ with **1** at 100 °C for 4 h (Scheme 2). When the ν(CO) bands in the IR spectrum of **5** are compared with those of related diphosphines (Table 1), the ν(CO) bands in **5** are observed to be 40−70 cm^{-1} higher than in (dppf)$Mo(CO)_4$ and about 10−20 cm^{-1} lower than in the fully perfluorinated ligand complex {$(CF_3)_2PCF_2CF_2P(CF_3)_2$}$Mo(CO)_4$. Consequently, these data confirm that dfmpf is indeed a ligand with electron-withdrawing power similar to that of dfmpe and dfepe.

In conclusion, we have synthesized and structurally characterized the new ferrocenyldiphosphine ligand dfmpf. The X-ray structure of (dfmpf)$PtCl_2$ gives a maximum cone angle of 126° for dfmpf, which is similar to that of dfepe, but dfmpf is a ligand with a larger bite angle (101°). The complex (dfmpf)$Mo(CO)_4$ was synthesized, and a comparison of ν(CO) IR data with the corresponding data for other diphosphines was made. The electronic influence of dfmpf was found to be similar to that of the other known perfluoroalkyldiphosphine ligands. The bulkier ferrocenyldiphosphine dfepf was also made. The X-ray structure of (dfepf)$PtCl_2$ gives a maximum cone angle for dfepf of 154°, which makes the ligand the bulkiest chelating bidentate (perfluoroalkyl)diphosphine yet synthesized.

Acknowledgment. We gratefully acknowledge the University of Oriente, Venezuela (scholarship to E.J.V.) for financial support.

Supporting Information Available: Text and figures giving detailed experimental procedures and details of the cone angle calculations and CIF files giving X-ray diffraction data for **1**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701244B

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(14) Experimental procedure and characterization of **1**: [Fe{η^5-$C_5H_4P(OPh)_2$}$_2$] (0.201 g, 0.325 mmol) was dissolved in ether (10 mL), and CsF (0.22 g, 1.46 mmol) and CF_3SiMe_3 (0.24 g, 1.69 mmol) were added. After it was stirred at room temperature for 14 h, the mixture was filtered and the solvent removed from the clear filtrate, giving the crude product as a dark orange oil. The product was recrystallized twice from hexane to give orange crystals of **1** (0.112 g, 66%). Mp: 49.8 °C. ^{31}P NMR (C_6D_6): $\delta -3.8$ (sept, $^2J_{PF} = 73$ Hz). ^{19}F NMR (C_6D_6): $\delta -53.9$ (d, $^2J_{PF} = 73$ Hz). ^{1}H NMR (C_6D_6): δ 3.99 (m, 4H), 4.12 (m, 4H). ^{13}C NMR (CD_2Cl_2): δ 60.1 (m), 73.5 (s), 74.2 (d, $^3J_{CP} = 18$ Hz), 126.5 (qdq, $^1J_{CF} = 321$ Hz, $^1J_{CP} = 20$ Hz, $^3J_{CF} = 6$ Hz). Anal. Calcd for $C_{14}H_8F_{12}FeP_2$: C, 32.21; H, 1.54. Found: C, 32.62; H, 1.49.

(15) Crystal data for **1**: $C_{14}H_8F_{12}FeP_2$, monoclinic, *C*2/*c*, $a = 17.536(1)$ Å, $b = 9.850(1)$ Å, $c = 12.428(1)$ Å, $\beta = 125.650(1)°$, $V = 1744.4(2)$ Å^3, $Z = 4$, $D_c = 1.988$ g cm^{-3}, $T = 150.0(1)$ K., $R_{int} = 0.0169$, 7417 reflections measured, 2542 unique reflections, 2261 reflections used, R1 = 0.0281, wR2 = 0.080.

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(18) Crystal data for **3**: $C_{14}H_8Cl_2F_{12}FeP_2Pt$, monoclinic, $P2_1/c$, $a = 9.661(1)$ Å, $b = 13.369(1)$ Å, $c = 17.265(1)$ Å, $\beta = 114.609(1)°$, $V = 2027.4(3)$ Å^3, $Z = 4$, $D_c = 2.582$ g cm^{-3}, $T = 150.0(1)$ K, $R_{int} = 0.0280$, 19 082 reflections measured, 5882 unique reflections, 5148 reflections used, R1 = 0.0255, wR2 = 0.0592.

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(20) Crystal data for **4**: $C_{18}H_8Cl_2F_{20}FeP_2Pt$, monoclinic, $P2_1/c$, $a = 16.293(1)$ Å, $b = 18.822(1)$ Å, $c = 18.758(1)$ Å, $\beta = 112.877(1)°$, $V = 5300.0(5)$ Å^3, $Z = 4$, $D_c = 2.476$ g cm^{-3}, $T = 150.0(1)$ K, $R_{int} = 0.0555$, 45 498 reflections measured, 15 451 unique reflections, 12 051 reflections used, R1 = 0.0423, wR2 = 0.1181.

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