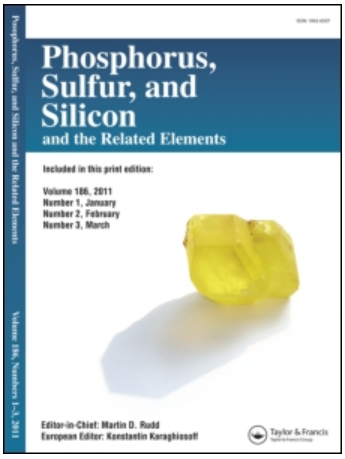

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The Bis(trifluoromethyl)phosphanide Anion and Novel Bis(trifluoromethyl)-phosphanido Complexes

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THE BIS(TRIFLUOROMETHYL)PHOSPHANIDE ANION AND NOVEL BIS(TRIFLUOROMETHYL)-PHOSPHANIDO COMPLEXES

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INTRODUCTION

Bidentate phosphane ligands play an important role in asymmetric catalysis. The bidentate phosphane ligands are most frequently synthesized reacting chiral ditosylates and diarylphosphanide anions. The extension of this procedure to the synthesis of bis(perfluoroorgano)phosphane chelate ligands requires nucleophilic $P(R_F)_2$ group transfer reagents. In 1972, J. Grobe and R. Demuth prepared mercury bis{bis(trifluoromethyl)phosphanide}, $Hg[P(CF_3)_2]_2$, by treatment of divinylmercury with bis(trifluoromethyl)phosphane, $HP(CF_3)_2$.[1] The new mercury compound was characterized solely by its ^{19}F NMR spectrum, and attempts to isolate the species were not successful. In a footnote, the authors mentioned that the reaction time decreased in the series $HgMe_2 > Hg(SMe)_2 > Hg(CH{=}CH_2)_2 > Hg(CN)_2$. Based on these results, we have investigated the reaction between cyanides and $HP(CF_3)_2$ with the aim to prepare a $P(CF_3)_2^-$ synthon.

RESULTS AND DISCUSSION

Treatment of $HP(CF_3)_2$ with $Hg(CN)_2$, suspended in THF or diglyme, gives HCN and $Hg(CN)P(CF_3)_2$ and $Hg[P(CF_3)_2]_2$, the relative amounts depending on the chosen stoichiometry:

$$Hg(CN)_2 + HP(CF_3)_2 \xrightarrow[-HCN]{-30^\circ C} Hg(CN)P(CF_3)_2 \xrightarrow[-HCN]{-30^\circ C} Hg[P(CF_3)_2]_2. \quad (1)$$

With an excess of $HP(CF_3)_2$, complete conversion to $Hg[P(CF_3)_2]_2$ is achieved. Upon warming to ambient temperature, this compound

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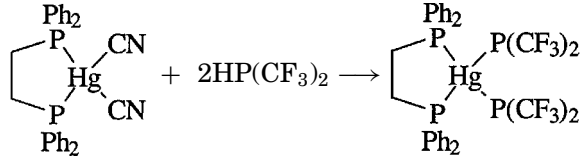
decomposes slowly, both in THF and in diglyme solution to elemental mercury and tetrakis(trifluoromethyl)diphosphane, $(CF_3)_2PP(CF_3)_2$. The rate of the thermal decomposition of $Hg[P(CF_3)_2]_2$ decreases with increasing donor strength of the solvent. This indicates that $Hg[P(CF_3)_2]_2$ is stabilized due to formation of 18 valence electron complexes, $[Hg\{P(CF_3)_2\}D_2]$. The intermediate formation of the rather instable mercurial is avoided by reacting phosphane adducts of $Hg(CN)_2$ with excessive $HP(CF_3)_2$. Thus, 1,2-bis(diphenylphosphanyl)ethanedicyanomercury, $[Hg(CN)_2(dppe)]$, was reacted at room temperature in CH_2Cl_2 with a slight excess of $HP(CF_3)_2$. After removal of the volatile compounds, the bis(trifluoromethyl)phosphanido complex $[Hg\{P(CF_3)_2\}_2(dppe)]$ is obtained as a white powder in almost quantitative yield:



(2)

In a preliminary study we have investigated the synthetic potential of the complexes $[Hg\{P(CF_3)_2\}_2(dppe)]$ and $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$, as well as that of the homoleptic compound $Hg[P(CF_3)_2]_2$ with respect to electrophilic substrates. While the halides in iodoalkanes or chlorodiphenylphosphane are readily replaced by the phosphanido group, no reaction with alkyl tosylates was observed.[2]

Salt-like compounds containing the $P(CF_3)_2^-$ anion are suggested to be most suitable $P(CF_3)_2$ group transfer reagents in S_N2 type reactions. The displacement of a weaker acid by a stronger acid during the reaction of $HP(CF_3)_2$ with KCN in DMF at $-50^\circ C$ leads to the formation of the $P(CF_3)_2^-$ anion, which is detected in low-temperature NMR experiments. Reaction mixtures containing $KP(CF_3)_2$ decompose rapidly above $-50^\circ C$. To increase the stability of the $P(CF_3)_2^-$ salts, a cation of lower Lewis acidity is needed:

$$[cat]CN + HP(CF_3)_2 \xrightarrow[-50^\circ C]{} HCN + [cat]^+[P(CF_3)_2]^-,$$
$$[cat] = [NEt_4], \quad [18\text{-C-6-K}]\ 100\%. \tag{3}$$

The neat phosphanides $[NEt_4]P(CF_3)_2$ and [18-crown-6-K]$P(CF_3)_2$ obtained by this procedure are stable up to $140^\circ C$.[3] The bis(trifluoromethyl)phosphanide ion, $P(CF_3)_2^-$,[3] decomposes slowly above $-30^\circ C$ in CH_2Cl_2 and THF solution. An increase of thermal stability of the $P(CF_3)_2^-$ moiety is observed if excess CS_2 is added, forming

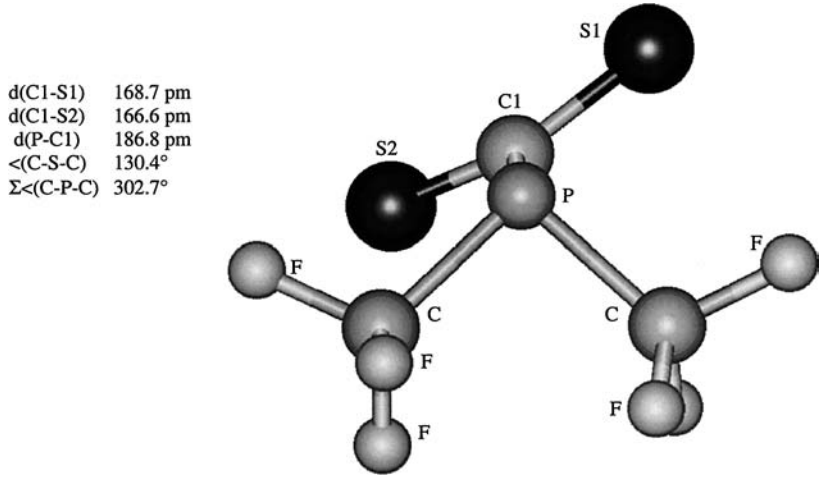


FIGURE 1 Geometry of the $[P(CF_3)_2CS_2]^-$ ion optimized at the B3PW91/6-311G′ level.

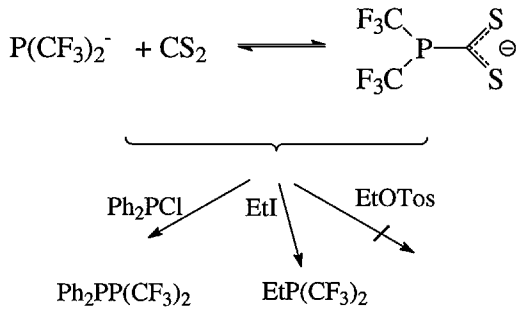
dark-red solutions. The $P(CF_3)_2^-$ moiety is stabilized due to a donor acceptor adduct formation:

$$[cat]P(CF_3)_2 + CS_2 \rightleftharpoons [cat][P(CF_3)_2CS_2],$$

$$[cat]^+ = [NEt_4]^+, \quad [18\text{-Crown-6-K}]^+. \tag{4}$$

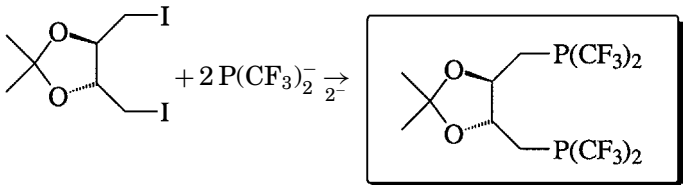
The CS_2 adduct is isolated in quantitatively yield and characterized by multinuclear NMR spectroscopy, elemental analysis, and vibrational spectroscopy. Reacting KCN and $HP(CF_3)_2$ in the presence of excess CS_2 allows the isolation of the potassium salt. The observed vibrational frequencies are in excellent agreement with calculated frequencies at the B3PW91/6-311G′ level of theory. The two rotation enantiomers, along the P—CS_2 bond (Figure 1), are of equal energy.

The increase of thermal stability in solution, adding CS_2, is accompanied by a reduced nucleophilicity of the $P(CF_3)_2^-$ moiety.



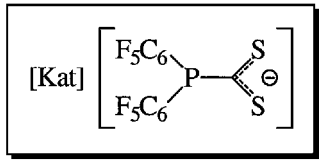
(5)

An increase in thermal stability without major decrease in nucleophilicity is observed in acetone and DMF solution. This allows nucleophilic displacement reactions with alkyl tosylates. Although there is no direct NMR spectroscopic evidence for the formation of a $P(CF_3)_2^-$ adduct with acetone or DMF, reaction with tetrakis(trifluoromethyl)diphosphane, $(CF_3)_2PP(CF_3)_2$, giving $(CF_3)_2PCMe_2OP(CF_3)_2$ proves the intermediate formation of an acetone adduct; however, attempts to substitute chiral tosylates failed so far. Substitution of the tosylate groups by iodine according to the Finkelstein procedure allows the following nucleophilic substitution by $P(CF_3)_2$ groups:



(6)

To synthesize salts of bis(pentafluorophenyl)phosphanide, bis(pentafluorophenyl)phosphane, $HP(C_6F_5)_2$, was treated with cyanide salts at low temperature. The thermally unstable $P(C_6F_5)_2^-$ ion decomposes even at $-78°C$ in CH_2Cl_2 or acetone solution giving polymeric material. Reaction in the presence of excess CS_2 allows the isolation of the thermally sensitive CS_2 adduct in a 70% yield.



(7)

$[Kat]^+ = [18\text{-crown-6-K}]^+$

The 18-crown-6-K salt crystallizes with one solvent molecule, CH_2Cl_2, in the monoclinic space group $P2_1/n$. The structure of the $[(C_6F_5)_2PCS_2]$ anion (Figure 2) is in excellent agreement with the theoretical model at the B3PW91 level of theory and corresponds to the structure of the $[Ph_2PCS_2]$ anion.[4]

The pure orange-red solid, as well as solutions with excess CS_2, decompose slowly upon warming to ambient temperature.

To synthesize bidentate bis(perfluoroorgano)phosphane–containing ligands, a new synthetic strategy is necessary which does not involve $P(R_F)_2^-$ ions. The use of functional phosphanides would result in a functional bis(phosphanyl) system which should be transferable into perfluoroorganyl systems. Dicyanophosphanide salts[5] react quantitatively

	x-ray	B3PW91 6311G'
d(C1-S1)	167.6	168.1 pm
d(C1-S2)	166.3	167.1 pm
d(P-C1)	186.9	186.2 pm
<(S-C-S)	129.3°	130.8°
Σ<(C-P-C)	311.1°	312.3°

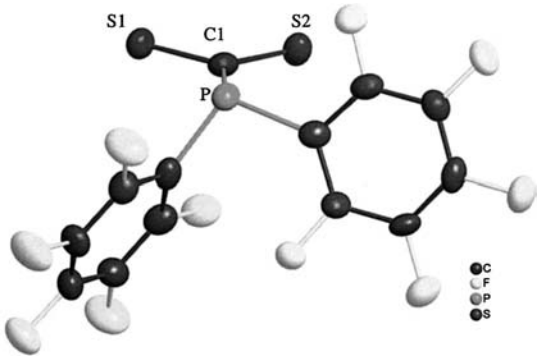
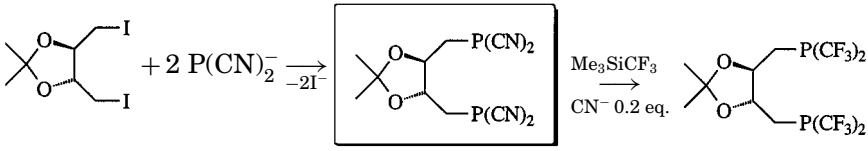


FIGURE 2 Perspective drawing of the $[(C_6F_5)_2PCS_2]$ anion in the compound [18-crown-6-K] $[(C_6F_5)_2PCS_2]{*}CH_2Cl_2$.

with alkyl tosylates to $RP(CN)_2$ derivatives which are transformed into $RP(CF_3)_2$ and $RP(C_6F_5)_2$ derivatives by a cyanide-initiated reaction with Me_3SiCF_3 and $Me_3SiC_6F_5$, respectively.[6]



(8)

The intermediately formed bis(dicyanophosphanyl) system leads after treatment with excess Me_3SiCF_3 and 0.2 eq. of [18-crown-6-K]CN to NMR and mass spectroscopic evidence for the formation of a comparable bis{bis(trifluoromethyl)phosphanyl} system. Investigations to isolate bis{bis(trifluoromethyl)phosphanyl} and bis{bis(pentafluorophenyl)phosphanyl} systems and their implementation in asymmetric catalysis are in progress.

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