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Synthesis of a Functional C_2-Symmetrical Bidentate Diphenylphosphonite DIOP Derivative and Its Conversion into the Corresponding π-Acidic Bis(pentafluorophenyl) and Bis(*p*-tetrafluoropyridyl) Compounds**

Berthold Hoge* and Patricia Panne[a]

Dedicated to Professor Josef Hahn on the occasion of his 65th birthday

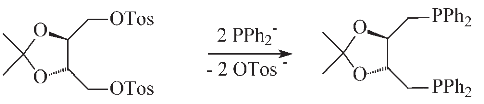
Abstract: The reaction of a C_2-symmetric diiodo compound, 1,4-dideoxy-1,4-diiodo-2,3,-*O*-isopropyliden-L-threitole, with $[K([18]crown\text{-}6)]P(CN)_2$ led to the generation of a corresponding bidentate dicyanophosphorus derivative. The in situ reaction with excess methanol and phenol yielded the corresponding bidentate dimethyl- and diphenylphosphonites, respectively. The isolated liquids were characterized by multinuclear NMR spectroscopy, elemental analysis, and mass spectrometry. The bidentate diphenylphosphonite ligand (a diphenoxyphosphane derivative) represents one of the very few functional bidentate phosphane derivatives: a DIOP [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphane) modification, in which the phenyl groups at the phosphorus atoms are replaced by functional phenoxy groups. Treatment of the bidentate diphenylphosphonite derivative with C_6F_5MgBr and p-C_5NF_4MgBr allowed the isolation and full characterization of the comparable bidentate bis(pentafluorophenyl) and bis(*p*-tetrafluoropyridyl)phosphanes. The ligand properties of the novel bidentate ligand systems were evaluated through the synthesis and vibrational investigation of their tetracarbonyl–molybdenum and cyclopentadienyl–iron complexes. The π acidity of the synthesized ligands increases in the order methoxy- < phenoxy- < pentafluorophenyl- < *p*-tetrafluoropyridyl phosphane.

Keywords: chirality · Lewis acids · P ligands · phosphonite · phosphanide

Introduction

Chiral, bidentate phosphane ligands play an important role in asymmetric catalysis. The main activities in the development of chiral phosphane ligands with catalytic efficiency are focused on the variation of the so-called chiral backbone.[1] The aim of our work is a systematic variation of the phosphorus substituents for one given chiral backbone. This kind of variation should allow a fine tuning of the catalytic activity of the corresponding chiral phosphane transition-metal complexes by the steric and electronic effects of the phosphorus atom bearing different substituents. Because Lewis acids play a key role as catalysts in organic synthesis, electron-poor phosphane ligands, containing electron-withdrawing groups at the phosphorus atom, are desirable.[2]

Chiral, bidentate phosphane ligands, such as DIOP, [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphane), are usually prepared by reacting chiral 1,2-, 1,3-, or 1,4-ditosylates with diarylphosphanides,[3] as shown in Equation (1):



1 DIOP (1)

By applying this procedure to the synthesis of a bis(trifluoromethyl)phosphane chelate ligand **3** [Eq. (2)], we investigated the stabilization of the $P(CF_3)_2^-$ ion in the presence of acetone, which allowed the synthesis of the first example of a bidentate bis(perfluoroorganyl)phosphane ligand. The strong π acidity of the bidentate ligand was demonstrated by conducting a structural and vibrational

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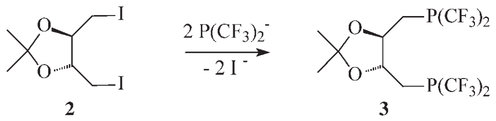
[a] Priv.-Doz. Dr. B. Hoge, Dr. P. Panne
Institut für Anorganische Chemie, Universität zu Köln
Greinstr. 6, 50939 Köln (Germany)
Fax: (+49) 221-470-5196
E-mail: b.hoge@uni-koeln.de

[**] DIOP = [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphane)



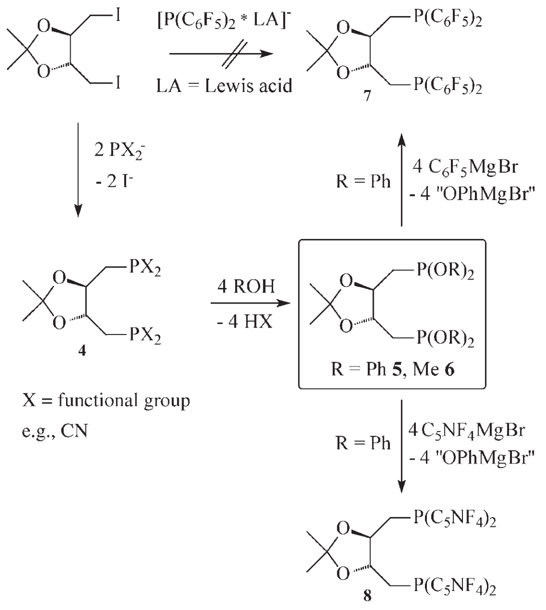
(2)

analysis of a corresponding tetracarbonyl–molybdenum complex.[4]

With the aim of synthesizing a corresponding bis(pentafluorophenyl) derivative we investigated the stabilization of the $P(C_6F_5)_2^-$ ion in the presence of weak Lewis acids, such as Hg^{2+} ions,[5] as well as CS_2.[6] However, all attempts to carry out the desired substitution of iodine by $P(C_6F_5)_2$ groups have been unsuccessful.[7]

To allow the synthesis of a whole series of chiral, bidentate bis(perfluoroorganyl)phosphane derivatives, the application of a phosphanide derivative, PX_2^-, with functional groups X that can be replaced by other nucleophilic groups, seems to be favorable. The adoption of a functional phosphanide, PX_2^-, would result in the synthesis of a functional bidentate phosphane derivative **4** that should be capable of transformation into different phosphane derivatives.

Here, we report the application of the dicyanophosphanide ion[8] $P(CN)_2^-$, which acts as a functional phosphanide PX_2^- and allows the synthesis of phosphane derivative **4** and its corresponding diphenyl- and dimethylphosphonite derivatives **5** and **6**, respectively (Scheme 1).



Scheme 1. Strategy for the synthesis of chiral, electron-poor phosphane ligands **5**–**8**.

The diphenylphosphonite system **5** (a diphenoxyphosphane derivative) still exhibits the properties of a functional phosphane. Upon treatment with pentafluorophenyl and *p*-tetrafluoropyridyl Grignard reagents it can be transformed into the corresponding bis(pentafluorophenyl) and bis(*p*-tetrafluoropyridyl) derivatives **7** and **8**, respectively.

The coordination properties of the bidentate phosphane ligands **5**–**8** were evaluated by conducting a vibrational study of the corresponding tetracarbonyl–molybdenum and cyclopentadienylcarbonyl–iron complexes.

Results and Discussion

In the literature, three examples of functional phosphanides are described that are, in principal, useful for the synthesis of chiral, bidentate phosphane derivatives, such as **4**. These are the well-known, strongly basic PH_2^- and $P(SiMe_3)_2^-$ ions, and the less-basic $P(CN)_2^-$ ion.

Application of the dicyanophosphanide ion would result in the synthesis of dicyanophosphane derivatives. As demonstrated previously, dicyanophosphanes can be transformed easily into the corresponding bis(trifluoromethyl)- and bis(pentafluorophenyl)phosphane derivatives by employing the cyanide-induced reactions with Me_3SiCF_3 and $Me_3SiC_6F_5$, respectively [Eq. (3)]:[9]

$$PhP(CN)_2 + 2\,Me_3SiR_f \rightarrow PhP(R_f)_2 + 2\,Me_3SiCN \qquad R_f = CF_3,\ C_6F_5 \tag{3}$$

The dicyanophosphanide ion, $P(CN)_2^-$, presented by Schmidpeter and co-workers in 1977, represents a stable, nucleophilic, and functional phosphanide ion that can be accessed through the cyanide degeneration of white phosphorus [Eq. (4)]. The reaction of cyanides with $P(CN)_3$ followed by reductive elimination of dicyane [Eq. (5)] also gives $P(CN)_2^-$ salts. Reaction of $P(CN)_3$ with diethylphosphonate salts [Eq. (6)][8] is best suited for the preparative synthesis of $P(CN)_2^-$ salts.[10],,

$$n/4\,P_4 + 2\,CN^- \rightarrow P(CN)_2^- + (P_{n-1})^- \tag{4}$$

$$P(CN)_3 + CN^- \rightarrow [P(CN)_4]^- \rightarrow P(CN)_2^- + NC{-}CN \tag{5}$$

$$P(CN)_3 + (EtO)_2PO^- \rightarrow P(CN)_2^- + NCPO(OEt)_2 \tag{6}$$

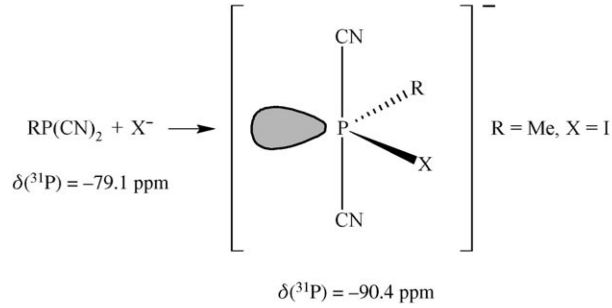
In the classical synthesis of cyanophosphanes, chlorophosphanes are reacted with silver cyanide,[11] a process that is cost-intensive and less useful for the synthesis of large amounts of $P(CN)_3$. However, a very convenient preparative access to $P(CN)_3$, on a 10-g scale, is given by the reaction of PCl_3 and HCN in the presence of triethylamine [Eq. (7)]:

$$PCl_3 + 3\,HCN + 3\,NEt_3 \rightarrow 3\,[NEt_3H]Cl + P(CN)_3 \tag{7}$$

The use of $P(CN)_2^-$ salts in nucleophilic displacement reactions was investigated. Schmidtpeter and co-workers reported the successful nucleophilic substitution of alkylhalides upon treatment with $P(CN)_2^-$ salts. In our own investigations we treated ethyl tosylate with [K([18]crown-6)]$P(CN)_2$, which led to $EtP(CN)_2$ as the sole product in a clean reaction. However, the less-reactive chiral ditosylate derivative **1** exhibits no reaction upon treatment with

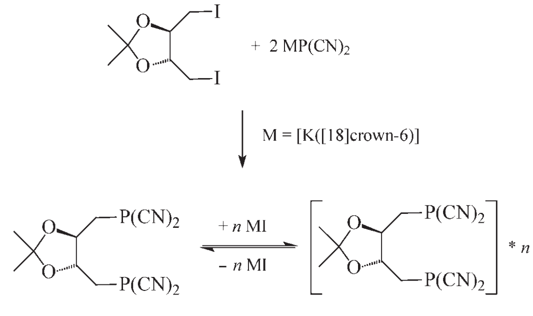
$P(CN)_2^-$ salts, whereas the rather more-reactive diiodo compound **2** shows a smooth reaction upon treatment with $P(CN)_2^-$ salts.[12]

The synthesis of dicyanoorganylphosphanes through nucleophilic substitution of iodide ions causes problems because the product tends to add the produced iodide ions with formation of phosphoranide ions [Eq. (8)], as demonstrated by Dillon and co-workers:[13]



(8)

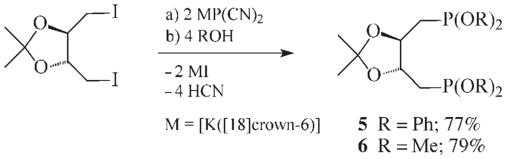
NMR spectra of the reaction mixture from the reaction of the diiodo compound **2** with $P(CN)_2^-$ salts exhibit the resonances of excess $P(CN)_2^-$ at −193 ppm as well as two additional resonances at −70 and −90 ppm. The formation of two reaction products could be explained by the formation of dicyano(iodo)phosphoranides [Eq. (9)]. The assignment of the product resonances is based on a comparison with the resonances of dicyanomethylphosphane and the dicyano(iodo)methylphoshoranide ion [Eqs. (8) and (9)].



9; $\delta(^{31}P) = -70$ ppm **10**; $\delta(^{31}P) = -90$ ppm (9)

The two products **9** and **10** are formed in varying amounts. The free dicyanophosphane derivative **9** always represents the minor product, formed in less than 20 % yield. The products can be separated from a stoichiometric reaction mixture by slow addition of diethyl ether at −30 °C. The neutral dicyanophosphane derivative **9** remains in solution, however, the salt **10** forms colorless crystals. Due to the extreme sensitivity of the single crystals towards hydrolysis and oxygen, we have not yet been able to characterize the product by performing either structural or vibrational investigations.

Further evidence that compound **10** represents a phosphoranide is given by the resistance towards reaction with Me_3SiCF_3 and $Me_3SiC_6F_5$. To facilitate the synthesis of the target bis(pentafluorophenyl) derivative **7** we tried to shift the equilibrium between the products **9** and **10** [Eq. (9)] towards the free compound **9**, which should be capable of transformation into the desired bis(pentafluorophenyl) derivative **7**. Unfortunately, the product ratio could be only slightly influenced by solvent or temperature variations. Even the addition of iodophilic Lewis acids, such as HgI_2, did not lead to a significant shift of the product ratio towards the free compound **9**. Because we were not able to transform the products directly into the desired bis(pentafluorophenyl) derivative **7**, we transformed compounds **9** and **10** into the corresponding phosphonite derivatives **5** and **6** by addition of excess phenol and methanol, respectively, to the reaction mixture of the diiodo compound **2** and $[K([18]crown\text{-}6)]P(CN)_2$ [Eq. (10)].

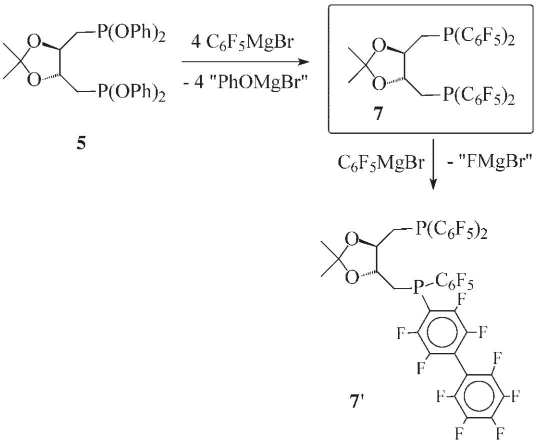


(10)

Saltlike compounds were separated from the reaction mixtures by the addition of hexane. The separated solutions were evaporated to yield the phosphonite derivatives contaminated with minor amounts of free crown ether. To remove the crown ether, the crude product was dissolved in a concentrated NaI solution in acetone to trap the crown ether as its sodium complex. The phosphonite derivatives **5** and **6** were isolated in an overall yield of 77 and 79 %, respectively, in the form of colorless liquids that could be easily manipulated by using standard Schlenk techniques. Upon exposure to air, slow hydrolysis occurred, followed by oxidation. The compounds were characterized by elemental analysis, mass spectrometry, and multinuclear NMR spectroscopy. The ^{31}P NMR resonances for compounds **5** and **6** of 178.3 and 183.8 ppm, respectively, are within the typical region for organyl phosphonite derivatives. The diastereomeric nature of the two −OR groups attached at each phosphorus atom are apparent from the ^{13}C NMR spectra. For example, the two diastereomeric methyl groups of derivative **6** exhibit resonances at 54.3 and 54.7 ppm with $^2J(P,H)$ couplings of 12 and 13 Hz, respectively.

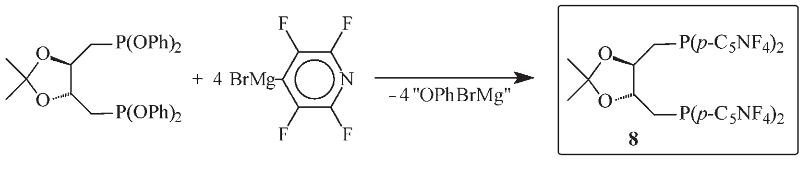
Because the phosphorus-bonded phenoxy groups can be replaced by various nucleophiles, compound **5** still represents a functional derivative that can react with pentafluorophenyl and *p*-tetrafluoropyridyl Grignard reagents to form the corresponding bis(pentafluorophenyl)phosphane and bis(*p*-tetrafluoropyridyl) derivatives **7** and **8**, [Eqs. (11) and (12)]. Both compounds were obtained by an aqueous workup procedure, followed by liquid chromatography on silica gel. They were recrystallized as white to pale-yellow solids and were fully characterized.

Product **7** was always contaminated by traces of a nonafluorobiphenyl derivative **7′** [Eq. (11)]. The formation of the side product is caused by nucleophilic attack of excess C_6F_5MgBr on a C_6F_5 group already attached at the phosphorus atom. A di- or oligomerization of the Grignard substrate, C_6F_5MgBr, as observed to some extent for C_6F_5MgCl,[14] seems to be unlikely. To reduce the amount of **7′** it was necessary to monitor the addition of a freshly prepared Et_2O solution of C_6F_5MgBr to a solution of **5** in THF by ^{31}P NMR spectroscopy. Stopping the addition directly after a complete transformation of **5** to **7** reduced the amount of **7′** to less than 1 %.



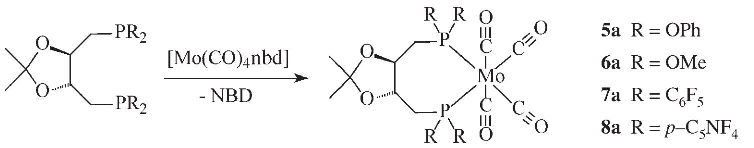
(11)

A more convenient method of preventing formation of the nonafluorobiphenyl derivative **7′** is the deactivation of the *para* position of the phenyl ring towards nucleophilic substitution. The formation of the side products discussed, such as **7′**, can be excluded by an exchange of the *para* CF unit by an isolobal nitrogen atom. The displacement of the phenoxy groups of **5** by *p*-tetrafluoropyridyl groups is, therefore, selective. As expected, an excess of *p*-C_5NF_4MgBr[14,15] does not lead to the formation of any side products.



(12)

To evaluate the coordination properties of the synthesized π-acidic ligands **5**–**8**, the corresponding tetracarbonyl–molybdenum complexes were synthesized by treating solutions of the ligands in CH_2Cl_2 at room temperature with $[Mo(CO)_4(nbd)]$ (NBD = norbornadiene). The reactions of **5** and **6** with $[Mo(CO)_4(nbd)]$ were complete within 3 h at room temperature, whereas only 80 % of the strongly π-acidic ligands **7** and **8** were coordinated after 8 h at room temperature. The complexes **5a**–**8a**, as well as $[Mo(CO)_4(nbd)]$, are not stable in the reaction mixture, and an extension of the reaction time favors the formation of side products.



5a R = OPh
6a R = OMe
7a R = C_6F_5
8a R = *p*–C_5NF_4

(13)

The chemical difference between the two diastereomeric pentafluorophenyl groups attached at each phosphorus atom of the C_2-symmetric ligand **7** causes the appearance of five multiplets in the ^{19}F NMR spectrum. The resonances of the fluorine atoms in the *para* and *meta* positions of the two diastereomeric C_6F_5 rings at around −150 and −160 ppm are each separated by 0.3 ppm, whereas the two resonances of the *ortho* fluorine atoms at −130 ppm could not be resolved. The coordination of **7** to a $Mo(CO)_4$ moiety increases the chemical difference of the two diastereomeric C_6F_5 groups in **7a**. This results in a more-extended separation of the two sets of *ortho*, *meta*, and *para* resonances in the ^{19}F NMR spectrum by 2.1, 1.2, and 3.7 ppm, respectively (Figure 1).

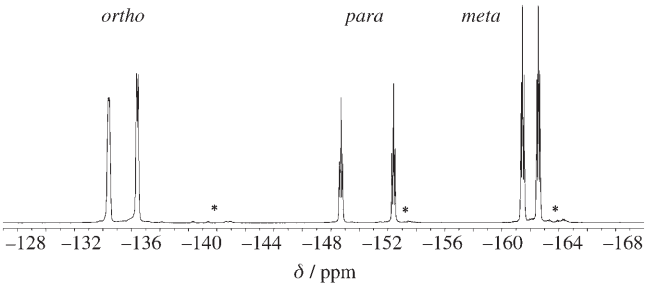
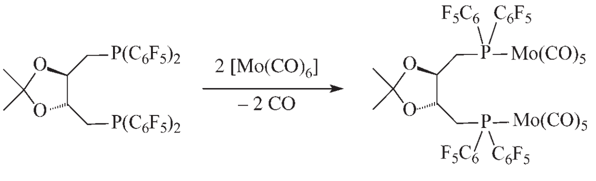


Figure 1. ^{19}F NMR spectrum of **7a** (see text). Signals marked with asterisks belong to nonafluorobiphenyl derivatives [see **7′** in Eq. (10)].

Refluxing **7** with $Mo(CO)_6$ in acetonitrile or irradiation of a solution in THF with a UV lamp leads to the formation of a dinuclear compound **7a′** with a $Mo(CO)_5$ moiety coordinated at each phosphorus atom [Eq. (14)]. For the dinuclear compound **7a′** the two sets of the *ortho*, *meta*, and *para* ^{19}F NMR resonances are separated by 1.3, 1.5, and 0.1 ppm, respectively.

Surprisingly, the largest separation of the resonances belonging to the diastereomeric fluorine atoms of the mononu-



7a'

(14)

clear chelate complex **7a** was observed for the fluorine atoms in the *para* position. In contrast, the dinuclear complex **7a′** exhibited the smallest chemical difference for the *para*-oriented fluorine atoms.

The highest CO stretching modes of the mononuclear complexes **5a**–**8a** are listed in Table 1. As expected, the frequencies of the carbonyl complexes are strongly dependent on the electronic nature of the substituents R on the phosphorus atoms (Table 1), and increase in the series R = Ph, OMe, OPh, C_6F_5, p-C_5NF_4, up to CF_3. This trend can be interpreted by using the classical σ donation and π back-bonding dualism in terms of an increasing π acidity of the phosphane ligands discussed. The trend observed is in accordance with data of comparable nonchiral diphosphane complexes (Table 1).

Table 1. Highest CO stretching mode of tetracarbonyl–molybdenum complexes.

L_2 with respect to 2L	$\tilde{\nu}$(CO) [cm^{-1}]	R	$\tilde{\nu}$(CO) [cm^{-1}]
2 PF_3	2087[16]		
F_2P PF_2	2074[17]	CF_3	2073[4]
$(CF_3)_2P$ $P(CF_3)_2$	2063[18]		
		p-C_5NF_4	2047
$(C_6F_5)_2P$ $P(C_6F_5)_2$	2041[19]	C_6F_5	2041
		OPh	2038
$(MeO)_2P$ $P(OMe)_2$	2033[20]	OMe	2031
Ph_2P PPh_2	2020[21]	Ph/Ar[a]	2014–2018[22]
Et_2P PEt_2	2012[21]		

[a] Ar = o-$MeOC_6H_4$, o-$Me_2NC_6H_4$, o-$(MeO)_2C_6H_3$.

The highest CO valence mode of the p-tetrafluoropyridyl-substituted complex **8a** is shifted by 6 cm^{-1} to higher energy relative to the pentafluorophenyl derivative **7a**, which classifies the p-C_5NF_4 group as being the stronger electron-withdrawing substituent. This interpretation is in accordance with a recent quantum-chemical concept[7] that uses the phosphorus–carbon distances in corresponding arylphosphanides, $[ArPH]^-$, as an indicator for the evaluation of the electron-withdrawing effect of aryl groups exerted on a phosphorus atom. Corresponding quantum-chemical calculations at the B3PW91/6-311G(d,p) level of theory suggest that the electron-withdrawing effect of perfluoroaryl groups can be increased by a successive substitution of fluorine atoms by CF_3 groups, or made even stronger upon successive substitution of CF units by isolobal nitrogen atoms. By considering these ideas the p-C_5NF_4 group was predicted to be a stronger electron-withdrawing substituent than a C_6F_5 group, in accordance with the vibrational investigation of tetracarbonyl–molybdenum complexes bearing p-C_5NF_4- and C_6F_5-substituted phosphane ligands discussed above (Table 1).

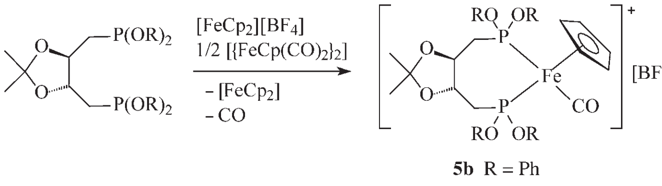
The strong electron-withdrawing nature of the p-C_5NF_4 group (which exceeds that of a C_6F_5 group) effects an increased stabilization of phosphinous acids, R_2POH, with respect to the tautomeric phosphane oxides, $R_2P(O)H$.[23]

In contrast to the tetracarbonyl–molybdenum complexes **5a**–**8a** that were synthesized to evaluate the coordination properties of the correlated phosphane ligands, diphosphane iron complexes are successfully used in homogeneous catalysis.[24]

The achiral Lewis acid $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(thf)][BF_4]$ is used in several catalytic processes,[25] such as Diels–Alder reactions,[26] whereas the less-Lewis-acidic phosphane complex $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(thf)][BF_4]$ exhibits no such catalytic activity.[27] However, upon substitution of PPh_3 by the stronger π-acidic $P(OMe)_3$ ligand, the resulting complex $[Fe(\eta^5\text{-}C_5H_5)(CO)P(OMe)_3(thf)][BF_4]$ does exhibit a catalytic activity towards Diels–Alder reactions.[27] This example demonstrates the important influence of the substituents at the phosphorus atoms on the catalytic activity of the resulting transition-metal phosphane complexes.

With the aim to synthesize potential catalytically active chiral Lewis acids, the phosphane ligands **5**–**8** were reacted with a reagent mixture of $[Fe(\eta^5\text{-}C_5H_5)_2][BF_4]$ and $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$.[28] After stirring for 8 h in CH_2Cl_2, the mononuclear iron complexes **5b** and **6b** were separated from the reaction mixture [Eq. (15)] by column chromatography and were purified by recrystallization from an Et_2O/CH_2Cl_2 mixture. The white and bright-yellow crystalline materials **5b** and **6b** were obtained in 57 and 36% yields, respectively.

The diphenylphosphonite derivative **5b** crystallizes in the acentric monoclinic space group C_2 (no. 5) (a = 2938.3(4),



5b R = Ph
6b R = Me

(15)

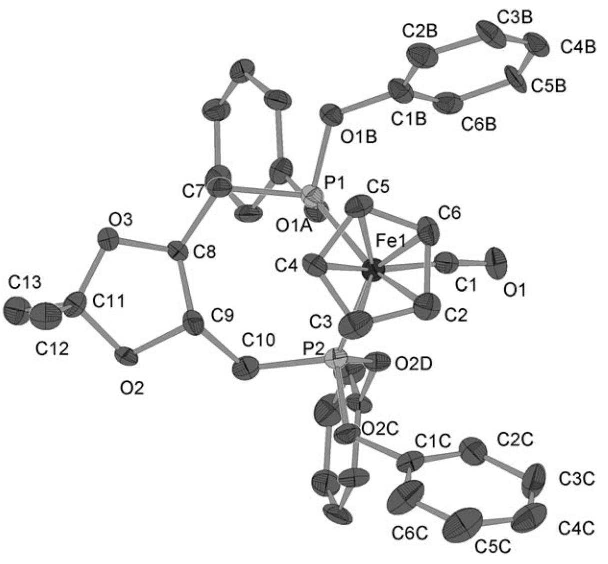


Figure 2. Thermal ellipsoid diagram of one of the two symmetry-independent cationic iron complexes **5b** as its tetrafluoroborate salt, and the atom numbering scheme. The hydrogen atoms and BF_4^- counterion have been omitted for clarity.

$b = 1024.2(1)$, $c = 2512.5(3)$ pm, $\beta = 100.63(1)°$). One of the symmetry-independent cations is shown in Figure 2. Selected bond lengths and angles of the two independent units are listed in Table 2. A comparison with literature data reveals that the phosphorus–iron distances of 214.7 to 215.8 pm, as well as the Fe–CO distances of 176 and 177 pm, are within the expected range.[29,30]

The ^{31}P NMR resonances of the iron complexes **5b** and **6b** are deshielded by about 30 and 23 pm relative to the free ligands **5** and **6**, respectively. The formerly chemically equivalent C_2-symmetric phosphorus atoms of the free ligands become diastereomeric upon coordination to the iron center. Although the resonance of **5b** represents a nonresolved singlet, the resonance of **6b** exhibits the expected AB spin-system splitting with a difference in chemical shift of 0.9 ppm and a ^2J(P,P) coupling of 86 Hz. Figure 3 shows the experimental proton-decoupled ^{31}P NMR spectrum (A) of complex **6b**, together with the calculated spectrum (B).

Table 2. Selected bond lengths [pm] and angles [°] of the two symmetry-independent molecules of the iron complex **5b**.

Fe1−P2	215.1(3)	P3-Fe2-P4	93.6(1)
Fe1−P1	215.7(3)	P2-Fe1-P1	93.3(1)
Fe1−C1	177(1)	C1-Fe1-C6	92.6(4)
Fe1−C2	211(1)	C1-Fe1-C5	123.1(5)
Fe1−C3	211(1)	C1-Fe1-P2	90.3(3)
Fe1−C4	212.9(8)	C1-Fe1-P1	93.8(3)
Fe1−C5	210.1(9)	C1C-O2C-P2	127.1(7)
Fe1−C6	208(1)	C1D-O2D-P2	125.8(6)
P1−O1B	160.9(7)	O1B-P1-O1A	105.6(4)
P1−O1A	162.0(7)	O1B-P1-C7	97.0(4)
P1−C7	182(1)	O1A-P1-C7	103.8(4)
P2−O2C	159.1(7)	O1B-P1-Fe1	116.2(3)
P2−O2D	162.3(6)	O1A-P1-Fe1	112.1(3)
P2−C10	180.4(9)	C7-P1-Fe1	120.0(4)
O1−C1	117(1)	O2C-P2-O2D	103.9(3)
O1A−C1A	142(1)	O2C-P2-C10	97.7(4)
O1B−C1B	141(1)	O2D-P2-C10	104.3(4)
O2−C11	143(1)	O2C-P2-Fe1	117.5(3)
O2−C9	146(1)	O2D-P2-Fe1	109.1(3)
O2C−C1C	143(1)	C10-P2-Fe1	122.2(3)
Fe2−P3	214.7(3)	C1A-O1A-P1	125.3(6)
Fe2−P4	215.8(3)	C1B-O1B-P1	122.8(6)

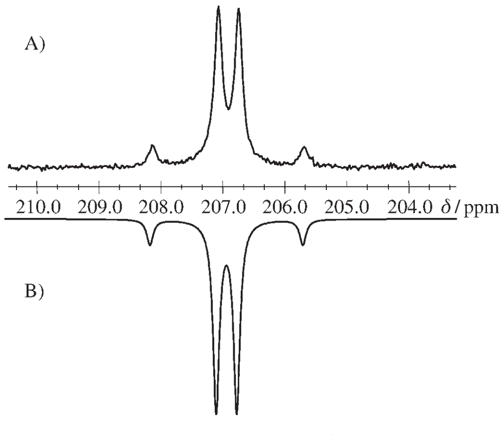
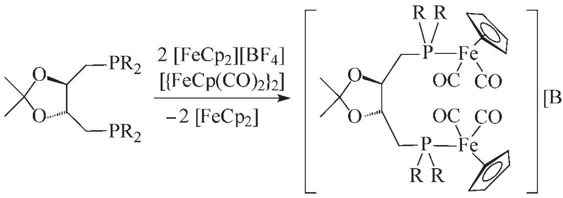


Figure 3. A) Experimental and B) calculated $^{31}P\{^1H\}$ NMR spectra of the iron complex **6b**.

The CO stretching mode of the diphenylphosphonite complex **5b** is shifted to higher energy by 11 cm^{-1} relative to the dimethylphosphonite derivative **6b** and describes the stronger π acidity of the phenyl-substituted phosphane ligand, which is in accordance with the trend observed for the comparable tetracarbonyl–molybdenum complexes **5a** and **6a** (Table 1).

The carbonyl group in **5b** and **6b** should be removable by UV irradiation, leading to reactive solvent adducts that represent potential chiral Lewis acids that should be capable of catalyzing asymmetric Diels–Alder reactions.[31]

The reaction of the bis(pentafluorophenyl)phosphane derivative **7** with the reagent combination of $[Fe(\eta^5\text{-}C_5H_5)_2][BF_4]$ and $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ does not lead to a mononuclear chelate complex, such as **5b** and **6b** [Eq. (15)], but results in the coordination of one $[FeCp(CO)_2]$ unit at only one phosphorus atom. This is supported by the observation of two new ^{31}P NMR resonances at 45.7 and −54.7 ppm for the coordinated and free phosphorus atoms, respectively. The intensity of the resonances for the mononuclear complex decreases as the excess of the iron-reagent combination increases, forming a nonchelate dinuclear iron complex **7b′** [Eq. (16)].



(16)

7b' $R = C_6F_5$
8b' $R = p\text{–}C_5NF_4$

As expected, both C_2-symmetric complexes **7b′** and **8b′** exhibit a sharp ^{31}P NMR resonance for the enantiotopic phosphorus atoms at 48.3 and 52.5 ppm, respectively. These resonances are deshielded by more than 100 ppm relative to the free ligands. The dinuclear character of the complexes **7b′** and **8b′** is supported by characteristic ESI mass spectra and the observation of two CO stretching modes of the $Fe(CO)_2$ moieties for both compounds. The CO stretching modes of the bis(*p*-tetrafluoropyridyl)phosphane derivative **8b′** at 2077 and 2038 cm^{-1} are shifted by 3 and 6 cm^{-1}, respectively, to higher frequencies, relative to the bis(pentafluorophenyl)phosphane complex **7b′**. The resulting classification of the bis(*p*-tetrafluoropyridyl)phosphane derivative as being the stronger π-acidic ligand is again in accordance with a previously presented quantum-chemical model,[7] and confirms the trend of the vibrational data of comparable mononuclear tetracarbonyl–molybdenum derivatives **7a** and **8a** (Table 1).

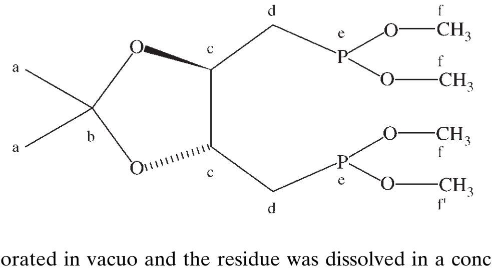
Experimental Section

Materials and apparatus: All chemicals were obtained from commercial sources and were used without further purification. Literature methods were used for the synthesis of 1,4-dideoxy-1,4-diiodo-2,3-*O*-isopropyliden-L-threitol, **2**.[32] Standard high-vacuum techniques were employed throughout all preparative procedures and nonvolatile compounds were handled under a dry N_2 atmosphere by using Schlenk techniques.

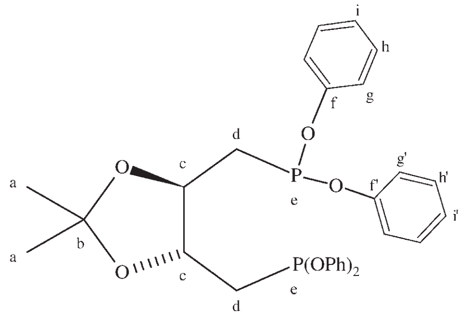
Infrared spectra were recorded by using a Nicolet-5PC-FTIR spectrometer and KBr pellets. Raman spectra were measured by using a Bruker FRA-106/s spectrometer with a Nd:YAG laser operating at $\lambda = 1064$ nm. The NMR spectra were recorded by using a Bruker Model AC200 spectrometer (^{31}P, 81.01 MHz; ^{19}F, 188.31 MHz; ^{1}H, 200.13 MHz) with positive shifts being downfield from the external standards (85% orthophosphoric acid (^{31}P), CCl_3F (^{19}F), and TMS (^{1}H)). Higher-order NMR spectra were calculated by using the program gNMR.[33] EI mass spectra were recorded by using a Finnigan MAT 95 spectrometer (20 eV) and ESI mass spectra were recorded by using a Finnigan MAT 900 (70 eV) spectrometer. Intensities were referenced to the most intense peak of a group. Isotope patterns for comparison were calculated by using the program Isopro.[34] Melting and visible decomposition points were determined by using a HWS Mainz 2000 apparatus. The carbon, hydrogen, and nitrogen analyses were carried out by using a HEKAtech Euro EA 3000 apparatus.

Syntheses

1,4-Dideoxy-1,4-bis(dimethoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol (6): [Na([18]crown-6)]P(CN)$_2$ (2.42 g, 6.54 mmol) and 1,4-dideoxy-1,4-diiodo-2,3-*O*-isopropyliden-L-threitol, **2**,(0.83 g, 2.17 mmol) were dissolved in 30 mL of THF and stirred for 8 h at RT. After addition of methanol (0.56 g, 17.48 mmol) and stirring for an additional hour at RT, saltlike compounds were precipitated upon addition of hexane. The filtrate was evaporated in vacuo and the residue was dissolved in a concentrated solution of NaI in acetone. After evaporation, the residue was extracted with hexane. Evaporation of the hexane yielded 0.54 g (1.72 mmol, 79%, with respect to **2**) of **6** as a colorless oil. $[\alpha]_D^{20} = -19°$ (hexane, $c = 0.12$). ^{1}H NMR (CDCl$_3$, RT): $\delta = 1.3$ (s, 6H^{a}), 1.6–1.9 (m, 4H^{d}), 3.5 (d, ^{2}J(P,H^{f}) = 4 Hz; 6H^{f}), 3.6 (d, ^{2}J(P,H) = 4 Hz; 6H$^{f'}$), 3.8 ppm (m, 2H^{c}); ^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta = 27.7$ (s, C^{a}), 37.3 (dd, ^{1}J(C,P) = 23 Hz, ^{4}J(C,P) = 2 Hz; C^{d}), 54.3 (d, ^{2}J(C,P) = 12 Hz; C^{f}), 54.7 (d, ^{2}J(C,P) = 13 Hz; C$^{f'}$), 78.1 (dd, ^{2}J(C,P) = 13 Hz, ^{3}J(C,P) = 7 Hz; C^{c}), 108.5 ppm (s, C^{b}); ^{31}P{^{1}H} NMR (CDCl$_3$, RT):$\delta = 183.8$ ppm (s); IR (KBr pellet): $\tilde{\nu} = 2985$ (m), 2949 (m), 2901 (sh), 2853 (sh), 1462 (w), 1417 (sh), 1377 (m), 1302 (s), 1215 (vs), 1097 (sh), 1041 (vs), 904 (sh), 880 (s), 844 (w), 803 (m), 775 (m), 697 cm^{-1} (m); MS (EI, 20 eV): *m/z* (%): 299 (13) $[M-CH_3]^+$, 221 (58) $[M-P(OMe)_2]^+$, 163 (63) $[C_6H_{12}O_3P]^+$, 93 (100) $[P(OMe)_2]^+$; elemental analysis calcd (%): C 42.04, H 7.70; found: C 42.56, H 8.52.

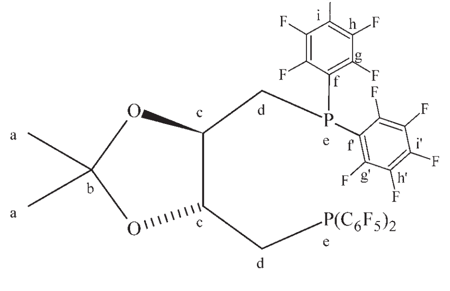


1,4-Dideoxy-1,4-bis(diphenoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol, 5: [Na([18]crown-6)]P(CN)$_2$ (13.40 g, 36.19 mmol) and 1,4-dideoxy-1,4-diiodo-2,3-*O*-isopropyliden-L-threitol, **2**, (4.60 g, 12.04 mmol) were dissolved in 30 mL of THF and stirred for 8 h at RT. After addition of phenol (4.77 g, 50.69 mmol) and stirring for an additional hour at RT, saltlike compounds were precipitated upon addition of hexane. The separated solution was evaporated in vacuo and the residue was dissolved in a concentrated solution of NaI in acetone. After evaporation, the residue was extracted with hexane. Evaporation of the hexane yielded 5.23 g (9.30 mmol, 77% with respect to **2**) of **5** as a colorless oil. $[\alpha]_D^{20} = -30°$ (hexane, $c = 0.27$).



^{1}H NMR (CDCl$_3$, RT): $\delta = 1.4$ (s, 6H^{a}), 1.9–2.4 (m, 4H^{d}), 4.1 (s, 2H^{c}), 6.8–7.3 ppm (m, 10H$^{g-i,g'-i'}$); ^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta = 27.0$ (s, C^{a}), 37.8 (d, ^{1}J(C,P) = 21 Hz; C^{d}), 77.2 (dd, ^{2}J(C,P) = 10, ^{3}J(C,P) = 7 Hz; C^{c}), 109.1 (s, C^{b}), 119.5 (d, ^{3}J(C,P) = 3 Hz; C^{g}), 119.7 (d, ^{3}J(C,P) = 3 Hz; C$^{g'}$), 123.4 (s, C$^{i,i'}$), 129.4 (s, C$^{h,h'}$), 155.2 (d, ^{2}J(C,P) = 6 Hz; C^{f}), 155.4 ppm (d, ^{2}J(C,P) = 5 Hz; C$^{f'}$); ^{31}P{^{1}H} NMR (CDCl$_3$, RT): $\delta = 178.3$ ppm (s); IR (KBr pellet): $\tilde{\nu} = 3263$ (m), 1604 (sh), 1593 (vs), 1491 (vs), 1454 (sh), 1381 (m), 1373 (w), 1221 (vs), 1198 (vs), 1165 (s), 1109 (s), 1070 (m), 1037 (w), 1024 (m), 927 (w), 881 (s), 862 (vs), 758 (s), 715 (w), 692 cm^{-1} (s); MS (EI, 20 eV): *m/z* (%): 563 (1) $[M]^+$, 547 (1) $[M-CH_3]^+$, 469 (100) $[M-OPh]^+$, 345 (38) $[M-P(OPh)_2]^+$, 217 (58) $[P(OPh)_2]^+$, 94 (3) $[PhOH]^+$; elemental analysis calcd (%): C 66.19, H 5.73; found: C 66.17, H 6.06.

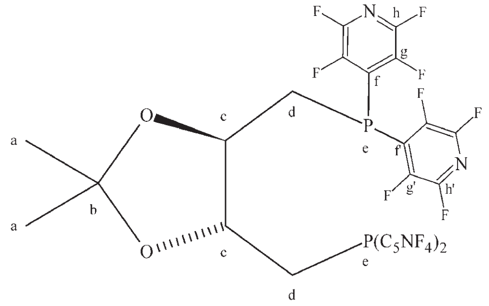
1,4-Dideoxy-1,4-bis[bis(pentafluorophenyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol (7): 1,4-Dideoxy-1,4-bis(diphenoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol, **5**, (2.90 g, 5.16 mmol) dissolved in 30 mL of THF was reacted with C_6F_5MgBr (7.69 g, 28.35 mmol) in 50 mL Et_2O. After stirring for 2 h at RT, the mixture was treated with hexane and washed with water and an aqueous concentrated NH_4Cl solution. The separated



organic layer was evaporated and the brown oily residue was purified by silica column chromatography (ethyl acetate/hexane 1:20). The resulting white solid was recrystallized from methanol, yielding 4.00 g (4.66 mmol, 90% with respect to **5**) of **7** as colorless crystals (m.p. 113 °C). $[\alpha]_D^{20} = -12°$ (hexane, $c=0.34$).

^{1}H NMR (CDCl$_3$, RT): $\delta=1.2$ (s, 6H^a), 2.6–3.1 (m, 4H^d), 4.1 ppm (s, 2H^c); ^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta=26.4$ (s, C^a), 54.6 (d, ^1J(C,P)=6 Hz; C^d), 78.2 (dd, ^2J(C,P)=14 Hz, ^3J(C,P)=12 Hz; C^c), 109.7 (s, C^b), 108 (m, C$^{f,f'}$), 134—151 ppm (m, C$^{g-i,g'-i'}$); ^{19}F NMR (CDCl$_3$, RT): $\delta=-129.9$ (m, F$^{g,g'}$), −149.4 (m, F^i), −149.7 (m, F$^{i'}$), −160.1 (m, F^h), −160.4 ppm (m, F$^{h'}$); ^{31}P{^{1}H} NMR (CDCl$_3$, RT): $\delta=-53.2$ ppm (quin, ^3J(P,F)=29 Hz); IR (KBr pellet): $\tilde{\nu}=2992$ (vw), 2938 (vw), 1644 (m), 1520 (vs), 1476 (vs), 1385 (m), 1291 (w), 1231 (w), 1177 (vw), 1092 (s), 1042 (vw), 1009 (vw), 976 (s), 895 (w), 839 (w), 814 (w), 639 (w), 509 (w), 426 cm^{-1} (w); Raman (int): $\tilde{\nu}=2988$ (40), 2938 (66), 2853 (23), 1641 (82), 1389 (31), 838 (31), 708 (17), 639 (16), 585 (94), 502 (100), 445 (70), 388 cm^{-1} (72); MS (EI, 20 eV): *m*/*z* (%): 843 (6) $[M-\mathrm{CH_3}]^+$, 493 (83) $[M-\mathrm{P(C_6F_5)_2}]^+$, 435 (100) $[\mathrm{C_{16}H_6F_{10}OP}]^+$, 365 (17) $[\mathrm{P(C_6F_5)_2}]^+$; elemental analysis calcd (%): C 43.38, H 1.41; found: C 43.33, H 1.50.

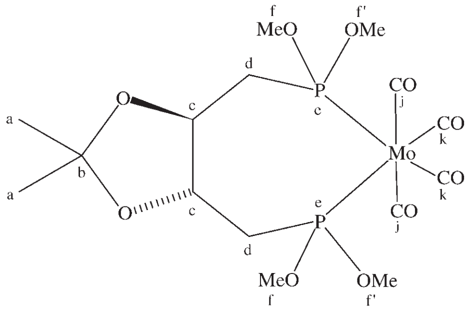
1,4-Dideoxy-1,4-bis[bis(*p*-tetrafluoropyridyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol (8): 1,4-Dideoxy-1,4-bis(diphenoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol, **5**, (2.40 g, 4.27 mmol) dissolved in 30 mL of THF was reacted with *p*-C$_5$NF$_4$MgBr (8.83 g, 34.72 mmol) in 50 mL Et$_2$O. After stirring for 2 h at RT, the reaction mixture was treated with hexane and washed with water and an aqueous concentrated NH$_4$Cl solution. The separated organic layer was evaporated and the brown oily residue was purified by silica column chromatography (ethyl acetate/hexane 1:20). The resulting white solid was recrystallized from hexane, giving a yield of 1.70 g (2.15 mmol, 50% with respect to **5**) of **8** as slightly yellow crystals (m.p. (decomp) 103 °C). $[\alpha]_D^{20} = -10°$ (CH$_2$Cl$_2$, $c=0.30$).



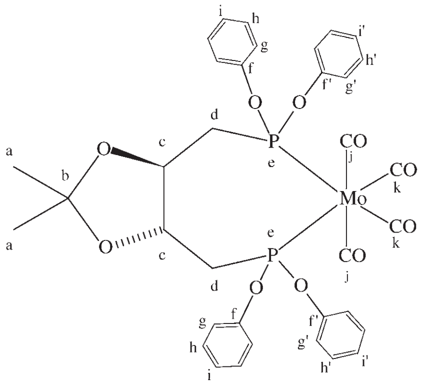
^{1}H NMR (CDCl$_3$, RT): $\delta=1.1$ (s, 6H^a), 2.6–3.1 (m, 4H^d), 4.0 ppm (s, 2H^c); ^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta=25.4$ (s, C^a), 53.7 (d, ^1J(C,P)=6 Hz; C^d), 77.3 (dd, ^2J(C,P)=12 Hz, ^3J(C,P)=12 Hz; C^c), 109.5 (s, C^b), 127 (m, C$^{f,f'}$), 137—146 ppm (m, C$^{g,h,g',h'}$); ^{19}F NMR (CDCl$_3$, RT): $\delta=-89.1$ (m, F^g), −89.4 (m, F$^{g'}$), −131.6 (m, F^h), −138.8 ppm (m, F$^{h'}$); ^{31}P{^{1}H} NMR (CDCl$_3$, RT): $\delta=-49.9$ ppm (quin, ^3J(P,F)=22 Hz); IR (KBr pellet): $\tilde{\nu}=$ 2926 (vw), 1655 (w), 1633 (m), 1472 (sh), 1451 (vs), 1399 (w), 1385 (w), 1259 (sh), 1237 (m), 1207 (w), 968 (w), 943 cm^{-1} (m); MS (EI, 20 eV): *m*/*z* (%): 775 (8) $[M-\mathrm{CH_3}^+]$, 715 (4) $[\mathrm{C_{24}H_6F_{16}N_4P_2}^+]$, 459 (33) $[M-\mathrm{P(C_5NF_4)_2}^+]$, 401 (100) $[\mathrm{C_{14}H_6F_8N_2OP}^+]$; elemental analysis calcd (%): C 41.03, N 7.09, H 1.53; found: C 42.12, N 7.23, H 1.70.

Tetracarbonyl{1,4-dideoxy-1,4-bis(dimethoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol-*P*,*P'*}molybdenum (6a): 1,4-Dideoxy-1,4-bis(dimethoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol, **6**, (0.30 g, 0.95 mmol) and [Mo(CO)$_4$(nbd)] (0.29 g, 0.97 mmol) were dissolved in 10 mL of CH$_2$Cl$_2$ and stirred for 3 h at RT. The filtered solution was evaporated in vacuo and the residue was extracted with hexane. Evaporation of the hexane yielded 0.13 g of a slightly yellow oil. The product **6a** contained minor amounts of [Mo(CO)$_4$(nbd)].

^{1}H NMR (CDCl$_3$, RT): $\delta=1.4$ (s, 6H^a), 1.9–2.4 (m, 4H^d), 3.5 (s, 6H^f), 3.6 (s, 6H$^{f'}$), 3.9 ppm (s, 2H^c); ^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta=22.9$ (s, C^a), 39.2 (AXX′ spin system with A=^{13}C^d, X=^{31}P, J(A,X)=23 Hz, J(A,X′)=−2 Hz, J(X,X′)=10 Hz), 48.1 (m, C^f), 48.3 (m, C$^{f'}$), 76.7 (AXX′ spin system with A=^{13}C^c, X=^{31}P, J(A,X)=19 Hz, J(A,X′)=−3 Hz, J(X,X′)=9 Hz), 103.8 (s, C^b), 204.3 (t, ^2J(C,P)=11 Hz; C^j), 209.2 ppm (dd, ^2J(C,P)$_{trans}$=34 Hz, ^2J(C,P)$_{cis}$=16 Hz; C^k); ^{31}P{^{1}H} NMR (CDCl$_3$, RT): $\delta=192.2$ ppm (s); IR (KBr pellet): $\tilde{\nu}=2986$ (vw), 2947 (vw), 2031 (s; CO), 1911 (vs), 1636 (w), 1458 (w), 1381 (w), 1244 (w), 1165 (vw), 1040 (m), 1015 (m), 889 (w), 820 (w), 781 (w), 710 (w), 604 (w), 589 (w), 572 cm^{-1} (w); MS (EI, 20 eV): *m*/*z* (%): 522 (4) $[M^+-\mathrm{CO}]$, 494 (4) $[M^+-2\,\mathrm{CO}]$, 466 (4) $[M^+-3\,\mathrm{CO}]$, 438 (4) $[M^+-4\,\mathrm{CO}]$, 300 (46) $[\mathrm{Mo(CO)_6(nbd)}]^+$, 272 (28) $[\mathrm{Mo(CO)_3(nbd)}]^+$, 244 (29) $[\mathrm{Mo(CO)_2(nbd)}]^+$, 216 (27) $[\mathrm{Mo(CO)(nbd)}]^+$, 188 (100) $[\mathrm{Mo(nbd)}]^+$; elemental analysis calcd (%): C 34.50, H 4.63; found: C 35.05, H 4.39.

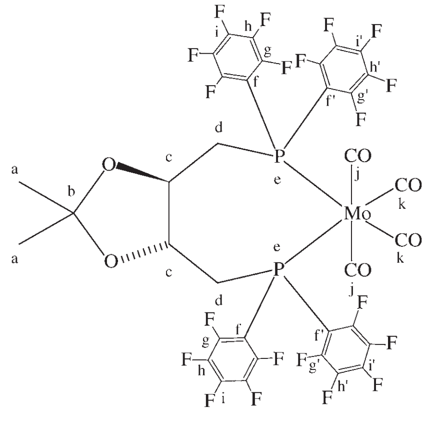


Tetracarbonyl{1,4-dideoxy-1,4-bis(diphenoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol-*P*,*P'*} molybdenum (5a): 1,4-Dideoxy-1,4-bis(diphenoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol, **5**, (0.17 g, 0.30 mmol) and [Mo(CO)$_4$(nbd)] (0.09 g, 0.30 mmol) were dissolved in 10 mL of CH$_2$Cl$_2$ and stirred for 3 h at RT. The filtered solution was evaporated in vacuo and the residue was extracted with hexane. Evaporation of the hexane yielded 0.12 g (0.16 mmol, 53%) of **5a** as a white solid.



^{1}H NMR (CDCl$_3$, RT): $\delta=1.4$ (s, 6H^a), 2.0–2.6 (m, 4H^d), 4.2 (s, 2H^c), 6.9–7.5 ppm (m, 10H$^{g-i,g'-i'}$); ^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta=22.9$ (s, C^a), 36.9 (d, ^1J(C,P)=23 Hz; C^d), 77.8 (s, C^c), 103.9 (s, C^b), 117.3 (s, C^g), 117.5 (d, ^3J(C,P)=3 Hz; C$^{g'}$), 121.0 (s, C^i), 121.2 (s, C$^{i'}$), 126.0 (s, C^h), 126.2 (s, C$^{h'}$), 148.6 (d, ^2J(C,P)=12 Hz; C^f), 149.2 (d, ^2J(C,P)=7 Hz; C$^{f'}$), 202.4 (t, ^2J(C,P)=11 Hz; C^j), 206.9 ppm (dd, ^2J(C,P)$_{trans}$=36 Hz, ^2J(C,P)$_{cis}$=14 Hz; C^k); ^{31}P{^{1}H} NMR (CDCl$_3$, RT): $\delta=190.4$ ppm (s); IR (KBr pellet): $\tilde{\nu}=$ 2986 (vw), 2038 (s; CO), 1925 (vs), 1592 (m), 1488 (s), 1455 (w), 1381 (w), 1211 (m), 1188 (s), 1162 (m), 1053 (w), 1024 (w), 883 (s), 761 (m), 690 cm^{-1} (m); MS (EI, 20 eV): *m*/*z* (%): 770 (17) $[M]^+$, 742 (8) $[M-\mathrm{CO}]^+$, 786 (96) $[M-3\,\mathrm{CO}]^+$, 758 (50) $[M-4\,\mathrm{CO}]^+$, 469 (8) $[M-\mathrm{Mo(CO)_4P(OPh)_2}]^+$, 217 (100) $[\mathrm{P(OPh)_2}]^+$, 94 (75) $[\mathrm{PhOH}]^+$; elemental analysis calcd (%): C 54.56, H 4.19; found: C 54.43, H 4.66.

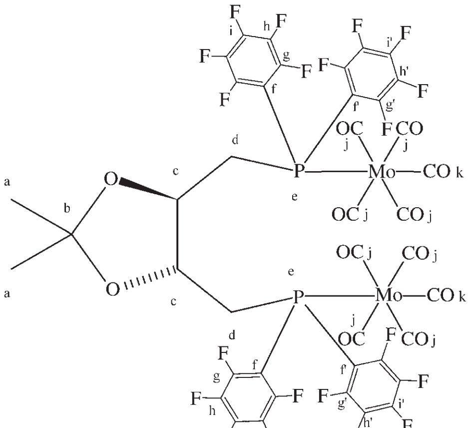
Tetracarbonyl{1,4-dideoxy-1,4-bis[bis(pentafluorophenyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol-*P*,*P'*} molybdenum (7a): 1,4-Dideoxy-1,4-bis[bis(pentafluorophenyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol, **7**, (0.30 g, 0.35 mmol) and [Mo(CO)$_4$(nbd)] (0.11 g, 0.37 mmol) were dissolved in 10 mL of CH$_2$Cl$_2$ and stirred for 3 h at RT. The filtered solution



was evaporated in vacuo and the residue was extracted with hexane. Evaporation of the hexane yielded 0.10 g (0.09 mmol, 26 % with respect to **7**) of **7a** as a white solid (m.p. (decomp) 130 °C).

^{1}H NMR (CDCl$_3$, RT): $\delta=1.3$ (s, 6H^a), 3.6–3.9 (m, 4H^d), 2.7 ppm (m, 2H^c); ^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta=26.5$ (s, C^a), 34.5 (m, C^d), 78.4 (dd, ^2J(C,P) = 12 Hz, ^3J(C,P) = 11 Hz; C^c), 109.8 (s, C^b), 105–113 (m, C$^{f,f'}$), 134–151 (m, C$^{g-i,g'-i'}$), 206 ppm (t, ^2J(C,P) = 8 Hz; C^{j,k}); ^{19}F NMR (CDCl$_3$, RT): $\delta=-132.3$ (m, F^g), −134.4 (m, F$^{g'}$), −148.7 (m, F^i), −152.4 (m, F$^{i'}$), −161.4 (m, F^h), −162.6 ppm (m, F$^{h'}$); ^{31}P{^{1}H} NMR (CDCl$_3$, RT): $\delta=-1.6$ ppm (s); IR (KBr pellet): $\tilde{\nu}=3439$ (w), 2990 (vw), 2870 (vw), 2082 (vw), 2041 (s; CO), 1952 (vs), 1935 (vs), 1918 (vs), 1641 (m), 1521 (s), 1473 (vs), 1385 (m), 1294 (w), 1245 (vw), 1144 (w), 1094 (s), 1064 (w), 979 (s), 886 (w), 607 (w), 580 cm^{-1} (m); MS (EI, 20 eV): *m*/*z* (%): 1066 (1) [*M*]$^+$, 1038 (1) [*M*−CO]$^+$, 1010 (1) [*M*−2CO]$^+$, 982 (1) [*M*−3CO]$^+$, 954 (1) [*M*−4CO]$^+$, 843 (38) [*M*−Mo(CO)$_4$CH$_3$]$^+$, 493 (46) [*M*−Mo(CO)$_4$P(C$_6$F$_5$)$_2$]$^+$, 435 (100) [C$_{16}$H$_6$F$_{10}$OP]$^+$, 365 (16) [P(C$_6$F$_5$)$_2$]$^+$; elemental analysis calcd (%): C 39.42, H 1.13; found: C 40.05, H 1.47.

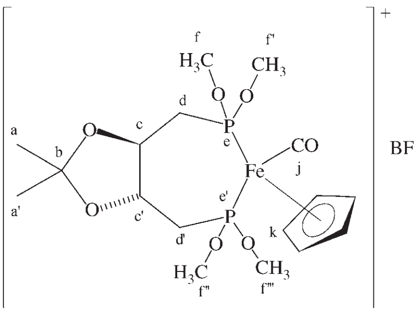
µ-{1,4-Dideoxy-1,4-bis[bis(pentafluorophenyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol-1κ*P*:2κ*P'*}bis[pentacarbonylmolybdenum] (7a'): [Mo(CO)$_6$] (2.00 g, 7.58 mmol) was dissolved in 100 mL of acetonitrile and refluxed for 8 h. The reaction mixture was evaporated, suspended in 100 mL of hexane, and treated with 1,4-dideoxy-1,4-bis[bis(pentafluorophenyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol, **7** (0.14 g, 0.16 mmol). After 2 h heating under reflux the suspension was filtered hot and the filtrate evaporated in vacuo yielding a yellow solid.



^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta=25.9$ (s, C^a), 34.2–34.5 (m, C^d), 70.6 (not assigned), 75.2 (not assigned), 78.0 (m, C^c), 110.6 (s, C^b), 109 (m, C$^{f,f'}$), 135–150 (m, C$^{g-i,g'-i'}$), 203.8 (d, ^2J(C,P) = 6 Hz; C^j), 208.0 ppm (d, ^2J(C,P) = 30 Hz; C^k); ^{19}F NMR (CDCl$_3$, RT): $\delta=-129.2$ (m, F^g), −130.5 (m, F$^{g'}$), −148.5 (m, F^i), −148.6 (m, F$^{i'}$), −158.6 (m, F^h), −160.1 ppm (m, F$^{h'}$); ^{31}P{^{1}H} NMR (CDCl$_3$, RT): $\delta=7.2$ ppm (s); IR (KBr pellet): $\tilde{\nu}=$ 2083 (s; CO), 1951 (vs), 1643 (w), 1522 (s), 1475 (s), 1387 (w), 1294 (vw), 1094 (s), 978 (m), 607 (m), 581 cm^{-1} (m); MS (EI, 20 eV): *m*/*z* (%): 1066 (2) [*M*]$^+$, 1038 (4) [*M*−CO]$^+$, 1010 (6) [*M*−2CO]$^+$, 982 (10) [*M*−3CO]$^+$, 954 (4) [*M*−4CO]$^+$, 842 (71) [*M*−Mo(CO)$_4$CH$_3$]$^+$, 782 (29) [C$_{28}$H$_4$F$_{20}$P$_2$]$^+$, 493 (46) [*M*−Mo(CO)$_4$P(C$_6$F$_5$)$_2$]$^+$, 435 (100) [C$_{16}$H$_6$F$_{10}$OP]$^+$, 365 (17) [P(C$_6$F$_5$)$_2$]$^+$; elemental analysis calcd (%): C 37.02, H 0.91; found: C 37.20, H 0.97.

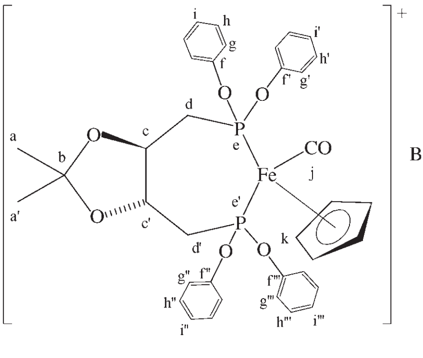
Attempted synthesis of tetracarbonyl{1,4-dideoxy-1,4-bis[bis(*p*-tetrafluoropyridin-4-yl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol-*P*,*P'*}molybdenum (8a): 1,4-Dideoxy-1,4-bis[bis(*p*-tetrafluorpyridiyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol, **7** (0.20 g, 0.25 mmol) and [Mo(CO)$_4$(nbd)] (0.08 g, 0.27 mmol) were dissolved in 10 mL of CH$_2$Cl$_2$. After stirring for 48 h at RT a portion of [Mo(CO)$_4$(nbd)] (0.10 g, 0.33 mmol) was added and the mixture was stirred for an additional 8 h. The reaction mixture was evaporated in vacuo and the residue was extracted with hexane. The residue of the evaporated hexane solution was investigated by infrared and NMR spectroscopy. Resonances at 10.3 and 6.6 ppm in the ^{31}P NMR spectrum indicated the possible formation of a dinuclear [Mo(CO)$_5$] complex **8a'** and a mononuclear [Mo(CO)$_4$] derivative **8a**, respectively. The highest CO infrared valence modes of these compounds were observed at 2084 and 2047 cm^{-1}, respectively. A separation of these compounds by silica gel column chromatography was not successful.

Carbonyl(η^5-cyclopentadienyl){1,4-dideoxy-1,4-bis(dimethoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol-*P*,*P'*}iron(II)tetrafluoroborate (6b): 1,4-Dideoxy-1,4-bis(dimethoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol, **6** (0.21 g, 0.67 mmol), [Fe(η^5-C$_5$H$_5$)$_2$][BF$_4$] (0.18 g, 0.66 mmol), and [{Fe(η^5-C$_5$H$_5$)(CO)$_2$}$_2$] (0.12 g, 0.34 mmol) were dissolved in 20 mL CH$_2$Cl$_2$ and the mixture was stirred for 8 h at RT. The evaporated residue was purified by silica gel column chromatography: 1) ethyl acetate/hexane 1:20; 2) CH$_2$Cl$_2$; 3) acetone. Evaporation of the acetone fraction and recrystallization from CH$_2$Cl$_2$/Et$_2$O yielded 0.13 g (0.24 mmol, 36 % with respect to **6**) of **6b** as a bright-yellow solid.



^{1}H NMR (CDCl$_3$, RT): $\delta=1.4$ (s, 6H$^{a,a'}$), 2.2–3.2 (m, 4H$^{d,d'}$), 3.6 (s, 6H$^{f,f',f'',f'''}$), 4.1 (br s), 2H$^{c,c'}$), 5.1 ppm (br s, 5H^k); ^{13}C{^{1}H} NMR (CDCl$_3$, RT): $\delta=23.1$ (s, C$^{a,a'}$), 35.5 (m, C^d), 37.3 (m, C$^{d'}$), 50.4 (m, C$^{f,f',f'',f'''}$), 73.1 (m, C^c), 73.2 (m, C$^{c'}$), 104.9 ppm (s, C^b); ^{19}F NMR (CDCl$_3$, RT): $\delta=-152.1$ ppm (s, BF$_4$); ^{31}P{^{1}H} NMR (CDCl$_3$, RT): $\delta=206.5$ (AB spin system, P^e), 207.4 ppm (AB spin system, ^2J(P^e,P$^{e'}$) = 86 Hz; P$^{e'}$); IR (KBr pellet): $\tilde{\nu}=2122$ (vw), 2986 (vw), 2954 (w), 1987 (s; CO), 1637 (vw), 1459 (w), 1375 (w), 1248 (m), 1165 (sh), 1083 (vs), 1014 (vs), 884 (m), 828 (m), 799 (m), 752 (m), 558 cm^{-1} (m); ESI-MS (positive mode, MeOH/CH$_2$Cl$_2$): *m*/*z* (%): 463 (100) [*M*−BF$_4$]$^+$; elemental analysis calcd (%): C 37.19, H 5.14; found: C 36.94, H 4.89.

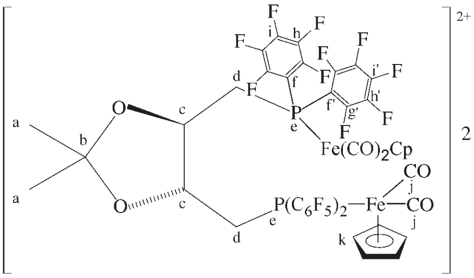
Carbonyl(η^5-cyclopentadienyl){1,4-dideoxy-1,4-bis(diphenoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol-*P*,*P'*}iron(II)tetrafluoroborate (5b): 1,4-Dideoxy-1,4-bis(diphenoxyphosphanyl)-2,3-*O*-isopropyliden-L-threitol, **5** (0.38 g, 0.68 mmol), [Fe(η^5-C$_5$H$_5$)$_2$][BF$_4$] (0.19 g, 0.70 mmol), and [{Fe(η^5-C$_5$H$_5$)(CO)$_2$}$_2$] (0.12 g, 0.34 mmol) were dissolved in 20 mL of CH$_2$Cl$_2$ and stirred for 8 h at RT. The evaporated residue was purified under a nitro-



gen atmosphere by silica gel column chromatography: 1) ethyl acetate/hexane 1:20; 2) CH_2Cl_2; 3) acetone. Evaporation of the acetone fraction and recrystallization from CH_2Cl/Et_2O yielded 0.31 g (0.39 mmol, 57 % with respect to **5**) of **5b** as a colorless solid (m.p. (decomp) 180 °C).

^{1}H NMR ($CDCl_3$, RT): $\delta = 1.1$ (s, $6H^a$), 1.4 (s, $6H^{a'}$), 2.4–4.3 (m, $6H^{c,c',d,d'}$), 4.8 (s, $5H^k$), 7.3 ppm (m, $10H^{g-i,g'-i',g''-i'',g'''-i'''}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): $\delta = 26.9$ (s, C^a), 27.1 (s, $C^{a'}$), 40.4–43.5 (m, $C^{d,d'}$), 73.0–76.0 (s, $C^{c,c'}$), 86.0 (s, C^k), 109.5 (s, C^b), 120.4 (s, C^g), 120.9 (s, $C^{g'}$), 121.3 (s, $C^{g''}$), 121.5 (s, $C^{g'''}$), 126.1–126.4 (m, $Ci^{i',i'',i'''}$), 130.9–131.1 (m, $C^{h,h',h'',h'''}$), 152.0 (m, $C^{f,f',f'',f'''}$), 212.9 ppm (t, $^2J(C,P) = 32$ Hz; C^j); ^{19}F NMR ($CDCl_3$, RT): $\delta = -151.7$ ppm (s, BF_4); $^{31}P\{^1H\}$ NMR ($CDCl_3$, RT): $\delta = 207.9$ ppm (s, $P^{e,e'}$); IR (KBr pellet): $\tilde{\nu} = 2984$ (w), 2932 (w), 2066 (vw), 1998 (vs; CO), 1590 (s), 1487 (vs), 1456 (w), 1422 (vw), 1375 (m), 1189 (s), 1163 (s), 1883 (vs), 1058 (vs), 916 (vs), 900 (vs), 784 (m), 761 (s), 728 (w), 692 (m), 616 (w), 582 (m), 564 cm^{-1} (m); ESI-MS (positive mode, $MeOH/CH_2Cl_2$): m/z (%): 1003 (100) $[M+FeCp(CO)_3]^+$, 739 (46) $[M+CO-BF_4]^+$, 711 (58) $[M-BF_4]^+$, 683 (8) $[M-BF_4CO]^+$; elemental analysis calcd (%): C 56.67, H 4.67; found: C 56.15, H 4.67.

μ-{1,4-Dideoxy-1,4-bis[bis(pentafluorophenyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol-1κ*P*:2κ*P'*}bis[dicarbonyl(η⁵-cyclopentadienyl)iron]bis(tetrafluoroborate) (7b'): 1,4-Dideoxy-1,4-bis(pentafluorophenyl)-2,3-*O*-isopropyliden-L-threitol, **7** (0.27 g, 0.31 mmol), $[Fe(\eta^5\text{-}C_5H_5)_2][BF_4]$ (0.22 g, 0.81 mmol), and $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ (0.14 g, 0.40 mmol) were dissolved in 20 mL of CH_2Cl_2 and the mixture was stirred for 8 h at RT. The evaporated residue was purified under a nitrogen atmosphere by silica gel column chromatography: 1) hexane; 2) CH_2Cl_2; 3) CH_2Cl_2/acetone 1:1. Evaporation of the CH_2Cl_2/acetone fraction and recrystallization from CH_2Cl_2/Et_2O yielded 0.14 g (0.10 mmol, 32 % with respect to **7**) of **7b'** as a colorless solid (m.p. (decomp) 180 °C).



^{1}H NMR ($CDCl_3$, RT): $\delta = 1.2$ (s, $6H^a$), 3.3–3.9 (m, $4H^d$), 4.4 (m, $2H^c$), 5.7 ppm (s, $10H^k$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, RT): $\delta = 26.8$ (s, C^a), 35.5–36.0 (m, C^d), 78.1–78.4 (m, C^c), 90.6 (s, C^k), 112.7 (s, C^b), 109 (m, $C^{f,f'}$), 136–150 (m, $C^{g-i,g'-i'}$), 209.2 ppm (pseudo-t, $^2J(C,P) = 20$ Hz; $C^{j,j'}$); ^{19}F NMR ($CDCl_3$, RT): $\delta = -129.2$ (m, $8F^{g,g'}$), -145.4 (m, $2F^i$), -146.8 (m, $2F^{i'}$), -158.2 (m, $4F^h$), -158.4 (m, $4F^{h'}$), -149.7 ppm (s, $2BF_4$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, RT): $\delta = 48.3$ ppm (s); IR (KBr pellet): $\tilde{\nu} = 3122$ (vw), 2989 (vw), 2939 (vw), 2074 (s; CO), 2032 (s; CO), 1645 (m), 1525 (s), 1476 (vs), 1429 (vw), 1388 (m), 1297 (w), 1240 (vw), 1097 (vs), 1060 (sh), 980 (s), 890 (vw), 600 (w), 572 (m), 549 cm^{-1} (m); ESI-MS (positive mode, $MeOH/CH_2Cl_2$): m/z (%): 1299 (100) $[M-BF_4]^+$, 1243 (52) $[M-BF_4(CO)_2]^+$, 1035 (96) $[M-FeCp(CO)_2BF_4]^+$, 976 (17) $[M-FeCp(CO)_4BF_4]^+$; elemental analysis calcd (%): C 39.00, H 1.60; found: C 38.71, H 1.53.

μ-{1,4-Dideoxy-1,4-bis[bis(*p*-tetrafluoropyridyl)phosphanyl]-2,3-*O*-isopropyliden-L-threitol-1κ*P*:2κ*P'*}bis[dicarbonyl(η⁵-cyclopentadienyl)iron]bis(tetrafluoroborate) (8b'): 1,4-Dideoxy-1,4-bis(*p*-tetrafluoropyridyl)-2,3-*O*-isopropyliden-L-threitol, **8** (0.30 g, 0.38 mmol), $[Fe(\eta^5\text{-}C_5H_5)_2][BF_4]$ (0.31 g, 1.14 mmol), and $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ (0.20 g, 0.57 mmol) were dissolved in 30 mL of CH_2Cl_2 and the mixture was stirred for 48 h at RT. The evaporated residue was purified under a nitrogen atmosphere by silica gel column chromatography: 1) ethyl acetate/hexane 1:20; 2) CH_2Cl_2; 3) acetone. As the evaporated acetone fraction still contained the free ligand **7**, the crude product was dissolved in CH_2Cl_2 treated with $[Fe(\eta^5\text{-}C_5H_5)_2][BF_4]$ (0.21 g, 0.77 mmol), and $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ (0.13 g, 0.37 mmol), and the mixture was stirred for one week at RT. After an additional separation by silica gel column chromatography the product (0.20 g) was contaminated with a BF_4 salt, as indicated in the ^{19}F NMR spectrum that exhibited a resonance for the BF_4 moiety that was too intense with respect to the intensities of the resonances for the C_6F_5 groups. ^{19}F NMR ($CDCl_3$, RT): $\delta = -87.0/-87.4$ (*ortho*-F, rel. int. 8.0), -127.0 (*meta*-F, rel. int. 7.9), -148.3 ppm (BF_4, rel. int. 55); ^{31}P NMR ($CDCl_3$, RT): $\delta = 52.5$ ppm; IR (KBr pellet): $\tilde{\nu} = 2977$ (m), 2877 (m), 2077 (s; CO), 2038 (s; CO), 1636 (m), 1457 (vs), 1385 (w), 1239 (s), 1084 (vs), 946 (m), 575 cm^{-1} (m); ESI-MS (positive mode, $MeOH/CH_2Cl_2$): m/z (%): 967 (100) $[M-FeCp(CO)_2BF_4]^+$, 911 (67) $[M-FeCp(CO)_4BF_4]^+$, 572 (54) $[M-(BF_4)_2]^{2+}$.

Single-crystal structure determination: Data collection for X-ray structure determination was performed by using a STOE IPDS II diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (71.073 pm). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data (X-Shape 2.01, Crystal Optimisation for Numerical Absorption Correction (C) 2001 Stoe & Cie GmbH, Darmstadt). The programs used in this work are the Stoe X-Area (X-Area 1.16, Stoe & Cie GmbH, Darmstadt, 2003), including X-RED and X-Shape for data reduction and numerical absorption correction (X-RED32 1.03, Stoe Data Reduction Program (C), 2002, Stoe & Cie GmbH, Darmstadt), and X-Step32 program (X-STEP32 1.06f, 2000, Stoe & Cie GmbH, Darmstadt), including SHELXS-97 (G. M. Sheldrick, SHELXS-97, University of Göttingen, **1998**) and SHELXL-97 (G. M. Sheldrick, SHELXL-97, University of Göttingen, **1997**) for structure solution and refinement. All hydrogen atoms were placed in idealized positions and constrained to ride on the coordinates of the previous atom. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Intensity data for $C_{37}H_{37}O_7P_2FeBF_4$ (798.27 $g\,mol^{-1}$) was collected at 170 K; colorless transparent plate, monoclinic space group C_2 (no. 5); $a = 2938.3(4)$ $b = 1024.2(1)$ $c = 2512.5(3)$ pm, $\beta = 100.63(1)°$, $V = 7.431\ nm^3$, $Z = 8$, $\rho_{calcd} = 1.427\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.560\ cm^{-1}$, $F(000) = 3296$, 43 613 reflections with $2.8 < 2\theta < 54.7°$, 16 381 independent reflections in structure solution and refinement for 937 parameters, Flack $x = 0.03(3)$, R_1 $[I \geq 2\sigma(I)] = 0.077$, wR_2 (all data) $= 0.110$, $w = 1/\{\sigma^2(F_0^2) + 0.0108(F_0^2 + 2F_c^2)/3]^2\}$.

CCDC 608264 contains the supplementary crystallographic data for this paper (compound **6**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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