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Synthesis and Properties of Mercury Bis(trifluoromethyl)phosphanides and Their Phosphane Complexes

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The thermally unstable compounds $Hg(CN)P(CF_3)_2$ and $Hg[P(CF_3)_2]_2$ were obtained by reactions of mercury cyanide and bis(trifluoromethyl)phosphane in solution and characterized by multinuclear NMR spectroscopy. An increase in thermal stability is observed when the products form 18 valence electron complexes. The compounds $[Hg\{P(CF_3)_2\}_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphanyl)ethane) and $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$ have been isolated in almost quantitative yield by reacting $[Hg(CN)_2(dppe)]$ or $[Hg(CN)_2(Me_3P)_2]$ with $HP(CF_3)_2$. $[Hg\{P(CF_3)_2\}_2(dppe)]$ crystallizes in the triclinic space group $P\bar{1}$. The mercury atom is coordinated in a distorted tetrahedral fashion. The Hg−P(CF$_3$)$_2$ bonds, ca. 250 pm, are significantly longer than those of the mercury bis(phosphanides) $Hg(PR_2)_2$ with R = *t*-Bu, 245 pm, or $SiMe_3$, 241 pm. These easily accessible compounds $[Hg\{P(CF_3)_2\}_2(dppe)]$ and $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$ act as nucleophilic bis(trifluoromethyl)phosphane group transfer reagents.

Introduction

Bidentate phosphane ligands play an important role in asymmetric catalysis.[1] The Lewis acid properties of metal catalysts are influenced by ancillary ligand effects, so the study of strongly electron-withdrawing phosphane ligands on potentially catalytic metal centers is of interest. Strong electron-withdrawing CF_3 groups, attached to the coordinating phosphorus atoms, will have a strong impact on the ligand properties, e.g. decreasing the σ donation ability while simultaneously increasing the π acidity of the phosphorus atom.

Chiral bidentate phosphane ligands are usually prepared from chiral tosylates and diarylphosphanides. For the synthesis of chiral bidentate 1,2-bis[bis(trifluoromethyl)phosphanyl]ethanes nucleophilic $P(CF_3)_2$ group transfer reagents are desirable. The sodium and cesium bis(trifluoromethyl)phosphanides have been characterized by NMR spectroscopy, but reaction with the solvent prevented their isolation.[2,3] In addition, these salts are thermally quite unstable. They decompose into perfluoro-2-phosphapropene and the corresponding metal fluoride.

$$M[P(CF_3)_2] \longrightarrow MF + F_2C{=}P{-}CF_3 \qquad (1)$$

Such elimination reactions are a well-known problem in the chemistry of (trifluoromethyl)metal compounds. For example, $LiCF_3$[4] or $M(CF_3)_2$ (M = Zn, Cd)[5] decompose at low temperatures by elimination of difluorocarbene and formation of metal fluorides. On the other hand, trifluoromethyl derivatives of less electropositive metals such as mercury show enhanced thermal stability, e.g. bis(trifluoromethyl)mercury is a common reagent in nucleophilic trifluoromethyl group transfer reactions.[4]

Metal compounds with covalently bonded, nonbridging bis(trifluoromethyl)phosphanido groups are potential $P(CF_3)_2^-$ synthons. While transition metal phosphanides with electron-rich substituents on the phosphorus are converted by iodomethane to quaternary phosphonium salts,[6] electron-poor bis(trifluoromethyl)phosphanido complexes such as $Cp(CO)_3CrP(CF_3)_2$ react selectively with iodomethane by cleavage of the metal phosphorus bond and formation of $MeP(CF_3)_2$ and $Cp(CO)_3CrI$.[7] In principle, this nucleophilic displacement of iodide by the phosphanide is well suited for the synthesis of alkyl bis(trifluoromethyl)phosphanes. Because the hitherto known nonbridged bis(trifluoromethyl)phosphanido complexes $Cp(CO)_2FeP(CF_3)_2$[8] and $Cp(CO)_3MP(CF_3)_2$ (M = Cr, Mo, W),[9] as well as $(CO)_5M'P(CF_3)_2$ (M′ = Mn, Re),[10] are tedious to synthesize, these compounds appear to be hardly suitable for preparative chemistry.

In 1972, Grobe and Demuth prepared mercury bis{bis(trifluoromethyl)phosphanide}, $Hg[P(CF_3)_2]_2$, by treatment of divinylmercury with bis(trifluoromethyl)phosphane, $HP(CF_3)_2$.[11] 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 $HgMe_2 > Hg(SMe)_2 > Hg(CH{=}CH_2)_2 > Hg(CN)_2$.[11]

On the basis of these results, we have reinvestigated the reaction between $Hg(CN)_2$ and $HP(CF_3)_2$ with the aim to prepare $Hg[P(CF_3)_2]_2$ on a larger scale and to explore its capabilities as a $P(CF_3)_2^-$ synthon. Such synthons are not only desirable for the synthesis of π-acidic bis(trifluoromethyl)phosphane ligands but may also be useful in the selective synthesis of bis(tri-

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fluoromethyl)phosphanido transition metal complexes with nonbridging $P(CF_3)_2$ groups. To our knowledge, $Cp(CO)_2FeP(CF_3)_2$ is the only structurally characterized transition metal complex of this type.[12]

Experimental Section

Materials and Apparatus. Chemicals were obtained from commercial sources and used without further purification. Modified literature methods were used for the synthesis of $HP(CF_3)_2$.[13] Instead of Me_3SnH the less volatile Bu_3SnH was used for the reduction of $(CF_3)_2PBr$. This allows easily separation by fractional condensation after reacting for 30 min at 0 °C. Bromobis(trifluoromethyl)phosphane was synthesized treating neat $(CF_3)_2PNEt_2$[14] with gaseous HBr at −78 °C. *Caution! The toxic compounds $(CF_3)_2PBr$ as well as $(CF_3)_2PH$ react violently with air*. The known complex $[Hg(CN)_2(dppe)]$[15] was synthesized reacting $Hg(CN)_2$ in THF with the corresponding phosphane ligand and fully characterized.

Solvents were purified by standard methods.[16] Standard high-vacuum techniques were employed throughout all preparative procedures; nonvolatile compounds were handled in a dry N_2 atmosphere by using Schlenk techniques.

Differential thermal analysis was carried out on a Netzsch model STA 409-Skimmer instrument. Infrared spectra were recorded on a Nicolet-5PC FT-IR spectrometer as KBr pellets. Raman spectra were obtained with a Bruker FRA-106/s spectrometer, with a Nd:YAG laser operating at $\lambda = 1064$ nm.

The NMR spectra were recorded on Bruker model AMX 300 (^{199}Hg, 53.51 MHz; ^{13}C, 75.47 MHz; ^{31}P, 121.50 MHz; ^{19}F, 282.35 MHz) and Bruker AC200 spectrometers (^{31}P, 81.01 MHz; ^{19}F 188.31 MHz; ^{13}C, 50.32 MHz; ^{1}H, 200.13 MHz) with positive shifts being downfield from the external standards $HgMe_2$ (^{199}Hg), 85% orthophosphoric acid (^{31}P), CCl_3F (^{19}F), and TMS (^{13}C and ^{1}H). High-order NMR spectra were calculated with the program gNMR.[17]

Preparation of (1,2-Bis(diphenylphosphanyl)ethane)bis(bis(trifluoromethyl)phosphanido)mercury, $[Hg\{P(CF_3)_2\}_2(dppe)]$. A 0.83 g (4.90 mmol) amount of $HP(CF_3)_2$ was condensed onto a solution of 1.30 g (2.00 mmol) of $[Hg(CN)_2(dppe)]$ in 10 mL of CH_2Cl_2 at −196 °C. After the mixture was warmed to room temperature and stirred for 10 min, the volatile compounds were removed in vacuo, giving 1.80 g (1.92 mmol; 96% yield) of $[Hg\{P(CF_3)_2\}_2(dppe)]$ as a white solid. DTA/TG analysis: exothermic decomposition peak at 142 °C. Anal. Found (calcd for $C_{30}H_{24}F_{12}HgP_4$): Hg, 21.1 (21.4); P, 13.0 (13.2); F, 24.1 (24.3); C, 37.9 (38.5); H, 2.7 (2.6). Infrared spectrum (cm^{-1}) (KBr pellet): 3061 m, 2917 w, 2361 m, 2343 m, 1575 vw, 1485 m, 1438 s, 1417 w, 1334 vw, 1306 w, 1265 w, 1197 m, 1157 vs, 1117 vs, 1090 vs, 1027 m, 1000 m, 971 w, 866 w, 823 w, 742 s, 692 s, 669 m, 650 w, 617 vw, 563 vw, 520 m, 479 w, 456 m. Raman (cm^{-1}): 3062 (100), 2975 (18), 2911 (25), 1585 (50), 1098 (20), 1027 (23), 1000 (70), 734 (13), 450 (7), 378 (8), 189 (35), 88 (90). Mass spectrum (EI, 20 eV) {*m/z* (%) [assignment]}: 540 (8) $[Hg[P(CF_3)_2]_2^+]$; 398 (25) $[Ph_2PC_2H_4PPh_2^+]$; 371 (19) $[HgP(CF_3)_2^+]$; 289 (16) $[Ph_2PCPh(CH_3)^+]$; 275 (6) $[Ph_2PCPhH^+]$; 262 (15) $[Ph_3P^+]$; 202 (2) $[Hg^+]$; 185 (18) $[PPh_2^+]$; 169 (51) $[P(CF_3)_2^+]$; 108 (23) $[PPh^+]$; 69 (100) $[CF_3^+]$; 28 (7) $[C_2H_4^+]$. For NMR spectroscopic data, see Table 2.

Preparation of Dicyanobis(trimethylphosphane)mercury, $[Hg(CN)_2(Me_3P)_2]$. A 16.00 mmol amount of PMe_3 was condensed onto a reaction mixture containing 2.00 g (7.92 mmol) of $Hg(CN)_2$ in 10 mL of THF. After the mixture was stirring at room temperature for 30 min, all volatiles were removed in vacuo yielding 3.20 g (7.90 g) of $[Hg(CN)_2(Me_3P)_2]$ as a white solid. DTA/TG analysis: exothermic decomposition peak at 142−143 °C. Anal. Found (calcd for $C_8H_{18}HgN_2P_2$): Hg, 48.7 (49.5); N, 6.8 (6.9); C, 24.0 (23.7); H, 4.6 (4.5). Infrared spectrum (cm^{-1}) (KBr pellet): 2990 vw, 2974 vw, 2913 vw, 2133 vw, 1434 m, 1427 m, 1293 w, 965 vs, 863 vw, 852 vw, 753 m, 674 vw. Raman (cm^{-1}): 2984 (50), 2911 (100), 2133 (40), 1417 (8), 750 (10), 681 (10), 259 (10), 155 (17), 84 (12). Mass spectrum (EI, 20 eV) {*m/z* (%) [assignment]}: 254 (10) $[Hg(CN)_2^+]$; 228 (2) $[HgCN^+]$; 202 (8) $[Hg^+]$; 76 (71) $[P(CH_3)_3^+]$; 61 (100) $[P(CH_3)_2^+]$. NMR (CH_2Cl_2; 213 K): $\delta(^{31}P)$ −20.8 ppm; $^{1}J(^{31}P^{199}Hg)$ 3195 Hz.

Table 1. Crystal Data and Details of Data Collection and Structure Refinement for $[Hg\{P(CF_3)_2\}_2(dppe)]$[a]

compd	$[Hg\{P(CF_3)_2\}_2(dppe)]$
fw	1873.92
cryst system	triclinic
space group	$P\bar{1}$
lattice params	$a = 1003.4(2)$ pm, $\alpha = 91.42(2)°$
	$b = 1029.9(2)$ pm, $\beta = 93.98(2)°$
	$c = 1819.2(4)$ pm, $\gamma = 105.89(2)°$
cell vol	1.8019(6) nm^3
formula units/unit cell	$Z = 1$
D_{calc}	1.727 Mg m^{-3}
μ_{calc}(Mo Kα)	4.530 mm^{-1}
F(000)	904
cryst size	0.1 × 0.12 × 0.2 mm
2θ range	$4.24 \le 2\theta \le 48.34°$
obsd reflcns ($I_0 > 2\sigma(I)$)	3923
no. of params	425
goodness of fit	1.090
R1; wR2 ($I_0 > 2\sigma(I)$)	0.0869; 0.2208
R1; wR2 (all data)	0.1106; 0.2372
$\Delta\rho_{min/max}$	$(-4.861/9.190) \times 10^{-6}$ pm^{-3}

[a] Weighting $w^{-1} = \sigma^2(|F_o|^2) + (aP)^2 + bP$ with $P = (|F_o|^2 + 2|F_c|^2)/3$; extinction $F_c^* = kF_c[1 + 0.001|F_c|^2\lambda^3/\sin(2\theta)]^{-1/4}$; $R = \Sigma|\,|F_o| - |F_c|\,|/\Sigma|F_o|$, $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$, and $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$.

Preparation of Bis[bis(trifluoromethyl)phosphanido]bis(trimethylphosphane)mercury, $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$. A 0.71 g (1.75 mmol) amount of $[Hg(CN)_2(Me_3P)_2]$ was dissolved in 5 mL of CH_2Cl_2. A 4.80 mmol amount of $HP(CF_3)_2$ was condensed onto the reaction mixture and stirred for 10 min at room temperature. After removal of all volatile materials in vacuo, 1.09 g (1.58 mmol) of $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$ (yield 90%) was obtained as a white powder. DTA/TG analysis: exothermic decomposition peak at 157 °C. Anal. Found (calcd for $C_{10}H_{18}F_{12}HgP_4$): Hg, 28.9 (29.0); P, 17.8 (17.9); F, 33.0 (33.0); C, 17.6 (17.4); H, 2.7 (2.7). Infrared spectrum (cm^{-1}) (KBr pellet): 2983 w, 2918 w, 2816 w, 2161 w, 1425 s, 1297 s, 1214 s, 1151 vs, 1106 vs, 1081 vs, 952 vs, 865 vw, 803 vw, 744 m, 732 w, 671 vw, 583 vw, 559 w, 506 vw, 456 m. Raman (cm^{-1}): 2985 (31), 2915 (100), 2809 (10), 1423 (12), 1145 (6), 1106 (6), 1085 (7), 952 (6), 745 (16), 733 (17), 673 (20), 454 (8), 373 (9), 328 (7), 289 (11), 261 (12), 176 (33), 149 (24), 81 (17). Mass spectrum (EI, 20 eV) {*m/z* (%) [assignment]}: 540 (32) $[Hg[P(CF_3)_2]_2^+]$; 371 (77) $[HgP(CF_3)_2^+]$; 202 (2) $[Hg^+]$; 169 (42) $[P(CF_3)_2^+]$; 119 (10) $[FPCF_3^+]$; 100 (19) $[C_2F_4/PCF_3^+]$; 76 (75) $[P(CH_3)_3^+]$; 69 (95) $[CF_3^+]$; 61 (100) $[P(CH_3)_2^+]$; 45 (16) $[PCH_2^+]$. For NMR spectroscopic data, see Table 2.

Nucleophilic Displacement Reactions. Solutions of $Hg[P(CF_3)_2]_2$, $[Hg\{P(CF_3)_2\}_2(dppe)]$, and $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$ were treated at −30 °C with an excess of ethyl tosylate, iodoethane, and Ph_2PCl. The temperature was raised overnight to room temperature, and the products $EtP(CF_3)_2$[18] and $Ph_2PP(CF_3)_2$ were identified by multinuclear NMR spectroscopy. NMR spectroscopic data for $Ph_2PP(CF_3)_2$ (CH_2Cl_2; RT): $\delta(^{31}PPh_2)$ −30.1 ppm; $\delta(^{31}P(CF_3)_2)$ 4.7 ppm; $\delta(^{19}F)$ −46.9 ppm; ^{1}J(PP) 180.0 Hz; ^{2}J(PF) 59.9 Hz; ^{3}J(PF) 9.0 Hz.

Crystal Structure Determination. Crystals of $[Hg\{P(CF_3)_2\}_2(dppe)]$ were grown by cooling a saturated toluene solution from room temperature to −20 °C. A colorless small single crystal was selected and sealed in a glass fiber ($d = 0.3$ mm). Single-crystal X-ray data of the compound were collected on an image plate diffractometer (STOE

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Table 2. NMR Spectroscopic Data for Mercury Bis(trifluoromethyl)phosphanide Derivatives

	$\delta(^{199}Hg)$	$\delta(^{19}F)$	$\delta(^{31}P)$	$\delta(^{13}CF_3)$	$^2J(PF)$	$^3J(HgF)$	$^1J(HgP)$	$^1J(PCF_3)$	$\delta(^{31}P_{lig})$	$^1J(HgP_{lig})$
$Hg(CN)P(CF_3)_2$[b]	−1237	−39. 7	−8.6	133.6	58.7	231.8	1682	37.5		
$Hg[P(CF_3)_2]_2$[c]	−1090	−39. 8	1.8	134.2	54.2	187.8	822.6	42.3		
$[Hg\{P(CF_3)_2\}_2(dppe)]$[d]	−293	−39. 4	−5.2	136.9	54	138	623	50.4	11.1	115
$[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$[e]	−192	−39. 0	−7.3	138.3	51	115	n.o.	55	−21.9	1526

[a] Chemical shifts in ppm; coupling constants in Hz; n.o. = not observed or not resolved. [b]In diglyme at 243 K; internal lock C_6D_6 and external lock acetone-*d*$_6$. [c]In diglyme at 243 K; internal lock C_6D_6 and external lock acetone-*d*$_6$; $^2J(PP)$ 12; $^4J(PF)$ 1.0; $^1J(CF)$ 317.9; $^4J(FF)$ 8.0; $^3J(PC)$ 0.8 Hz. [d]In CH_2Cl_2 at 220 K; internl lock C_6D_6 and external lock acetone-*d*$_6$; $^3J(CF)$ 317.8; $^3J(CF)$ 7.0; $^2J(P_{CF_3}P_{ligand})$ 44; $^1J(CF)$ 317.8; $^3J(CF)$ 7.0 Hz. Ligand data: $\delta(^{13}C_{dppe})$ 133.5; 132.3; 130.8; 130.2; 24.3 ppm; $\delta(^1H_{dppe})$ 8.4; 3.8 ppm. [e]In CH_2Cl_2 at 210 K; internal lock C_6D_6 and external lock acetone-*d*$_6$; $^1J(CF)$ 317; $^4J(FF)$ 8.0; $^3J(CF)$ 8 Hz. Ligand data: $\delta(^{13}C_{PMe_3})$ 14.9 ppm; $^1J(PC)$ 19.5 Hz; $\delta(^1H_{PMe_3})$ 2.5 ppm; $^2J(PH)$ 8.6 Hz.

Table 3. Characteristic Infrared and Raman Data of the $HgP(CF_3)_2$ Unit of the Complexes $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$ and $[Hg\{P(CF_3)_2\}_2(dppe)]$ (cm^{-1})

$[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$		$[Hg\{P(CF_3)_2\}_2(dppe)]$		
IR	Raman	IR	Raman	assgnt
		1197 m		$\nu(CF)$
1151 vs	1145(6)	1157 vs		$\nu(CF)$
1106 vs	1106(6)	1117 vs		$\nu(CF)$
1081 vs	1085(7)	1090 vs		$\nu(CF)$
732 w	733(17)	742 s	734(13)	$\delta(CF_3)$
583 vw				$\delta_{as}(CF_3)$
559 vw		563 vw		$\delta_a(CF_3)$
456 m	454(8)	456 m	450(7)	$\nu(PC_2)$
	373(9)		378(8)	$\delta(CPC)/\rho(CF_3)$
	176(33)		189(35)	$\nu(Hg-P)$

IPDS) using graphite-monochromatized Mo Kα radiation (λ = 71.069 pm).[19] The structure was solved by direct methods (SHELXS-86) and Fourier synthesis.[20] The refinement[21] was done by full-matrix least-squares procedures using anisotropic thermal parameters. The H atoms were placed in idealized positions with one thermal parameter for all H atoms of one molecule. Further details are given in Table 1. A selection of bond distances and angles is given in Table 4.

Results and Discussion

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

$$Hg(CN)_2 + HP(CF_3)_2 \xrightarrow[-HCN]{-30\ °C} Hg(CN)P(CF_3)_2 \xrightarrow[-HCN]{-30\ °C} Hg[P(CF_3)_2]_2 \quad (2)$$

With an excess of $HP(CF_3)_2$ complete conversion to $Hg[P(CF_3)_2]_2$ is achieved. Upon being warmed to ambient temperature, this compound decomposes slowly both in THF and in diglyme solution to elemental mercury and tetrakis(trifluoromethyl)diphosphane, $(CF_3)_2PP(CF_3)_2$:

$$Hg[P(CF_3)_2]_2 \xrightarrow{RT} Hg + (CF_3)_2P-P(CF_3)_2 \quad (3)$$

Similarly, all attempts to isolate $Hg[P(CF_3)_2]_2$ by removing the solvent, HCN, and excess of $HP(CF_3)_2$ in vacuo at low temperatures failed due to decomposition (eq 3).

When the complex is dissolved in THF, neither $^{199}Hg-^{19}F$ nor $^{199}Hg-^{31}P$ couplings are detectable in the NMR spectra due to phosphanide exchange phenomena via solvated $[Hg\{P(CF_3)_2\}_3]^-$ and $[HgP(CF_3)_2]^+$. If diglyme is used as the solvent, the ^{199}Hg satellite spectra are clearly observed at −30 °C which allows a full characterization of the products $Hg(CN)P(CF_3)_2$ and $Hg[P(CF_3)_2]_2$ by multinuclear NMR spectroscopy (see Table 2). The substitution of one cyanide group by a $P(CF_3)_2$ group causes a low-field shift in the ^{199}Hg NMR spectrum of about 260 ppm relative to $Hg(CN)_2$ ($\delta(^{199}Hg)$ −1495 ppm); substitution of the second cyanide is accompanied by an additional low-field shift of approximately 150 ppm. The absolute value of $^1J(HgP)$ of 1682 Hz for $Hg(CN)P(CF_3)_2$ is dramatically reduced to 822 Hz by substitution of the cyanide by a second $P(CF_3)_2$ phosphanide group.

Table 4. Selected Bond Lengths (pm) and Angles (deg) for $[Hg\{P(CF_3)_2\}_2(dppe)]$

Hg1−P1	271.7(4)	C1−F13	133(3)
Hg1−P2	250.3(4)	C1−F12	135(3)
Hg1−P3	248.6(5)	C1−F11	136(3)
Hg1−P4	257.1(4)	C2−F22	131(3)
P1−C11	182(2)	C2−F21	135(2)
P1−C5	183(2)	C2−F23	136(2)
P2−C3	187(2)	C3−F33	133(2)
P2−C4	187(2)	C3−F32	133(3)
P3−C1	187(2)	C3−F31	137(3)
P3−C2	189(2)	C4−F42	132(3)
P4−C6	184(2)	C4−F41	136(3)
P4−C41	183(2)	C4−F43	136(2)
P3−Hg1−P2	122.88(15)	P3−Hg1−P1	108.5(2)
P3−Hg1−P4	118.03(15)	P2−Hg1−P1	97.56(14)
P2−Hg1−P4	115.7(2)	P4−Hg1−P1	80.74(13)
C3−P2−C4	98.6(11)	C1−P3−C2	96.7(10)
C3−P2−Hg1	100.4(8)	C1−P3−Hg1	101.7(7)
C4−P2−Hg 1	103.4(7)	C2−P3−Hg1	101.4(7)

For $Hg[P(CF_3)_2]_2$ the $^2J(PF)$ and the long-range $^4J(PF)$ couplings with values of 54.2 and 1.0 Hz, respectively, give rise to a magnetic nonequivalence of the two $P(CF_3)_2$ moieties, resulting in a high-order $[AX_6]_2M$ spin system with A = P, X = F, and M = ^{199}Hg. Both high-order ^{199}Hg (Figure 1) and ^{31}P NMR spectra (Figure 2) are in excellent agreement with the simulated spectra displayed in the respective bottom traces.

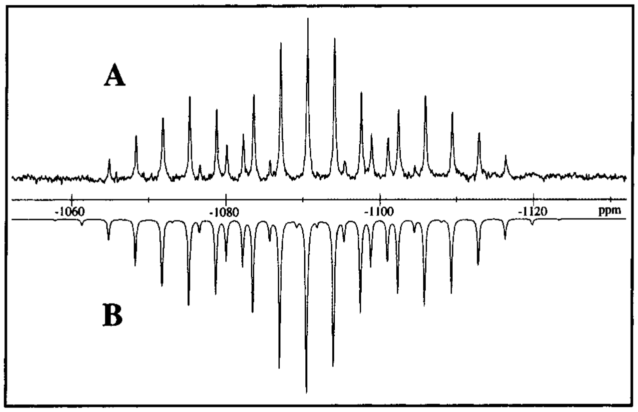

Figure 1. Experimental (A) and simulated (B) ^{199}Hg NMR spectrum of $Hg[P(CF_3)_2]_2$. The spectrum was recorded at 220 K by means of DEPT polarization transfer from ^{19}F (1849 scans, 32 K data points, spectral with 27 800 Hz, relaxation delay 2 s, variable pulse length 32E, no decoupling).

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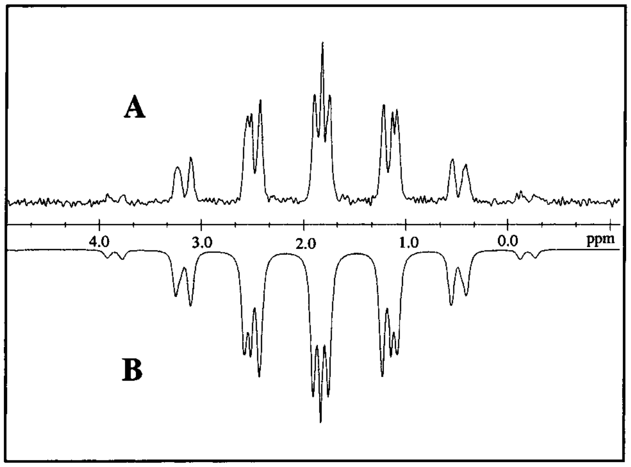
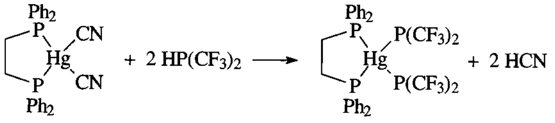


Figure 2. Experimental (A) and calculated (B) ^{31}P NMR spectrum of $Hg[P(CF_3)_2]_2$.

The rate of the thermal decomposition of $Hg[P(CF_3)_2]_2$ decreases with increasing donor strength of the solvent; e.g., the compound is stable at room temperature in pyridine solution. This indicates that $Hg[P(CF_3)_2]_2$ is stabilized due to formation of 18 valence electron complexes, $[Hg\{P(CF_3)_2\}_2D_2]$. Removal of these donor molecules during the working up procedure results in the decomposition to elemental mercury and $(CF_3)_2PP(CF_3)_2$. For this rather soft Lewis acid, phosphanes may be regarded as suitable ligands. 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)ethane)dicyanomercury, $[Hg(CN)_2(dppe)]$,[15] 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.



(4)

The moderately air stable product shows no sign of decomposition over a period of several months in an inert gas atmosphere at room temperature. The exothermic decomposition temperature of 142 °C was determined by DTA/TG measurement. To study the stabilization by nonchelating phosphanes we have prepared $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$ by reacting the novel compound $[Hg(CN)_2(Me_3P)_2]$ with $HP(CF_3)_2$. The decomposition temperature of the trimethylphosphane complex which has been fully characterized is increased by 15 °C as compared with the dppe complex as a result of the higher donor strength of Me_3P.

As compared with a diglyme solution of $Hg[P(CF_3)_2]_2$, the ^{199}Hg NMR resonances of the phosphane complexes $[Hg\{P(CF_3)_2\}_2(dppe)]$ (Figure 3) and $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$ appear at distinctive lower fields, −293 and −192 ppm, respectively (see Table 2). A comparable low-field shift of about 1145 ppm is observed of $HgCl_2$ complexed by two triphenylphosphane ligands.[22] The coordination of the mercury atom by four phosphorus atoms in the complex $[Hg\{P(CF_3)_2\}_2(dppe)]$ is indicated by the triplet of triplet splitting of the ^{199}Hg NMR resonance as shown in Figure 3.

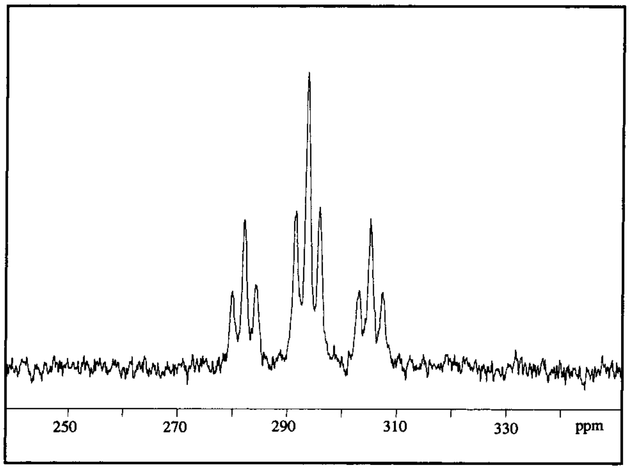


Figure 3. ^{19}F-decoupled ^{199}Hg NMR spectrum of $[Hg\{P(CF_3)_2\}_2(dppe)]$.

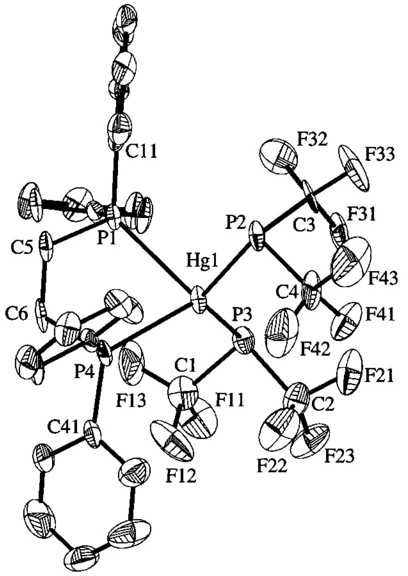


Figure 4. Perspective drawing of the complex $[Hg\{P(CF_3)_2\}_2(dppe)]$ with 50% thermal ellipsoids.

The analysis of the vibrational spectra, based on earlier assignments,[23] locates the symmetric $\nu(Hg-P(CF_3)_2)$ stretching mode of the complex $[Hg\{P(CF_3)_2\}_2(dppe)]$ at 189 cm^{-1} (see Table 3). The stronger donor Me_3P in $[Hg\{P(CF_3)_2\}_2(Me_3P)_2]$ causes the $v(Hg-P(CF_3)_2)$ mode to decrease by 13 cm^{-1}. However, these $\nu(Hg-PR_2)$ frequencies are significantly lower than the value of 370 cm^{-1} which has been reported for $Hg[P(t\text{-}Bu)_2]_2$.[24]

The crystal structure of $[Hg\{P(CF_3)_2\}_2(dppe)]$ has been determined by X-ray diffraction (Figure 4). The strongly distorted tetrahedral coordination of the mercury center is apparent from the P−Hg−P bond angles for the $(CF_3)_2P-Hg-P(CF_3)_2$ and $Ph_2P-Hg-PPh_2$ units of 122.9 and 80.7°, respectively, the four $Ph_2P-Hg-P(CF_3)_2$ angles being 118.0, 115.7, 108.5, and 97.6°. In an alternate description the complex may be regarded as a distorted triangular, spanned by the phosphorus atoms P_2, P_3, and P_4, the fourth coordination by P_1 being much weaker. The Hg−P distances are of special interest (Table 4). It is well-known that metal−P bond lengths for fluorinated

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Table 5. Hg−P Bond Distances Together with the Corresponding $^1J(^{31}P^{199}Hg)$ Coupling Constants of Phosphane Mercury Complexes $[Hg(X)_2(R_3P)_2]$[15,28]

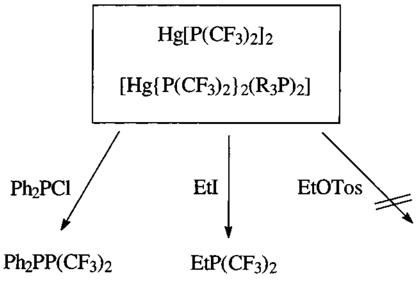
phosphane $(R_3P)_2$	anion X	d(HgP) (pm)	$^1J(^{31}P^{199}Hg)$ (Hz)
$(Ph_3P)_2$	NO_3	245	5928
$(Ph_3P)_2$	SCN	249	3726
$(Ph_3P)_2$	I	257	3074
$(Ph_3P)_2$	CN	259/243	2617
dppe	CN	261/253	1817[a]
dppe	$P(CF_3)_2$	272/257[a]	115[a]

[a] This work; in CH_2Cl_2 at 220 K; internal lock C_6D_6 and external lock acetone-d_6.

phosphanes are significantly shorter than corresponding alkylphosphane M−P bond lengths.[25] The opposite trend is observed for phosphanide ligands. The Hg−$P(CF_3)_2$ bonds, 249 and 250 pm, are slightly longer than those in $Hg[P(t\text{-}Bu)_2]_2$, 244 and 245 pm,[26] or $Hg[P(SiMe_3)_2]_2$, 240 and 241 pm.[27]

With values of 272 and 257 pm the two Hg−P bonds of the dppe ligand are significantly different. The Hg−P distance of 272 pm is longer than the sum of the covalent radii[28] but clearly lower than the sum of their van der Waals radii (335pm).[29] Different Hg−P bond lengths have also been observed in polymeric $[Hg(CN)_2(dppe)]$ with 261 and 253 pm[15] as well as in monomeric $[Hg(CN)_2(Ph_3P)_2]$ with 259 and 243 pm.[28] An interesting correlation exists between the $^1J(^{199}Hg^{31}P)$ coupling constant and the Hg−P bond length in the compounds $[Hg(X)_2(R_3P)_2]$ as shown in Table 5. For these compounds the Hg−P bond lengths increases with a decreasing of the $^1J(^{199}Hg^{31}P)$ coupling constant.

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.

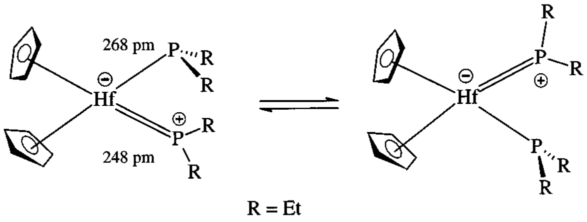


(5)

Conclusion

In this paper a convenient synthesis for mercury bis(trifluoromethyl)phosphanides is described. The thermally unstable $Hg[P(CF_3)_2]_2$ is stabilized by addition of donors and formation of 18 valence electron donor acceptor adducts. Structural data demonstrate, compared with binary $Hg(PR_2)_2$ compounds, a weakening of the Hg−PR_2 bonds in the complexes $[Hg\{P(CF_3)_2\}_2(R_3P)_2]$. The destabilization of the Hg−PR_2 bond is compensated by the kinetic stabilization of the complex.

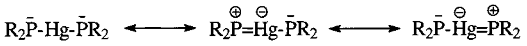
Electronically unsaturated transition metal phosphanides such as the complexes $Cp_2M(PR_2)_2$ (M = Zr, Hf; R = Alkyl, Ph)[30] have been shown to exhibit a phosphanido/phosphenium bonding dualism.[31] In the solid state they contain both a phosphanido and a phosphenium ligand which interconvert rapidly on the NMR time scale in solution:



(6)

X-ray structural results indicate that the Hf−P bond length for the planar phosphenium ligand of the R = Et derivative is 248.8 pm, while the corresponding bond length for the pyramidal phosphido ligand is about 20 pm longer. The pyramidal phosphanido ligand, which may be described as a nucleophilic PR_2^- unit, is in contrast to the planar electrophilic phosphenium PR_2^+ cation, which is stabilized by p$\pi\angle$dπ bond contribution.

For a mercury bis(phosphanide) compound, $Hg(PR_2)_2$, the following mesomeric structures consequently might be formulated: The resonance structures **B** and **C** contain both nucleophilic and electrophilic phosphorus atoms. This approach explains why two phosphorus atoms smoothly combine with reductive elimination of elemental mercury. The formal opposite charges of the two phosphorus atoms based on a phosphenium bonding contribution may become real in a ligand exchange process as is it observed by NMR experiments. However, also a radical decay via elimination of two $P(CF_3)_2$ radicals cannot be fully excluded. The stabilization of $Hg[P(CF_3)_2]_2$ by donors is ascribed to the electronic saturation of the mercury atom which does not allow phosphenium bonding contributions as it is proven by the pyramidality of the $P(CF_3)_2$ phosphanide ligands in the complex $[Hg\{P(CF_3)_2\}_2(dppe)]$ by X-ray crystallography (Figure 4).



$$R_2\bar{P}\text{-}Hg\text{-}\bar{P}R_2 \longleftrightarrow R_2\overset{\oplus}{P}{=}\overset{\ominus}{Hg}\text{-}\bar{P}R_2 \longleftrightarrow R_2\bar{P}\text{-}\overset{\ominus}{Hg}{=}\overset{\oplus}{P}R_2 \qquad (7)$$

A **B** **C**

The easy to handle complexes are suitable tools for nucleophilic substitutions. Further investigations to synthesize chiral bidentate bis(trifluoromethyl)phosphane containing ligands for use in asymmetric catalysis are in progress.

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Supporting Information Available: A crystallographic file in CIF format for the compound $[Hg\{P(CF_3)_2\}_2(dppe)]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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