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Synthesis of the First Chiral Bidendate Bis(trifluoromethyl)phosphane Ligand through Stabilization of the Bis(trifluoromethyl)phosphanide Anion in the Presence of Acetone

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Dedicated to Professor Karl Otto Christe on the occasion of his 70th birthday

Abstract: Lewis acid/Lewis base adduct formation of the $P(CF_3)_2^-$ ion and acetone leads to a reduced negative hyperconjugation and, therefore, limits the C–F bond activation. The resulting increased thermal stability of the $P(CF_3)_2^-$ ion in the presence of acetone allows selective substitutions and enables the synthesis of the first example of a chiral, bidentate bis(trifluoromethyl)phosphane ligand: a DIOP derivative, [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphane), in which the phenyl groups at the phosphorus atoms are replaced by strong electron-withdrawing trifluoromethyl groups. The resulting high electron-acceptor strength of the synthesized bidentate $(CF_3)_2P$ ligand is demonstrated by a structural and vibrational study of the corresponding tetracarbonyl–molybdenum complex. The stabilization of the $P(CF_3)_2^-$ ion in the presence of acetone is based on the formation of a dynamic Lewis acid/Lewis base couple, $(CF_3)_2PC(CH_3)_2O^-$. Although there is no spectroscopic evidence for the formation of the formulated alcoholate ion, the intermediate formation of $(CF_3)_2PC(CH_3)_2O^-$ could be proved through the reaction with $(CF_3)_2PP(CF_3)_2$, which yields the novel phosphane–phosphinite ligand $(CF_3)_2PC(CH_3)_2OP(CF_3)_2$. This ligand readily forms square-planar Pt(II) complexes upon treatment with solid $PtCl_2$.

Keywords: chirality • diphosphanes • Lewis acids • Lewis bases • phosphorus

Introduction

The catalytic activity of a chiral phosphane ligand containing transition-metal complexes is strongly influenced by the electronic and steric properties of the substituents on the phosphorus atom. Because Lewis acids play a key role as catalysts in organic synthesis, electron-poor phosphane ligands that contain electron-withdrawing groups at the phosphorus atoms are of considerable interest.[1] For example, Kündig and co-workers successfully used chiral bidentate bis(pentafluorophenyl)phosphinite ligands to create weak iron- and ruthenium-containing Lewis acids to activate enals and effectively catalyze their asymmetric Diels–Alder reactions with dienes and 1,3-dipolar cycloaddition reactions with nitrones.[2] In addition, electron-poor phosphane ligands (partly fluorinated BINAP derivatives) were shown, in some cases, to be more efficient in asymmetric hydrogenations than their nonfluorinated counterparts.[3]

The influence of electron-poor phosphane ligands is described by using the nonsymmetric diphosphane complexes $[M(Cl)_2Ph_2PCH_2CH_2P(CF_3)_2]$ with M = Pd, Pt as examples.[4] Due to the strong π acidity of the CF_3-substituted phosphorus atom and the resulting strong π-backbonding contribution, the phosphorus–metal distances are shortened by 6 and 7 pm, respectively, relative to the corresponding distance between the metal and the nonfluorinated diphenyl-substituted phosphorus atom (see Figure 1).

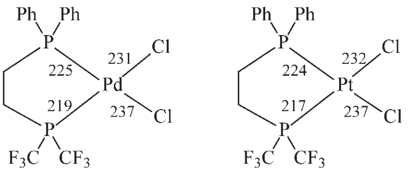

Figure 1. Bond lengths (pm) of $[M(Cl)_2Ph_2PCH_2CH_2P(CF_3)_2]$ (M = Pd, Pt).[4]

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The weak σ basicity of trifluoromethyl-substituted phosphanes[5] causes these ligands to exhibit a lower *trans* effect than the nonfluorinated phosphane derivatives. This results in a shortening of the Pt−Cl bond *trans* to the trifluoromethyl-substituted phosphorus atom of around 6 pm relative to the Pt−Cl bond *trans*-coordinated with respect to the Ph_2P moiety.

This special bonding situation is brought about by electronic contributions rather than by steric effects. Although CF_3 groups are smaller than phenyl groups, the steric shielding of a transition metal by the coordination of a $(CF_3)_2P$ unit is nearly identical to that afforded by a Ph_2P unit, as demonstrated in the Tolman concept.[6] The cone angles of the bis(trifluoromethyl) derivatives $HP(CF_3)_2$ and $CH_3P(CF_3)_2$, 120 and 131°, respectively, are close to those of the diphenyl derivatives $HPPh_2$ and CH_3PPh_2, 126 and 136°, respectively. Considering the comparable steric shielding of a transition metal by the coordination of either a $(CF_3)_2P$ or Ph_2P unit and the special bonding situation of trifluoromethyl-substituted phosphane ligands mentioned above, chiral bis(trifluoromethyl)phosphane ligands should exhibit special features in asymmetric catalysis. However, no example of a chiral bidentate bis(perfluoroorganyl)phosphane derivative has been reported so far.

Here, we report the stabilization of the $P(CF_3)_2^-$ ion in the presence of acetone, which allows the successful synthesis of the first example of a bidentate bis(trifluoromethyl)phosphane ligand: a DIOP derivative, [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphane), in which the phenyl groups at the phosphorus atoms are replaced by strong electron-withdrawing trifluoromethyl groups. The strong π acidity of the bidentate ligand is demonstrated by structural and vibrational analysis of the corresponding tetracarbonyl–molybdenum complex.

Results and Discussion

Chiral bidentate phosphane ligands, such as DIOP, are most frequently synthesized through a nucleophilic displacement reaction involving diphenylphosphanide ions [Eq. (1)]:[7]

X = I (**1a**), OTos (**1b**) DIOP (1)

With the aim of synthesizing the analogue bidentate bis(trifluoromethyl)phosphane derivative, we investigated the use of $P(CF_3)_2^-$ ions in nucleophilic displacement reactions.[8] Due to the strong negative hyperconjugation of the $P(CF_3)_2^-$ ion and the resulting C−F bond activation, the use of $P(CF_3)_2^-$ salts in nucleophilic displacement reactions effects an increased formation of byproducts. To generate a selective nucleophilic $P(CF_3)_2^-$ synthon, it is of considerable interest to lower the negative hyperconjugation. This special bonding situation can be described by the Kohn–Sham HOMO and HOMO-1 of the $P(CF_3)_2^-$ ion, depicted in Figure 2.

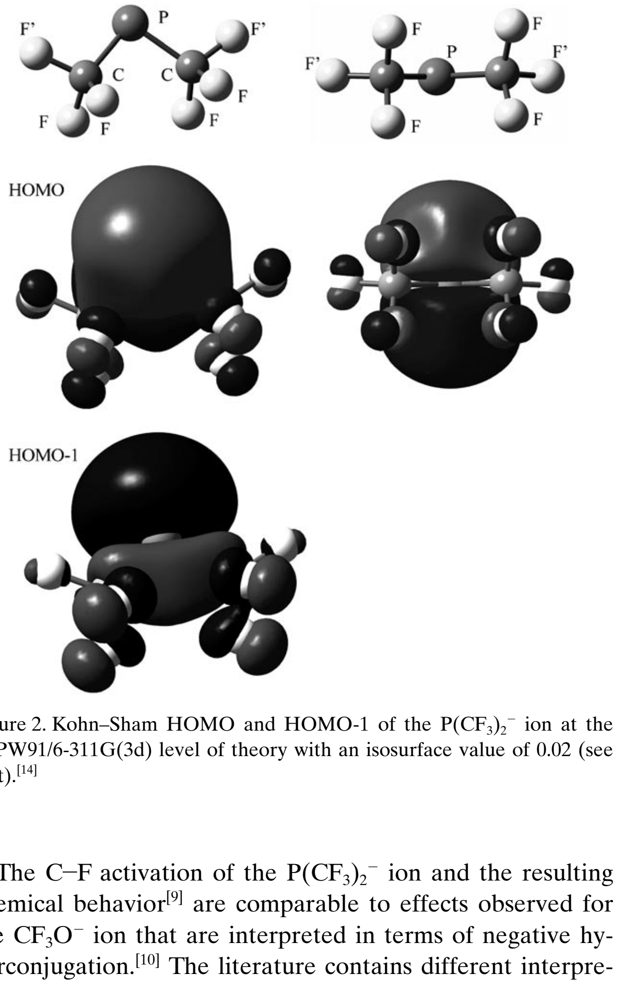


Figure 2. Kohn–Sham HOMO and HOMO-1 of the $P(CF_3)_2^-$ ion at the B3PW91/6-311G(3d) level of theory with an isosurface value of 0.02 (see text).[14]

The C−F activation of the $P(CF_3)_2^-$ ion and the resulting chemical behavior[9] are comparable to effects observed for the CF_3O^- ion that are interpreted in terms of negative hyperconjugation.[10] The literature contains different interpretations of hyperconjugation.[11,12] The term hyperconjugation was originally employed to denote σ→π* delocalization, whereas a partial delocalization of π-electron density into an adjoining σ* orbital is defined as a negative hyperconjugation.[13] The symmetry designations σ and π are used in a local sense to denote the symmetry of a localized bond or lone-pair orbital with respect to a local two-center bond axis within a polyatomic molecule. Both types of hyperconjugation act to build π-bond character into bonds that nominally have only σ character, at the expense of weakening adjoining π(σ) bonds through the population of σ*(π*) orbitals, respectively.[13] Figure 2 depicts two views of the Kohn–Sham HOMO of the $P(CF_3)_2^-$ ion. The interaction of the π density along the C-P-C plane with the orbital spheres concentrated at the fluorine atoms above and below the C-P-C plane fulfils, in principle, the terms of a negative hyperconjugation. In contrast, the interaction of the π density with the orbital spheres at the fluorine atoms close to the C-P-C plane (F′ in Figure 2) is best described by a π(PC)→π*(CF) interaction. The HOMO-1 isosurface, shown at the bottom of Figure 2, might be interpreted in terms of a hyperconjugation: $\sigma(\mathrm{PC})\rightarrow\pi^*(\mathrm{CF})$ delocalization.

As described earlier, the negative hyperconjugation of the $P(CF_3)_2^-$ ion[9] can be reduced by the addition of weak non-fluorophilic Lewis acids, such as CS_2,[15] or Hg^{2+} and Ag^+ ions.[16] The reduced negative hyperconjugation is accompanied by an increased thermal stability of the $P(CF_3)_2^-$ ion in solution, which is based on the formation of dynamic Lewis acid/Lewis base ($P(CF_3)_2^-$) adducts [Eq. (2)]:

$$P(CF_3)_2^- + LA \rightleftharpoons [(CF_3)_2P{-}LA]^- \qquad (2)$$

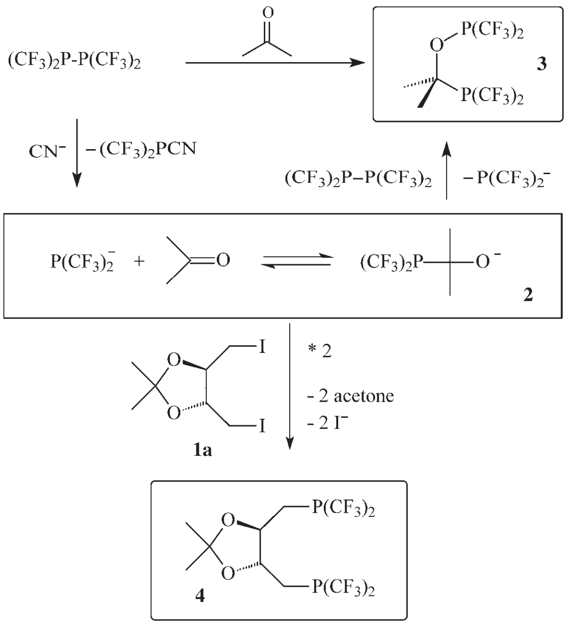
in which LA = Lewis acid, Hg^{2+}, Ag^+, CS_2, or acetone.

The decreased negative hyperconjugation and, therefore, reduced C–F bond activation of the dynamic Lewis acid/Lewis base adducts permits selective nucleophilic displacement reactions. However, the reduced electron density at the phosphorus atom is accompanied by a reduced nucleophilicity of these dynamic adducts. This explains why we were unsuccessful so far in using these systems in Equation (2) for the synthesis of chiral compounds.

A very weak Lewis acid that is able to increase the decomposition temperature of the $P(CF_3)_2^-$ ion in solution from −30 °C up to 0 °C is acetone. Following addition of CS_2 to a solution containing the $P(CF_3)_2^-$ ion in THF or CH_2Cl_2, adduct formation can be monitored by multinuclear NMR spectroscopy. In contrast, the addition of acetone to a solution containing the $P(CF_3)_2^-$ ion gives no significant change in the NMR spectra. These findings imply that if LA = acetone, the reaction shown in Equation (2) will shift towards the left.

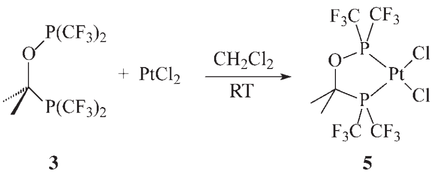
However, evidence for the intermediate formation of the Lewis acid/Lewis base adduct $(CF_3)_2P{-}C(CH_3)_2{-}O^-$, **2**, is given by the addition of $(CF_3)_2P{-}P(CF_3)_2$ to a solution of $[K([18]crown\text{-}6)]P(CF_3)_2$ in acetone. The dynamic alcoholate ion $(CF_3)_2P{-}C(CH_3)_2{-}O^-$ causes a nucleophilic cleavage of the phosphorus–phosphorus bond of $(CF_3)_2P{-}P(CF_3)_2$, leading to the novel compound $(CF_3)_2P{-}C(CH_3)_2{-}O{-}P(CF_3)_2$, **3**, and the regeneration of a $P(CF_3)_2^-$ ion. Due to the regeneration of the $P(CF_3)_2^-$ ion, this reaction sequence may be considered to be a base-catalyzed addition of $(CF_3)_2P{-}P(CF_3)_2$ to the carbonyl function of acetone (Scheme 1). Besides the $P(CF_3)_2^-$ ion, other nucleophiles, such as cyanides or pyridine, are also suitable to initiate the addition. Upon using [K([18]crown-6)]CN for the initiation step (Scheme 1), $(CF_3)_2PCN$ is formed upon the nucleophilic cleavage of $(CF_3)_2P{-}P(CF_3)_2$ and can be characterized by ^{19}F and ^{31}P NMR spectroscopy (^{19}F NMR: $\delta = -50.8$ ppm (d); ^{31}P NMR: $\delta = -41.4$ ppm (sept), $^2J(P,F) = 80.7$ Hz).

The thermally unstable, neat, colorless liquid $(CF_3)_2P{-}C(CH_3)_2{-}O{-}P(CF_3)_2$, **3**, is obtained in 75 % yield after fractional condensation of a reaction mixture of [K([18]crown-6)]CN in acetone with excess of $(CF_3)_2P{-}P(CF_3)_2$. The proton-decoupled ^{31}P NMR spectrum of the purified product exhibits two phosphorus resonances, one at 79.2 ppm for the oxygen-bonded phosphorus atom and one at 23.3 ppm for the phosphorus atom connected through a carbon atom. Each resonance exhibits a characteristic septet of doublet splitting. The septet splitting is caused by $^2J(P,F)$ couplings of 87 and 73 Hz, respectively, and the doublet splitting is caused by a $^3J(P,P)$ coupling of 5 Hz. Although the neat product slowly decomposes at room temperature to a mixture that was not further analyzed, diluted acetone or CH_2Cl_2 solutions can be stored for several weeks at room temperature in an inert gas atmosphere.



Scheme 1. Stabilization of the $P(CF_3)_2^-$ ion in the presence of acetone (cation: [K([18]crown-6)]).

Treatment of a CH_2Cl_2 solution of $(CF_3)_2PC(CH_3)_2OP(CF_3)_2$ with an excess of solid $PtCl_2$ yields selectively the corresponding Pt^{II} complex **5**:



(3)

The Pt^{II} complex was characterized through the mass balance of the reaction, mass spectrometry (characteristic isotopic pattern), and multinuclear NMR spectroscopy. Figure 3 shows the proton-decoupled ^{31}P NMR spectrum of the Pt^{II} complex. The phosphorus resonances, each exhibiting a doublet of septets pattern, are surrounded by ^{195}Pt satellites. Both resonances are deshielded, in contrast to the resonances of the free ligand. Upon coordination to the platinum center the value of the phosphorus–phosphorus coupling constant is increased from 5 to 13 Hz.

Although $P(CF_3)_2^-$ salts are principally useful reagents in nucleophilic substitutions of alkyl tosylates,[9] we were unable to substitute tosyl groups (OTos) in the less-reactive

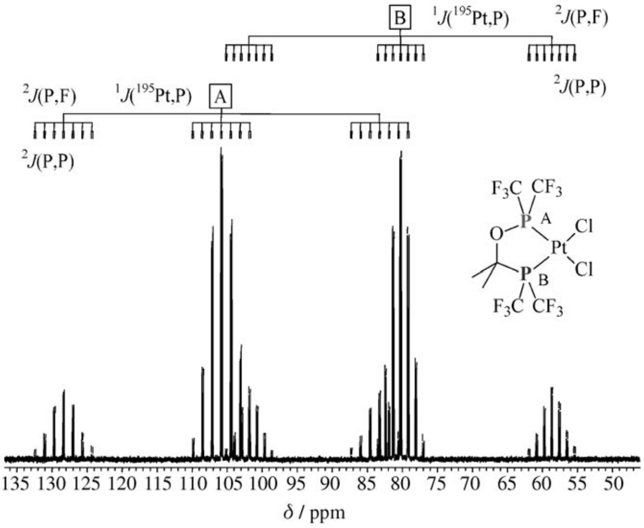
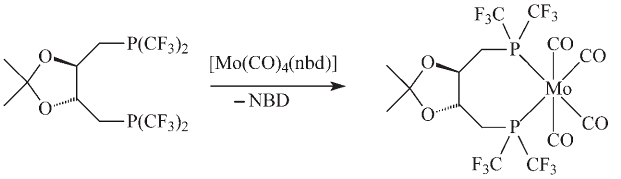


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of the Pt^{II} complex **5**.

chiral derivative **1b** upon treatment with $P(CF_3)_2^-$ salts, even in the presence of acetone.

In contrast, the diiodo derivative **1a** could be transformed into the corresponding bidentate bis(trifluoromethyl)phosphane derivative upon treatment with an excess of $[K([18]crown-6)]P(CF_3)_2$ in the presence of acetone. The exchange was complete within 72 h at −20 °C. After evaporation of all volatiles and extraction of the residue with hexane, a colorless oil was obtained that was contaminated with free crown ether. To separate the crown ether, the crude product was dissolved in an acetone solution of NaI to trap the crown ether as a sodium complex. After evaporation and extraction of the residue with hexane, the bidentate $P(CF_3)_2$ derivative **4** was obtained as a colorless oil in 53 % yield. The product was characterized by elemental analysis, mass spectrometry, and multinuclear NMR spectroscopy (Figure 4).

To investigate the coordination properties of the ligand **4**, the tetracarbonyl–molybdenum complex was synthesized through treatment of a solution of **4** in CH_2Cl_2 with an excess of $[Mo(CO)_4(nbd)]$ (NBD = norbornadiene) [Eq. (4)]. Mass spectrometric investigation of the selectively formed complex enabled detection of the molecular peak with its characteristic isotopic pattern that is in excellent agreement with calculated data. Due to the coordination of the chiral ligand to the $Mo(CO)_4$ moiety, the chemical difference between the two CF_3 groups attached at each phosphorus atom could be resolved in the ^{19}F NMR experiment. The two resonances at −59.1 and −61.5 ppm both exhibit a doublet of quartets splitting. The doublet splittings are caused by $^2J(P,F)$ couplings of 72.3 and 74.5 Hz, respectively, whereas the quartet splitting of 7.6 Hz is the result of the $^4J(F,F)$ coupling between the two chemically different CF_3 groups. The ^{31}P NMR resonance at 65.0 ppm exhibits a complex higher-order splitting, as shown in Figure 5. The observed resonance is in good agreement with a calculated $AA'X_6Y_6$ spin system ($A,A' = {}^{31}P$; $X,Y = {}^{19}F$).



(4)

4 **6**

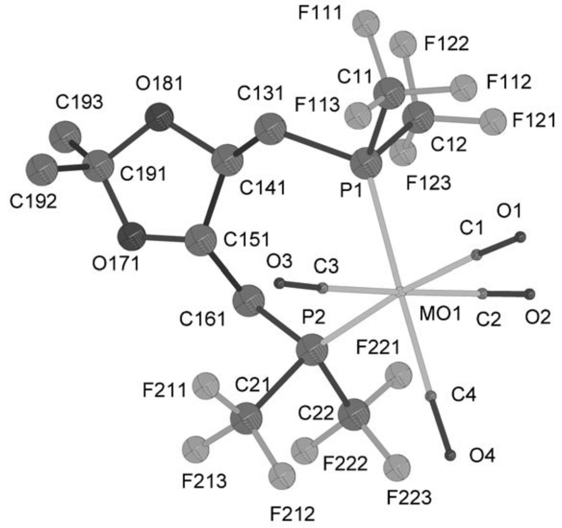


Figure 4. Simplified molecular structure and atom-numbering scheme of one of the two symmetry-independent molecules of the chiral molybdenum complex **6**. Selected bond lengths (pm): Mo1−P1 242.9(2), Mo1−P2 242.6(2), Mo2−P3 243.1(2), Mo2−P4 243.8(2), Mo1−C1 200.2(8), Mo1−C4 201.5(8), Mo1−C3 203.5(9), Mo1−C2 204.3(9), C1−O1 116.5(8), C2−O2 115.0(9), C3−O3 115.1(9), C4−O4 115.7(9), P1−C131 1.837(6), P1−C12 1.866(10), P1−C11 188.0(8), C11−F111 132.5(8), C11−F112 134.2(9), C11−F113 135(1), C12−F122 133.8(9), C12−F123 134(1), C12−F121 134.2(8).

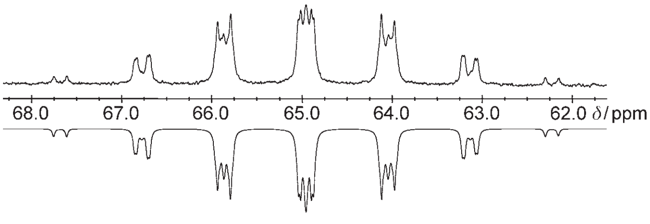


Figure 5. Experimental (top) and calculated (bottom) ^{31}P NMR spectrum of the chiral molybdenum complex **6**.

The molybdenum complex **6** crystallizes in the chiral orthorhombic space group $P2_12_12_1$ with two molecules in the asymmetric unit.[17] The molecular structure of one of the two symmetry-independent molecules is shown in Figure 4, and proves that the chiral information of the starting diiodo derivative (**1a**) is still present in the synthesized bis(trifluoromethyl)phosphane derivative **4**.

The strong π acidity of the chiral ligand **4** is demonstrated by the relatively short Mo–P distances (Figure 4) that are shortened by an average of 10 pm with respect to related nonfluorinated diarylphosphane derivatives.[18]

The high acceptor strength of the $P(CF_3)_2$ ligand is also supported by the highest infrared CO stretching mode of the tetracarbonyl–molybdenum complex **6** of 2073 cm^{-1}, which is shifted by more than 50 cm^{-1} to higher energy relative to an analogous bis(diphenylphosphino)ethylene complex, $[Mo(CO)_4Ph_2PCH_2CH_2PPh_2]$.[19] The observed infrared CO stretching frequency of the chiral complex is exceeded by only the trifluorophosphane derivative *cis*-$[Mo(CO)_4(PF_3)_2]$,[20] which has a value of 2087 cm^{-1}.

Conclusion

The reduced negative hyperconjugation that causes a reduced C−F activation of the $P(CF_3)_2^-$ ion in the presence of acetone allows the use of $P(CF_3)_2^-$ salts in selective nucleophilic displacement reactions. The increased thermal stability of the $P(CF_3)_2^-$ ion in the presence of acetone is based on the formation of a dynamic Lewis acid/Lewis base couple $(CF_3)_2PC(CH_3)_2O^-$. The intermediate formation of the alcoholate anion is supported by the base-catalyzed addition of $(CF_3)_2PP(CF_3)_2$ to the carbonyl group of acetone. The reaction sequence described represents the first example of a base-induced diphosphane addition to a carbonyl compound.

The stabilization of the $P(CF_3)_2^-$ ion in the presence of acetone is the key step in the synthesis of the first example of a chiral bidentate bis(perfluoroorganyl)phosphane derivative. The high electron-acceptor strength of the chiral bidentate $P(CF_3)_2$ ligand **4** could be demonstrated by structural and vibrational investigation of its tetracarbonyl–molybdenum complex **6**.

Experimental Section

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**.[21] Standard high-vacuum techniques were employed throughout all preparative procedures. Nonvolatile compounds were handled under a dry N_2 atmosphere by using Schlenk techniques.

Infrared spectra were recorded as KBr pellets by using a Nicolet-5PC-FTIR spectrometer. 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 Bruker Model AC200 spectrometers (^{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.[22] EI mass spectra were recorded by using a Finnigan MAT 95 spectrometer (20 eV). Intensities are referenced to the most intense peak of a group. Isotope patterns for comparison were calculated by using the program Isopro.[23] Melting and visible decomposition points were determined by using a HWS Mainz 2000 apparatus. C, H, and N analyses were carried out by using a HEKAtech Euro EA 3000 apparatus.

Syntheses

2-Bis(trifluoromethyl)phosphanyl-2-bis(trifluoromethyl)phosphinitopropane (3): A portion of tetrakis(trifluoromethyl)phosphane (2.54 g, 7.5 mmol) was condensed onto a mixture of [K([18]crown-6)]CN (170 mg, 0.5 mmol) and acetone (0.38 g, 6.5 mmol) at −196 °C. Upon slowly raising the temperature to RT the colorless suspension became a yellow solution. The volatile compounds were removed in dynamic vacuo by using −60 and −196 °C traps to separate the product from the excess of $(CF_3)_2PP(CF_3)_2$ and the formed $(CF_3)_2PCN$. After three steps of fractional condensation, the −60 °C trap contained 1.97 g (5.0 mmol, 77 %) of a colorless liquid identified as $(CF_3)_2PC(CH_3)_2OP(CF_3)_2$. The product could be stored for several months in sealed glass ampoules at −30 °C, exhibiting no sign of decomposition, but slowly decomposed at RT. ^{31}P NMR (acetone, RT): $\delta = 79.2$ (sept, d, $^{2}J(P,F) = 87$ Hz, $^{2}J(P,P) = 5$ Hz, $(CF_3)_2\mathit{P}O$), 23.3 ppm (sept, sept, d, $^{2}J(P,F) = 73$ Hz, $^{3}J(P,H) = 14$ Hz, $(CF_3)_2\mathit{P}$); ^{19}F NMR (acetone, RT): $\delta = -63.9$ (d, $(C\mathit{F}_3)_2PO$), −49.2 ppm (d, $(C\mathit{F}_3)_2P$); MS (EI, 20 eV): *m*/*z* (%): 396 (58) $[M]^+$, 227 (95) $[M-P(CF_3)_2]^+$, 211 (100) $[M-OP(CF_3)_2]^+$, 170 (24) $[HP(CF_3)_2]^+$, 98 (40) $[CH_3CH_2CF]^+$, 83 (45) $[CF_3CH_2]^+$, 69 (12) $[CF_3]^+$, 58 (36) $[(CH_3)_2CO]^+$, 43 (38) $[CH_3CO]^+$.

Dichloro[2-bis(trifluoromethyl)phosphanyl-2-bis(trifluoromethyl)phosphinitopropane]platinum (5): A solution of $(CF_3)_2PC(CH_3)_2OP(CF_3)_2$ (1.19 g, 3 mmol) dissolved in CH_2Cl_2 (5 mL) was treated with $PtCl_2$ (0.70 g, 2.6 mmol). The resulting brown solution was stirred for 24 h at RT and evaporated to dryness yielding 1.73 g (2.6 mmol, 99 %) of $[Pt(Cl)_2(CF_3)_2PC(CH_3)_2OP(CF_3)_2]$. ^{1}H NMR ($CDCl_3$, RT): 1.9 ppm (d); ^{31}P NMR ($CDCl_3$, RT): $\delta = 105.7$ (sept, d, $^{1}J(^{195}Pt,P) = 3653$ Hz, $^{2}J(P,F) = 109$ Hz, $^{2}J(P,P) = 15$ Hz, $(CF_3)_2\mathit{P}O$), 80.2 ppm (sept, sept, d, $^{1}J(^{195}Pt,P) = 3496$ Hz, $^{2}J(P,F) = 87$ Hz, $^{3}J(P,H) = 13$ Hz, $(CF_3)_2\mathit{P}$); ^{19}F NMR ($CDCl_3$, RT): $\delta = -60.9$ (d, $^{3}J(^{195}Pt,P) = 35$ Hz $(C\mathit{F}_3)_2PO$), −50.5 ppm (d, $^{3}J(^{195}Pt,P) = 39$ Hz, $(C\mathit{F}_3)_2P$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, RT): $\delta = 25.1$ ppm (br, $C(\mathit{C}H_3)_2O$); MS (EI, 20 eV): *m*/*z* (%): 662 (100) $[M]^+$, 627 (50) $[M-Cl]^+$, 604 (5) $[M-(CH_3)_2CO]^+$, 590 (18) $[M-Cl_2]^+$, 458 (25) $[M-(CF_3)_2PCl]^+$, 404 (11) $[PtCl_2CH_3COPCFCF_3]^+$, 331 (26) $[PtPFCF_3OH]$, 69 (14) $[CF_3]^+$, 43 (46) $[CH_3CO]^+$.

1,4-Dideoxy-1,4-bis[bis(trifluoromethyl)phosphanyl-2,3-*O*-isopropyliden-L-threitol (4): A solution of 1,4-dideoxy-1,4-diiodo-2,3-*O*-isopropyliden-L-threitol (0.95 g, 2.5 mmol) in acetone (20 mL) was added to a mixture of $[K([18]crown\text{-}6)]P(CF_3)_2$ (4.84 g, 10.2 mmol) and acetone (50 mL) at −78 °C. After stirring the reaction mixture for 72 h at −20 °C, all volatiles were removed in vacuum and the residue was extracted several times with hexane (200 mL). The evaporated oily residue of the hexane solution was dissolved in 30 mL of a saturated NaI solution in acetone to trap free [18]crown-6 as its sodium complex. All volatiles were removed in vacuum. Compound **4** was extracted from the residue again with hexane and was obtained in 43 % yield (0.61 g, 1.3 mmol) as a colorless oil after distilling off the solvent. ^{1}H NMR ($[D_6]$acetone, RT): $\delta = 1.6$ (s, 6 H), 2.6–3.1 (m, 2 H), 4.5 ppm (m, 4 H); ^{13}C NMR ($[D_6]$acetone, RT): $\delta = 129.7$ (q, d, q, $^{1}J(C,F) = 318$ Hz, $^{1}J(C,P) = 24$ Hz, $^{3}J(C,F) = 6$ Hz, $\mathit{C}F_3$), 77.9 (t, $^{3}J(C,P) = 11$ Hz, $\mathit{C}H$), 26.9 (s, $\mathit{C}H_3$), 22.8 ppm (d, sept, $^{1}J(C,P) = 14$ Hz, $^{3}J(CF) = 3$ Hz, $\mathit{C}H_2$); ^{31}P NMR ($[D_6]$acetone, RT): $\delta = 0.2$ ppm (sept, $^{2}J(P,F) = 69$ Hz); ^{19}F NMR ($[D_6]$acetone, RT): $\delta = -54.2$ ppm (d); MS (EI, 20 eV): *m*/*z* (%): 451 (100) $[M-CH_3]^+$, 409 (35) $[M-CH_3COCH_2]^+$, 397 (50) $[M-CF_3]^+$, 391 (16) $[M-(CH_3)_2CO_2H]^+$, 339 (25) $[M-(CH_3)_2COCF_3]^+$, 297 (13) $[M-P(CF_3)_2]^+$, 85 (42) $[(CH)_3O_2CH_2]^+$, 59 (8) $[(CH_3)_2CO]^+$, 43 (22) $[CH_3CO]^+$; elemental analysis calcd (%) for $C_{11}H_{12}F_{12}O_2P_2$: H 2.6, C 28.3; found: H 2.7, C 28.9.

Tetracarbonyl{1,4-dideoxy-1,4-bis[bis(trifluoromethyl)phosphanyl-2,3-*O*-isopropyliden-L-threitol}molybdenum (6): 1,4-Dideoxy-1,4-bis-[bis(trifluoromethyl)phosphanyl-2,3-*O*-isopropyliden-L-threitol (0.24 g, 0.5 mmol) dissolved in CH_2Cl_2 (20 mL) was added to $[Mo(CO)_4(nbd)]$ (0.14 g, 0.5 mmol) dissolved in CH_2Cl_2 (20 mL) at −78 °C. The reaction mixture was stirred for 5 days at 0 °C and evaporated to dryness yielding 0.16 g of a pale-yellow solid. The crude product was contaminated with $[Mo(CO)_4(nbd)]$. Single crystals were obtained by slow distillation of hexane onto a saturated solution of the crude product in diethyl ether. ^{31}P NMR ($CDCl_3$, RT): $\delta = 65.0$ ppm ($^{2}J(P,F) = 72.5$ Hz, $^{2}J(P,F') = 74.7$ Hz, $^{4}J(P,F) = 0.4$ Hz, $^{4}J(P,F') = 0.4$ Hz, see Figure 5 and text); ^{19}F NMR

($CDCl_3$, RT): $\delta = -59.1$ (d, q, ^4J(F,F′) = 7.6 Hz), −61.5 ppm (d, q); MS of the crude product (EI, 20 eV): m/z (%): 674 (100) $[M]^+$, 659 (35) $[M-CH_3]^+$, 646 (32) $[M-CO]^+$, 618 (10) $[M-(CO)_2]^+$, 577 (24) $[M-CF_3CO]^+$, 560 (5) $[M-(CO)_2(CH_3)_2CO]^+$, 532 (34) $[M-(CO)_3(CH_3)_2CO]^+$, 383 (57) $[M-(CO)_3(CF_3)_3]^+$, 355 (65) $[M-(CO)_4(CF_3)_3{}^+]$, 302 (10) $[Mo(CO)_4(nbd)]^+$, 274 (6) $[Mo(CO)_3(nbd)]^+$, 246 (7) $[Mo(CO)_2(nbd)]^+$, 218 (5) $[Mo(CO)(nbd)]^+$, 190 (23) $[Mo(nbd)]^+$.

CCDC 210560 contains the crystallographic data for the structure of 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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[1] *Handbook of Lewis Acids—Application in Organic Synthesis* (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, **2000**.

[2] V. Alezra, G. Bernardinelli, C. Corminboeuf, U. Frey, E. P. Kündig, A. E. Merbach, C. M. Saudan, F. Viton, J. Weber, *J. Am. Chem. Soc.* **2004**, *126*, 4843, and references therein.

[3] S. Jeulin, S. Duprat de Paule, V. Ratovelomananna-Vidal, J.-P. Genêt, N. Champion, P. Dellis, *Angew. Chem.* **2004**, *116*, 324; *Angew. Chem. Int. Ed.* **2004**, *43*, 320.

[4] L. Manojlovic-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, *J. Chem. Soc. Chem. Commun.* **1974**, 999; I. Macleod, L. Manojlovic-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, R. Walker, *J. Organomet. Chem.* **1975**, *97*, C7.

[5] J. Apel, J. Grobe, *Z. Anorg. Allg. Chem.* **1979**, *453*, 53.

[6] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313; A. L. Fernandez, M. R. Wilson, A. Prock, W. P. Giering, *Organometallics* **2001**, *20*, 3429.

[7] See, for example: Y. Yamonaoi, T. Imamoto, *Rev. Heteroat. Chem.* **1999**, *20*, 227; J. Christoffers, U. Rößler, *Tetrahedron: Asymmetry* **1999**, *10*, 1207; H. Brunner, A. Terfort, *Tetrahedron: Asymmetry* **1995**, *6*, 919; I. Tüth, E. Hanson, *Tetrahedron: Asymmetry* **1990**, *1*, 895; J. Bakos, I. Tüth, B. Heil, L. Markü, *J. Organomet. Chem.* **1985**, *279*, 23; J. M. Brown, B. A. Murrer, *J. Chem. Soc. Perkin Trans. 2* **1982**, 489; P. A. MacNeil, N. K. Roberts, B. Bosnich, *J. Am. Chem. Soc.* **1981**, *103*, 2273; J. Köttner, G. Greber, *Chem. Ber.* **1980**, *113*, 2323; D. P. Riley, R. E. Shumate, *J. Org. Chem.* **1980**, *45*, 5187; M. D. Fryzuk, B. Bosnich, *J. Am. Chem. Soc.* **1978**, *100*, 5491; M. D. Fryzuk, B. Bosnich, *J. Am. Chem. Soc.* **1977**, *99*, 6260.

[8] B. Hoge, C. Thösen, T. Herrmann, P. Panne, I. Pantenburg, *J. Fluorine Chem.* **2004**, *125*, 831, and references therein.

[9] B. Hoge, C. Thösen, *Inorg. Chem.* **2001**, *40*, 3113; B. Hoge, C. Thösen, T. Herrmann, I. Pantenburg, *Inorg. Chem.* **2003**, *42*, 3633.

[10] K. B. Wiberg, *J. Am. Chem. Soc.* **1990**, *112*, 3379; W. B. Farnham, B. E. Smart, W. J. Middleton, J. C. Calabrese, D. A. Dixon, *J. Am. Chem. Soc.* **1985**, *107*, 4565; J. S. Francisco, I. H. William, *Mol. Phys.* **1984**, *52*, 743; F. Grein, L. J. Lawlor, *Theor. Chim. Acta.* **1983**, *63*, 161; K. O. Christe, E. C. Curtis, C. J. Schack, *Spectrochim. Acta, Part A* **1975**, *31*, 1035.

[11] W. Kutzelnigg, *Einführung in die Theoretische Chemie, Band 2: Die chemische Bindung*, Wiley-VCH, Weinheim, **2001**.

[12] U. Salzner, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1993**, *115*, 10231.

[13] A. E. Reed, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434.

[14] Gaussian 98 (Revision A.9), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[15] B. Hoge, C. Thösen, T. Herrmann, I. Pantenburg, *Inorg. Chem.* **2002**, *41*, 2260.

[16] B. Hoge, C. Thösen, I. Pantenburg, *Inorg. Chem.* **2001**, *40*, 3084; B. Hoge, C. Thösen, T. Herrmann, A. Vij, *Inorg. Chem.* **2004**, *43*, 1659.

[17] 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 1.06, Crystal Optimisation for Numerical Absorption Correction (C), 1999, 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-RED 1.22, Stoe Data Reduction Program (C), 2001, STOE & Cie GmbH, Darmstadt), and the WinGX suite of programs (L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837), including SIR-92 (A. Altomare, G. Cascarano, C. Giacovazzo, *J. Appl. Crystallogr.* **1993**, *26*, 343) and SHELXL-97 (G. M. Sheldrick, SHELXL-97, Programs for Crystal Structure Analysis, University of Göttingen, Göttingen (Germany), **1997**) for structure solution and refinement. All hydrogen atoms were placed in idealized positions and were constrained to ride on their parent atom (U_{iso} (C(H)) = 490, ($C(H_2)$) = 340, ($C(H_3)$) = 1170 pm^2). 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 $C_{15}H_{12}F_{12}O_6P_2Mo$ (674.13 $g\,mol^{-1}$) were collected in 157 frames at 170 K; light-yellow transparent plate 0.45 × 0.20 × 0.05 mm^3, orthorhombic space group $P2_12_12_1$ (no. 19); $a = 1336.6(1)$, $b = 1859.6(1)$, $c = 1894.8(2)$ pm, $V = 4709.5(7)\times10^6$ pm^3, $Z = 8$, $\rho_{calcd} = 1.902$ $g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.818$ cm^{-1}, $F(000) = 2640$; 55759 reflections with $3.1 < 2\theta < 54.7°$, 10509 independent reflections in structure solution and refinement for 653 parameters, Flack $x = -0.02(4)$; R_1 $[I \geq 2\sigma(I)] = 0.0391$, wR_2 (all data) = 0.0678, $w = 1/\{\sigma^2(F_0^2) + [0.0179(F_0^2 + 2F_c^2)/3]^2\}$.

[18] K. Burgess, M. J. Ohlmeyer, K. H. Whitmire, *Organometallics* **1992**, *11*, 3588.

[19] J. Chatt, H. R. Watson, *J. Chem. Soc.* **1961**, 4980.

[20] G. R. Dobson, I. W. Stolz, R. K. Sheline, *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 1.

[21] S. P. Khanapure, N. Naajafi, S. Manna, J. Yang, J. Rokach, *J. Org. Chem.*, **1995**, *60*, 7548.

[22] P. H. M. Budzelaar, gNMR Version 4.1, Cherwell Scientific, Oxford, UK, **1998**.

[23] M. Senko, Isopro 3.0, Shareware, Sunnyvale, CA.

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