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Synthesis and Coordination Chemistry (with Platinum(II) and Molybdenum(0)) of New Bis(bis(trifluoromethyl)phosphano)alkanes. Structure of a New Bis(phosphano)methanide Complex

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Two known and four new bis(phosphano)alkanes [$(CF_3)_2P(CH_2)_nP(CF_3)_2$, n = 1-3; $(CF_3)_2PCR(CH_3)P(CF_3)_2$, R = H, CH_3; $(CF_3)_2P(CF_2)_2P(CF_3)_2$] have been prepared in good yield by an improved procedure. $PtCl_2$ and $Mo(CO)_4$ complexes of these highly π-acidic ligands have been prepared by standard routes. Thus, displacement of benzonitrile from [$PtCl_2(PhCN)_2$] affords [$PtCl_2LL$] [LL = $(CF_3)_2P(CH_2)_nP(CF_3)_2$, n = 2, 3; LL = $(CF_3)_2PCR(CH_3)P(CF_3)_2$, R = H, CH_3; LL = $(CF_3)_2P(CF_2)_2P(CF_3)_2$]. Similarly, piperidine is displaced from *cis*-[$Mo(CO)_4$(piperidine)$_2$] to give [$Mo(CO)_4$(LL)], (LL = $(CF_3)_2P(CH_2)_nP(CF_3)_2$, n = 2, 3; LL = $(CF_3)_2P(CF_2)_2P(CF_3)_2$). Self-dehydrochlorination of [$PtCl_2\{(CF_3)_2PCH(CH_3)P(CF_3)_2\}$] in the solid state at 150 °C gives the complex [$Pt_2(\mu\text{-}Cl)_2\{(CF_3)_2PC(CH_3)P(CF_3)_2\}_2$] (**34**), shown by single-crystal X-ray crystallography to contain two chelating bis(phosphano)methanide ligands. **34** crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with cell dimensions a = 7.001 (2) Å, b = 12.612 (2) Å, c = 16.944 (4) Å, and β = 100.18 (2)°. The backbone P-C bond lengths of **34** (1.708 (8) and 1.686 (8) Å) are among the shortest measured for chelate complexes of bis(phosphano)methanides.

Introduction

Several trifluoromethylated bis(phosphano)alkanes, prepared by a variety of specific procedures, have been known for many years. Pyrolysis of C_2H_4, C_2F_4, or C_2H_2 with $(CF_3)_2PP(CF_3)_2$ in the presence of catalytic traces of iodine gave the bis(phosphano)alkanes $(CF_3)_2PCR_2CR_2P(CF_3)_2$ (R = H (**1**) or F (**2**)) and *trans*-$(CF_3)_2PCH{=}CHP(CF_3)_2$ (**3**), respectively.[1] Similarly at higher temperatures $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (**4**) was prepared from C_2H_4 and $(CH_3)_2PP(CH_3)_2$.[2] Prolonged photolysis of $(CF_3)_2PH$ and $CF_3C{\equiv}CCF_3$ gave $(CF_3)_2PCHCF_3CHCF_3P(CF_3)_2$ (**5**) along with *cis*- and *trans*-$(CF_3)_2PC(CF_3){=}CH(CF_3)$ (**6a** and **6b**) in low yields,[3] and in a related procedure, the unsymmetrical bis(phosphano)alkanes $Ph_2PCH_2CH_2PR_2$ (R = CF_3[4] (**7**) and C_6F_5[5] (**8**)) were obtained from reaction of $Ph_2PCH{=}CH_2$ and R_2PH in the presence of a radical initiator.

Reaction of **1** or **2** with $Ni(CO)_4$ gave the chelate complexes [$Ni(CO)_2\{(CF_3)_2PCR_2CR_2P(CF_3)_2\}$] (R = H (**9**); R = F (**10**)).[6] Displacement of more CO from **9** by **1** gave [$Ni(CO)\{(CF_3)_2PCH_2CH_2P(CF_3)_2\}_2$] (**11**), which contains both chelate and unidentate molecules of **1**.[6] The related bis(phosphanes) $(CF_3)_2PXP(CF_3)_2$ (X = O (**12**), S (**13**), NH (**14**), NCH_3 (**15**))[7] did not yield chelate complexes with [$Ni(CO)_4$]. Instead **12** gave [$Ni(CO)_2\{(CF_3)_2POP(CF_3)_2\}]_2$[7] (**16**) in which two $Ni(CO)_2$ moieties appear to be bridged by both bis(phosphanes) similar to the bridging bis(phosphano)methanes in [$Ni(CO)_2\{\mu\text{-}(CH_3)_2PCH_2P(CH_3)_2\}]_2$ (**17**).[8] In contrast **11-13** gave the "A"-frame complexes [$Ni_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}(CF_3)_2PXP(CF_3)_2\}_2$] (X = S (**18**), NH (**19**), NCH_3 (**20**)).[7,9,10] Monomeric chelate complexes [$MCl_2(Ph_2PCH_2CH_2PR_2)$] (M = Pd, R = CF_3[4] (**21**); M = Pt, R = CF_3 (**22**); R = C_6F_5 (**23**[5])) were obtained from **7** or **8** and [$MCl_2(PhCN)_2$] (M = Pt, Pd). Two of these **21** and **22**, are nearly isomorphous, with the most striking features of the molecular structures in each case being the extreme shortness of the $(CF_3)_2P$-M bonds (2.192 (1) Å[4] in **21** and 2.168 (3) Å[5] in **22**) and the respective trans M-Cl bonds (2.311 (4) Å[4] in **21** and 2.317 (3) Å[5] in **22**).

We report herein the details of a useful general synthetic method for the preparation of **1**, **2**, and the new bis(phosphano)alkanes $(CF_3)_2P(CH_2)_3P(CF_3)_2$ (**24**) and $(CF_3)_2PCRR'P(CF_3)_2$ (R = R' = H (**25**); R = H, R' = CH_3 (**26**); R = R' = CH_3 (**27**)) from $(CF_3)_2PP(CF_3)_2$ and the appropriate diiodoalkanes. In addition the coordination of these ligands to platinum(II) and molybdenum(0) was investigated.

Experimental Section

All reactions were performed in sealed glass tubes and standard vacuum-line techniques[11] were used throughout for the manipulation of volatile compounds. $(CF_3)_2PP(CF_3)_2$ was prepared[12] by the reduction of $(CF_3)_2PI$ with mercury. 1,1-Diiodoethane[13] and 2,2-diiodopropane[14] were prepared by literature methods. The other diiodoalkanes were commercial materials (Aldrich) that were used without further purification. [$PtCl_2(PhCN)_2$][15] and *cis*-[$Mo(piperidine)_2(CO)_4$][16] were prepared by standard methods.

^{19}F and ^{31}P NMR spectra of $CDCl_3$ solutions were recorded by using a Bruker WP400 instrument at the appropriate frequencies. ^1H and ^{13}C NMR spectra were similarly recorded by means of a Bruker AM300 spectrometer. ^{19}F and ^{31}P NMR shifts are quoted with respect to $CFCl_3$ and 85% H_3PO_4 respectively while ^1H and ^{13}C shifts are referenced to tetramethylsilane.

Infrared spectra of the bis(phosphano)alkanes were recorded for gases (ca. 0.5 mmHg pressure) in 10 cm path length cells with CsI windows on a Nicolet MX-1 spectrometer. Solution infrared spectra were recorded for $CHCl_3$ solutions in 0.5 mm path cells with NaCl windows on a Perkin-Elmer Model 457 spectrometer. Mass spectra were recorded on a Kratos MS50 instrument. Microanalyses of solids were obtained in this department while analyses of the volatile liquids were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of the Bis(phosphano)alkanes. Typically the diiodoalkane (1 mmol) and $(CF_3)_2PP(CF_3)_2$ (3 mmol) were heated to 130 °C in a sealed medium-walled Pyrex 5-mm NMR tube for between 1 and 3 days. The reaction was monitored by means of periodic ^1H and ^{19}F NMR spectra of the neat mixture recorded at room temperature. Reaction occurred slowly, but in most cases complete consumption of the diiodoalkanes was eventually achieved to give mixtures of $(CF_3)_2PI$, the bis(phosphano)alkane, some unreacted $(CF_3)_2PP(CF_3)_2$, and trace amounts of $(CF_3)_2PH$ and $(CF_3)_3P$. The bis(phosphano)alkanes, separated by fractional distillation through traps cooled to -23, -45, -63, -78, and -196 °C, condensed at either -23 or -45 °C (or both) and were obtained in yields exceeding 50% (with respect to the diiodoalkanes).

$(CF_3)_2PCH_2CH_2P(CF_3)_2$ (1). A yield of 55% of pure (by ^{19}F and ^1H NMR spectroscopy of the neat liquid) compound was obtained after a 24-h reaction. The infrared spectral data for **1** (ν_{CF} = 1198, 1168, 1147, and 1108 cm^{-1}) were identical with published data.[1,6] ^{13}C NMR: +127.87 ppm, quartets of doublets of quartets [$^1J_{C,F}$ = 318.9 Hz, $^1J_{CP}$ = 20.0 Hz, $^3J_{C,F}$ = 6.0 Hz; P(CF_3)$_2$]: +14.15 ppm, pseudotriplet AA'X

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$[|^1J_{C,P} + ^2J_{C,P}| = 33.7$ Hz, $^3J_{C,F}$ 1.3 Hz; $P(CH_2)_2P]$.

$(CF_3)_2PCF_2CF_2P(CF_3)_2$ (2). A yield of 60%, pure by ^{19}F NMR spectroscopy, was obtained. An infrared spectrum of **2** was identical with that of an authentic sample (ν_{CF} = 1208, 1173, 1155, and 1115 cm^{-1}).[1,6] ^{13}C NMR: +126.0 ppm, quartet of multiplets [$^1J_{C,F}$ = 323.0 Hz; $(CF_3)_2P$]; +121.0 ppm, multiplet [$P(CF_3)_2P$]. Yield was 50% after 48-h reaction time.

$(CF_3)_2PCH_2CH_2CH_2P(CF_3)_2$ (24). A yield of 67% of pure **24** (by ^{19}F and ^1H NMR spectroscopy of the neat liquid) was obtained after a 72-h reaction. IR (ν_{CF}): 1197, 1167, 1140, 1110 cm^{-1}. MS: *m/e* 380 (M^+): calcd *m/e* 380.1. Anal. Calcd for $C_7H_6F_{12}P_2$: C, 22.12; H, 1.59; F, 59.99; P, 16.30. Found: C, 21.72; H, 1.62; F, 60.37; P, 16.63. ^{13}C NMR: +128.59 ppm, quartet of doublets of quartets [$^1J_{C,F}$ = 318.3 Hz, $^1J_{C,P}$ = 21.3 Hz, $^3J_{C,F}$ = 6.1 Hz; $(CF_3)_2P$]; +20.56 ppm, triplet [$^2J_{C,P}$ = 20.2 Hz; $CH_2(CH_2P)_2$]; +20.30 ppm, pseudotriplet of multiplets AA′X [$|^1J_{C,P} + ^3J_{C,P}|$ = 27.6 Hz, $^3J_{C,F}$ = 2.2 Hz; $CH_2(CH_2P)_2$].

$(CF_3)_2PCH_2P(CF_3)_2$ (25). A yield of 100% of **25** was obtained after a 24-h reaction. IR (ν_{CF}): 1202, 1180, 1141, 1119 cm^{-1}. MS: *m/e* 352 (M^+); calcd *m/e* 352.0. Anal. Calcd for $C_5H_2F_{12}P_2$: C, 17.06; H, 0.57; F, 64.77; P, 17.60. Found: C, 16.67; H, 0.61; F, 65.48; P, 17.27. ^{13}C NMR: +127.81 ppm, quartet of doublets of quartets [$^1J_{C,F}$ = 324.5 Hz, $^1J_{C,P}$ = 12.0 Hz, $^3J_{C,F}$ = 6.0 Hz; $(CF_3)_2P$]; +8.83 ppm, triplet of multiplets [$^1J_{C,P}$ = 28.2 Hz, $^3J_{C,F}$ = 3.0 Hz; PCH_2P].

$(CF_3)_2PCH(CH_3)P(CF_3)_2$ (26). Sixteen hours of reaction time gave a 100% yield of **26**. IR (ν_{CF}): 1198, 1166, 1136, 1118 cm^{-1}). MS: *m/e* 366 (M^+); calcd *m/e* 366.0. Anal. Calcd for $C_6H_4F_{12}P_2$: C, 19.69; H, 1.10; P, 16.92. Found: C, 19.80; H, 1.13; P, 17.33. ^{13}C NMR +128.00 ppm, quartet of multiplets [$^1J_{C,F}$ = 340.0 Hz; $(CF_3)_2P$]; +21.90 ppm, triplet of multiplets [$^1J_{C,P}$ = 31.6 Hz, $^3J_{C,F}$ = 2.1 Hz; $PCH(CH_3)P$]; +12.98 ppm, triplet [$^2J_{C,P}$ = 14.0 Hz; $PCH(CH_3)P$].

$(CF_3)_2PC(CH_3)_2P(CF_3)_2$ (27). Twenty hours of reaction time gave ca. 67% yield of **27**, but at best as a 95% enriched mixture according to ^{19}F NMR spectroscopy even after repeated fractional distallation. The other species was tentatively identified as $(CF_3)_2PCH_2CH(CH_3)P(CF_3)_2$ on the basis of ^{19}F and ^1H NMR spectroscopy. The sample was used as prepared.

Pyrolysis of $(CF_3)_2PP(CF_3)_2$ with Other Iodoalkanes. (a) 1,4-Diiodobutane. An oil of low volatility was obtained whose NMR spectra (neat) showed the ^1H and ^{19}F signals that would be expected for $(CF_3)_2P(CH_2)_4P(CF_3)_2$ as a minor component (ϕ(F) −55.3, doublet, $^2J_{P,F}$ = 71.1 Hz; δ(H) 1.66, composite broad signal) of the total mixture. The major component of the mixture, unreacted 1,4-diiodobutane, could not be removed by fractional distillation.

(b) 1,4-Diiodopentane. An oil of low volatility was obtained from the reaction of this iodide and $(CF_3)_4P_2$. The product, which appeared to be free of contamination according to NMR spectroscopy (yield ~10%), was tentatively identified as $(CF_3)_2P(CH_2)_5P(CF_3)_2$ on the basis of ^1H, ^{13}C, and ^{19}F NMR spectroscopy (see Table III).

(c) *α,α′*-Diiodotoluene. A low yield of a product tentatively identified as $(CF_3)_2PCH(Ph)P(CF_3)_2$, on the basis of the similarity of the ^{19}F NMR spectra to spectra of **26**, was observed in the neat volatile components of the mixture resulting when $PhCHI_2$ was heated with $(CF_3)_4P_2$. Two $X_3AA'X'_3$ spin patterns (the X parts) were observed, ϕ(F) −50.41 and −51.52, $|^2J_{PF} + ^4J_{P,F}|$ = 78.3 and 88.1 Hz respectively, with $J_{F,F}$ = 7.5 Hz.

(d) Iodoform. An oil, 90% enriched in a single species, was obtained from reaction of CHI_3 and $(CF_3)_4P_2$. The product was tentatively identified as $[(CF_3)_2P]_3CH$: σ(P) +20.3, singlet (br); ϕ(F) −51.52, doublet (br), "$J_{P,F}$" = 86.0 Hz; δ(H) 2.47, quartet, $^2J_{H,P}$ = 4.1 Hz; yield ~13%.

(e) *trans*-Diiodoethene and 1,3-Diiodopropan-2-one. In each case decomposition of the organic components ensued, thus releasing iodine. $(CF_3)_2PI$ and $(CF_3)_2PP(CF_3)_2$ were the only fluorine-containing species in ^{19}F NMR spectra of the neat reaction mixtures.

Preparations of Platinum Complexes (28–32). Typically $[PtCl_2(PhCN)_2]$ (ca. 0.10 mmol), the bis(phosphano)alkanes (ca. 0.10 mmol), and chloroform (ca. 1 mL) were sealed in 5-mm glass reaction tubes. Initially yellow solutions formed at 70 °C. Within 5 min the solutions became colorless and cloudy, and after 10 min colorless microcrystalline precipitates of the monomeric chelate platinum complexes were evident. Compounds **28**, **30**, **31** and **33** were isolated by filtration of the cooled reaction mixtures. The reactions of ligands **2** and **25** gave soluble reaction products, and precipitates did not form despite prolonged cooling of their solutions to −35 °C.

$[PtCl_2\{(CF_3)_2PCH_2CH_2P(CF_3)_2\}]$ (28): yield 42%; mp 352 °C dec. MS: M^+ (250), $[M - Cl]^+$ (326), $[M - CF_2Cl]^+$ (71), $[M - C_2F_4Cl]^+$ (76), $[CF_3]^+$ (100, reference); figures in parentheses refer to relative intensities with respect to the reference (100). Anal. Calcd for $C_6H_4Cl_2F_{12}P_2Pt$: C, 11.40; H, 0.64; Cl, 11.22. Found: C, 11.59; H, 0.66; Cl, 11.13.

$[PtCl_2\{(CF_3)_2PCF_2CF_2P(CF_3)_2\}]$ (29): spectroscopic yield quantitative; assigned on the basis of ^{19}F and ^{31}P NMR spectroscopic evidence as the monomeric chelate. Despite repeated attempts a solid product was not obtained by crystallization.

$[PtCl_2\{(CF_3)_2P(CH_2)_3P(CF_3)_2\}]$ (30): yield 43%; mp 321 °C dec. MS: $[M - F]^+$ (137), $[M - Cl]^+$ (782), $[M - CF_2Cl]^+$ (107), $[CF_3]^+$ (100, reference). Anal. Calcd for $C_7H_6Cl_2F_{12}P_2Pt$: C, 13.01; H, 0.94; Cl, 10.98. Found: C, 13.34; H, 0.95; Cl, 11.91.

Reaction of $(CF_3)_2PCH_2P(CF_3)_2$ with $[PtCl_2(PhCN)_2]$. **25** (60 mg, 0.17 mmol) and $PtCl_2(PhCN)_2$ (74 mg, 0.16 mmol) and $CDCl_3$ (ca. 600 μL) in a sealed 5-mm NMR tube were warmed to 70 °C for 10 min. NMR spectroscopy indicated a complex product distribution (see text). Prolonged cooling to −35 °C gave no crystalline precipitates.

$[PtCl_2\{(CF_3)_2PCH(CH_3)P(CF_3)_2\}]$ (31): yield 72%. The compound sublimes below 200 °C before it melts. The yellow sublimate melts sharply at 216 °C. Anal. Calcd for $C_6H_4Cl_2F_{12}P_2Pt$: C, 11.40; H, 0.64; Cl, 11.22. Found: C, 11.38; H, 0.62; Cl, 11.30.

$[PtCl_2\{(CF_3)_2PC(CH_3)_2P(CF_3)_2\}]$ (32): yield 35%; mp 316 °C dec. MS: $[M - F]^+$ (37), $[M - Cl]^+$ (335), $[M - CF_3]^+$ (27), $[M - CF_3Cl]$ (42), $[CF_3]^+$ (100, reference). Anal. Calcd for $C_7H_6Cl_2F_{12}P_2Pt$: C, 13.01; H, 0.94; Cl, 10.98. Found: C, 13.25; H, 0.89; Cl, 11.39.

Preparation of $[Pt_2(\mu\text{-}Cl)_2\{(CF_3)_2PC(CH_3)P(CF_3)_2\}_2]$ (34). A sample of **31** (70.4 mg, 0.11 mmol) was sealed in a 30 × 1 cm glass reaction tube. The sample was heated to 150 °C for 1 h whereupon yellow crystals of **34** (40 mg, 60% yield), mp 216 °C, collected at the cooler end of the tube. MS: $[C_{10}H_1F_2P_3]^+$ (38), $[M/2 - PF_2]^+$ (105), $[M/2 - PCF_4]^+$ (75), $[M/2 - C_2F_6Cl]^+$ (77), $[CF_3]^+$ (100, reference). Anal. Calcd for $[C_6H_3ClF_{12}P_2Pt]_x$: C, 12.10; H, 0.51; Cl, 5.95. Found: C, 12.01; H, 0.52; Cl, 6.04. Mol wt 1191.13 ($x = 2$), from X-ray crystallography.

Preparation of the Molybdenum Complexes (35–37). Typically chloroform solutions (0.5 mL) containing 0.4 mmol each of *cis*-$[Mo(CO)_4(piperidine)_2]$ and bis(phosphano)alkane (**1**, **2**, or **24**) were heated to 80 °C for 1 h in sealed 5-mm NMR tubes. The extent of reaction was monitored by solution ^{19}F NMR spectroscopy, which showed that the reaction was complete within 30 min. The chloroform was removed in vacuo and the residue redissolved in methanol. The methanol solutions were then cooled to −78 °C overnight. Colorless crystalline samples of **35–37** were collected by filtration and dried in vacuo (2 h, 10^{-3} Torr).

$[Mo(CO)_4\{(CF_3)_2PCH_2CH_2P(CF_3)_2\}]$ (35): yield 55%; mp 90–91 °C. Anal. Calcd for $C_{10}H_4F_{12}MoO_4P_2$: C, 20.93; H, 0.70 (mol wt 573.9). Found: C, 20.87; H, 0.70 (mol wt 605.7 (benzene)). ($CHCl_3$): ν_{CO} 2063 (s), 1988 (vs), 1961 (vs) cm^{-1}; ν_{CF} 1208 (m), 1176 (vs), 1163 (vs), 1130 (vs), 1113 (s), 1101 (s), 1091 (s) cm^{-1}.

$[Mo(CO)_4\{(CF_3)_2PCF_2CF_2P(CF_3)_2\}]$ (36): yield 13%; mp ca 25 °C. Anal. Calcd for $C_{10}F_{16}MoO_4P_2$: C, 18.58; H, 0.00. Found: C, 18.02; H, 0.00. IR ($CHCl_3$): ν_{CO} 2082 (s), 1994 (vs), 1972 (s) cm^{-1}; ν_{CF} 1247 (vs), 1185 (vs), 1150 (vs), 1121 (vs), 1103 (s), 1009 (s) cm^{-1}.

$[Mo(CO)_4\{(CF_3)_2P(CH_2)_3P(CF_3)_2\}]$ (37): yield 25%; mp 111 °C. Anal. Calcd for $C_{11}H_6F_{12}MoO_4P_2$: C, 22.47; H, 1.03 (mol wt 588.0). Found: C, 22.65; H, 1.13 (mol wt 576 (benzene)). IR ($CHCl_3$): ν_{CO} 2065 (s), 1981 (vs), 1955 (vs) cm^{-1}; ν_{CF} 1200 (s), 1189 (s), 1152 (vs), 1108 (s) cm^{-1}.

X-ray Data Collection and Structure Solution for $[Pt_2(\mu\text{-}Cl)_2(\{(CF_3)_2P\}_2CCH_3)_2]$ (34).[17] A crystal of **34** was mounted in a nonspecific orientation on an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed by using Mo Kα radiation (λ = 0.71073 Å) with a graphite-crystal, incident-beam monochromator. The automatic peak search and reflection indexing programs[18] in conjunction with a cell reduction program showed the crystal to be monoclinic, and from the systematic absences ($h0l$, $h + l$ odd; $0k0$, k odd) the space group was determined to be $P2_1/n$, an alternative setting of $P2_1/c$ (No. 14).[19] Cell constants were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $14 < 2\theta < 24°$. The various crystal parameters and details of intensity collection for **34** are given in Table I.

The intensity data were collected at room temperature (23 °C) by using an ω–2θ scan ranging in speed from 10.1 to 1.4° min^{-1} (in ω). The variable scan rate was chosen to give $\sigma(I)/I \leq 0.03$ within a time limit of 50 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined

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(17) This X-ray crystallographic study comprises Report No. SR:030122-03-87 of the Structure Determination Laboratory, Department of Chemistry, University of Alberta.

(18) The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer with some local modifications and additions.

(19) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I.

Table I. Crystal Data and Details of Intensity Collection for **34**

formula: $C_{12}H_6Cl_2F_{24}P_4Pt_2$
fw: 1191.13
cryst size: 0.16 × 0.15 × 0.18 mm
syst abs: $h0l$ ($h + l$ odd), $0k0$ (k odd)
space group: monoclinic $P2_1/n$
radiation: Mo Kα (λ = 0.71073 Å)
unit cell params: a = 7.001 (2) Å, b = 12.612 (2) Å, c = 16.944 (4) Å, β = 100.18 (2)°
V 1472 Å^3
Z: 2
ρ_{calc}: 2.686 g cm^{-3}
linear abs coeff: 101.44 cm^{-1}
agreement factors R_1, R_2, GOF:[a] 0.037, 0.045, 1.41
cor applied: abs cor

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $R_2 = (\sum w(|F_o| - |F_c|)/\sum wF_o)^{1/2}$, GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

as a function of θ to compensate for the α_1–α_2 wavelength dispersion; the ω scan width = 0.60 + 0.35 tan θ.

Backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range to give a peak to background counting time of 2:1. Intensity measurements were made out to a maximum 2θ of 55°. Three reflections were chosen as standard reflections and were remeasured every 60 min of exposure time to monitor crystal and electronic stability over the course of data collection. A linear regression analysis of these standards showed a mean change in intensity of 3.4% (5.8%) over the time span of data collection, which was considered to be negligible.

Data Reduction. A total of 3807 reflections were collected and these were corrected for Lorentz, polarization, and background effects according to the following formulas:

$$I = \mathrm{SR}(\mathrm{SC} - RB)/Lp$$

$$\sigma(I) = \mathrm{SR}(\mathrm{SC} + RB) + (pI)/Lp$$

where SR is the scan rate, SC is the total scan count, R is the ratio of scan time to background time, B is the total background count, p is a factor to downweight intense reflections (chosen as 0.04 in this experiment), and Lp is the Lorentz and polarization correction term.

The data were corrected for absorption effects by using an empirical correction based on the absorption surface method of Walker and Stuart.[20] The maximum and minimum correction coefficients applied to F_o were 1.1974 and 0.7406, respectively. After equivalent forms were averaged (R factor for averaging is 0.065) and any systematically absent data were rejected, there were 3525 unique reflections of which 2232, having $I > 3\sigma(I)$, were used in the structure solution and refinement.

Structure Solution and Refinement. The volume of a unit cell indicates there are only two independent formula units present thus each molecule must sit on a center of symmetry as required by the space group. The structure was solved with a three-dimensional Patterson synthesis that gave the positional parameters for the Pt atom. The remaining nonhydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis.

Refinement[21] of atomic parameters was carried out by using full-matrix least-squares techniques on F_o minimizing the function $\sum w(|F_o| - |F_c|)$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes respectively, and the weighting factor w is given by $w = 4F_o/\sigma(F_o)$. The neutral-atom scattering factors were calculated from the analytical expression for the scattering factor curves.[22] The f' and f'' components of anomalous dispersion[23] were included in the calculations for all non-hydrogen atoms.

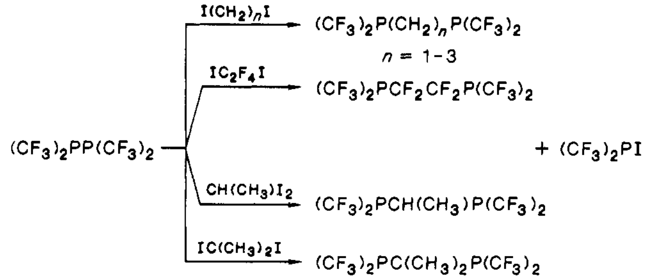
The hydrogen atoms of an ideal methyl group (C–H 0.95 Å and tetrahedral geometry) were fitted by least-squares techniques to peaks observed in a difference Fourier. These atoms were then included in the calculations with fixed, isotropic thermal parameters 1.2 times that of the attached atom and constrained to "ride" with this atom.

Table II. Final Positional (×10^3) and Thermal (×10^2) Parameters for **34**[a]

atom	x	y	z	U,[b] Å^2
Pt	159.17 (5)	90.83 (3)	55.87 (2)	3.289 (8)
Cl	−3.6 (4)	71.2 (2)	−79.2 (1)	4.96 (7)
P1	330.4 (3)	129.2 (2)	174.3 (1)	3.81 (7)
P2	323.0 (3)	240.4 (2)	53.1 (2)	4.17 (7)
F1	614 (1)	56.8 (7)	287.3 (5)	11.8 (3)
F2	632 (1)	6.2 (7)	171.3 (5)	11.7 (3)
F3	423 (1)	−63.4 (6)	234.8 (7)	13.2 (4)
F4	128 (1)	58.0 (7)	282.7 (5)	13.8 (4)
F5	35 (1)	203.7 (8)	232.6 (5)	10.8 (3)
F6	288 (1)	196.7 (8)	318.3 (4)	11.6 (4)
F7	398 (1)	244 (1)	−95.8 (5)	15.5 (5)
F8	604 (1)	325.0 (8)	−11.1 (6)	15.1 (4)
F9	597 (1)	163 (1)	−14.0 (6)	17.0 (4)
F10	77 (2)	359.6 (8)	−47.4 (6)	14.5 (5)
F11	280 (2)	447.5 (7)	32.5 (8)	14.2 (5)
F12	49 (1)	373.1 (7)	70.3 (6)	12.5 (4)
C1	436 (1)	243.5 (7)	149.5 (6)	4.2 (3)
C2	582 (2)	318 (1)	198.1 (8)	6.8 (4)
C3	508 (2)	23.8 (9)	220.7 (7)	6.8 (4)
C4	186 (2)	146.8 (9)	259.0 (7)	5.7 (4)
C5	490 (2)	243 (1)	−22.8 (7)	8.3 (5)
C6	177 (2)	361 (1)	22.9 (8)	7.0 (4)

[a] Atomic coordinates of the hydrogen atoms are available as supplementary material. [b] Estimated standard deviations in parentheses. [c] The equivalent isotropic thermal parameter U is given by $U = {}^1/_3\sum_{i=1}^{3} r_i^2$, where r_i are the root-mean-square amplitudes of vibration.

Scheme I



In the final cycle 200 parameters were refined by using 2232 observations having $I > 3\sigma(I)$. Included as a variable was a secondary extinction coefficient which refined to a value of 3.41 × 10^{-8}. The final agreement factors were R_1 = 0.037 and R_2 = 0.045. The largest shift in any parameter was 0.02 times its estimated standard deviation and the error in an observation of unit weight was 1.41e. An analysis of R_2 in terms of F_o, λ^{-1} sin θ, and various combinations of Miller indices showed no unusual trends. The highest peak in the final difference Fourier has a density of 1.7 (2) e Å^{-3}, is located 1 Å from the Pt atom and is without chemical significance. The final positional (×10^3) and thermal (×10^2) parameters for **34** are listed in Table II.

Results and Discussion

Phosphorus–phosphorus bond cleavage of $(CF_3)_2PP(CF_3)_2$ by CH_3I or CF_3I to give the tertiary phosphanes $(CF_3)_2PCH_3$ or $(CF_3)_3P$, respectively, and $(CF_3)_2PI$ has been known since 1960[24] (eq 1). High yields of two known and four new bis(bis(trifluoromethyl)phosphano)alkanes were successfully obtained by extension of the procedure to diiodoalkanes. Specifically the diiodoalkanes (1 equiv of $I(CH_2)_nI$ (n = 1–3), $CH(CH_3)I_2$, $IC(CH_3)I$, and IC_2F_4I) when heated with $(CF_3)_2PP(CF_3)_2$ (3 equiv) to 130 °C in sealed glass tubes for between one and three days yielded **1**, **2**, $(CF_3)_2P(CH_2)_3P(CF_3)_2$ (**24**), and $(CF_3)_2PCRR'P(CF_3)_2$ (R = R' = H (**25**), R = H, R' = CH_3 (**26**); R = R' = CH_3 (**27**) (Scheme I).

$$(CF_3)_2PP(CF_3)_2 + RI \rightarrow (CF_3)_2PR + (CF_3)_2PI \qquad (1)$$

The bis(phosphano)alkanes, all of which are moderately air-stable colorless liquids, were readily isolated from the common byproducts by high-vacuum fractional distillation. Diiodoalkanes with moderate amounts of contaminant iodine can be utilized in this synthesis. In these instances thermolysis of the volatile

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(20) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(21) The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package, Version 3 (1985, Delft, The Netherlands), rewritten for a Sun Microsystems computer and several locally written or modified programs.

(22) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. Table 2.2B.

(23) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. Table 2.3.1. Present distributor: D. Reidel, Dordrecht, The Netherlands.

(24) Cullen, W. R. *Can. J. Chem.* **1960**, *38*, 439.

Table III. ^1H, ^{19}F, and ^{31}P NMR Parameters of Phosphanoalkanes[a]

compd	ϕ_F	$J_{P,F}$, Hz	δ_H	$J_{H,P}$, Hz	σ_P
$(CF_3)_2PCH_2P(CF_3)_2$ (**25**)	−55.31	86.5	2.58 (t)[b]	2.75	−7.11
$(CF_3)_2PCH(CH_3)P(CF_3)_2$[c,d] (**26**)	−49.97	87.2	3.03 (q)	0	+10.94
	−51.73	96.5	1.71 (t of d)	8.7	
$(CF_3)_2PC(CH_3)_2P(CF_3)_2$ (**27**)	−48.54	95.2	1.64 (t)	9.5	
$(CF_3)_2PCH_2CH_2P(CF_3)_2$ (**1**)	−54.97	74.4	2.29 ("t")	"8.1"	+21.70
$(CF_3)_2PCH_2CH_2CH_2P(CF_3)_2$ (**24**)	−55.07 (d)	72.6	1.75 (m, $C-CH_2-C$)	...	−0.93
			1.98 (m, $C-CH_2P$)	...	
$(CF_3)_2P(CH_2)_5P(CF_3)_2$	−55.09 (d)	70.8	2.02 (m)	...	...
			1.67, 1.64 (m)	...	
$(CF_3)_2PCF_2CF_2P(CF_3)_2$[e] (**2**)	−48.46	84.3	...	...	−0.38
	−103.68	77.6	...	...	

[a] Recorded for $CDCl_3$ solutions at +25 °C relative to $CFCl_3$ (^{19}F, 376.5 MHz), TMS (^1H, 300.13 MHz), or 85% H_3PO_4(aq) (^{31}P, 161.9 MHz). Positive values indicate low-field shifts. [b] d = doublet, t = 1:2:1 triplet, "t" = pseudotriplet (second order), q = 1:3:3:1 quartet, m = multiplet. [c] $^4J_{F,F}$ = 7.5 Hz. [d] $^3J_{H,H}$ = 7.2 Hz. [e] $^4J_{F,F}$ = 6.6 Hz.

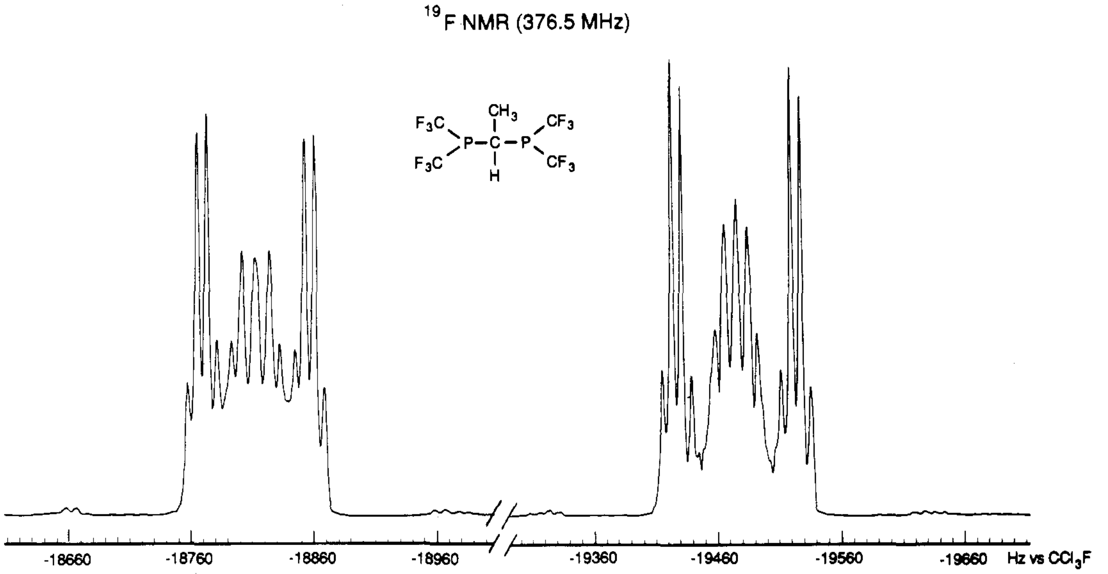

Figure 1. ^{19}F NMR spectrum of $(CF_3)_2PCH(CH_3)P(CF_3)_2$ (**26**). Each part of the spectrum corresponds to an $X_3AA'X'_3$ pattern of a pair of CF_3 groups. The $^2J_{PP}$ coupling can be seen as very weak lines approximately 100 Hz outside the edges of each central envelope.

products from a mercury reduction of the initial pyrolysis products (which converts $(CF_3)_2PI$ to $(CF_3)_2PP(CF_3)_2$[12]) makes it possible to isolate bis(phosphano)alkanes in good, though lower, yields than when pure reactants are used. Although the reaction is apparently general, repeated attempts to prepare pure phosphanes from several other iodoalkanes (*trans*-diiodoethene, α,α'-diiodotoluene, 1,3-diiodopropan-2-one, 1,4-di-iodobutane, 1,5-di-iodopentane, and iodoform; see Experimental Section) were complicated either by decomposition of the iodides at the reaction temperature or the formation of liquid products of insufficient volatility to permit efficient fractional distillation and purification.

The preparations of **1** and **2** described previously[1] are limited to C_2 carbon chains. Previous workers in our laboratory prepared **25** in 57% yield[25] by heating mixtures of $(CF_3)_2PI$ and CH_2I_2 over excess mercury to 150 °C in sealed tubes for 40 h. *Caution! Heating* $(CF_3)_2PP(CF_3)_2$ *(9.4 mmol),* CHI_3 *(6.4 mmol) over Hg (~130 mmol) to 140 °C in a Carius tube (30 mL) for 4 days gave no reaction. However, within 5 min at 160 °C a violent explosion occurred, the cause of which remains unknown.* Subsequently we have shown that the bis(phosphanes) are more conveniently prepared in as good or better yields without the need of mercury by simple thermolysis of $(CF_3)_2PP(CF_3)_2$ and diiodoalkanes for 1–3 days at 130 °C. A typical reaction of diiodoalkane (1 mmol) with $(CF_3)_2PP(CF_3)_2$ (3 mmol) is most conveniently performed in a sealed 5-mm medium-walled glass NMR tube (see Experimental Section). The progress of the reaction is easily monitored by using continuous-wave NMR experiments on unlocked samples. Although the total conversion of all $(CF_3)_2P$ groups to bis(phosphano)alkane cannot be achieved, the byproduct $(CF_3)_2PI$ can be easily separated from the reaction mixture. This advantage overshadows the limits to conversion. Recovered $(CF_3)_2PI$ can be easily transformed back to $(CF_3)_4P_2$ by reaction with mercury.[12]

Infrared and mass spectra and C, H, F, and P microanalyses of the new bis(phosphano)alkanes are fully consistent with their formulation.

NMR Spectroscopy of the Bis(phosphano)alkanes. ^1H, ^{19}F, and ^{31}P NMR spectroscopic details for the bis(phosphano)alkanes are given in Table III. The ^1H NMR spectra of **25**–**27** are first order while that of **24** consists of overlapping multiplets. ^1H NMR spectra of the methylene protons of **1** show a characteristic ("deceptively simple") pseudotriplet, due to the X part of an AXXX'X''X'''A' nuclear spin system.[26] The splitting between the outermost intense peaks, $|^2J_{P,H} + {}^3J_{P,H}|$, is 8.1 Hz and is comparable to the same coupling in $Ph_2PCH_2CH_2PPh_2$ (8.5 Hz),[26] the ^1H NMR spectrum of which more closely resembled a 1:2:1 triplet. The ^{19}F and ^{31}P NMR spectra of **1**, **25**, and **27** are best interpreted as the X and A parts respectively of $X_6AA'X'_6$ nuclear spin systems.[27] The ^{19}F NMR spectrum of **24** is a doublet while small doublet splittings in the outermost peaks of the ^{31}P NMR septet of **24** arise from a small $|^4J_{P,P}|$ coupling of 2.0 Hz.

The ^{19}F NMR spectrum of **26** comprises two signals corresponding to two pairs of CF_3 groups. Each pair resonates as an independent $X_3AA'X'_3$ nuclear spin system[27] (the X part) while there is only a single phosphorus resonance. A $^{19}F\{^{31}P\}$ NMR spectrum of **26** (Figure 1) consists of two quartets split by a geminal fluorine–fluorine coupling constant, $^4J_{F,F}$, of 7.5 Hz.

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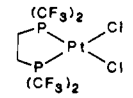
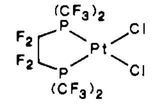
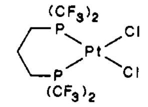
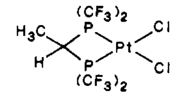
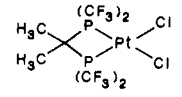
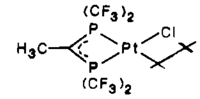
(25) Doty, L.; Sanger, A. R.; Cavell, R. G., unpublished results.

(26) Carty, A. J.; Harris, R. K. *Chem. Commun.* **1967**, 234.

(27) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

Table IV. NMR Spectroscopic Parameters for $[PtCl_n(P\frown P)]$ Complexes

	ϕ_F	$\lvert ^2J_{P,F} + ^4J_{P,F} \rvert$, Hz	$^3J_{F,Pt}$, Hz	σ_P	$\lvert ^2J_{P,P} \rvert$, Hz	$^1J_{P,Pt}$, Hz	δ_H	$J_{H,P}$, Hz
 **28**	−55.41[a]	91.8	39.2		0		1.47	$\lvert ^2J_{P,H} + ^3J_{P,H} \rvert$ = 14.3 Hz
 **29**	−48.11[d] −118.3[d]	102.4 $\lvert ^2J_{P,F} + ^3J_{P,F} \rvert$ = 76.0 Hz	36.5	+27.08 (m)	11.3	3258.5		
 **30**	−53.97[a]	85.2	36.5		0		2.49 (m, CH_2CH$_2$P) 2.11 (s, CH_2P)	
 **31**	−49.93[b] −54.66[b]	91.4 96.5 } $J_{F,F}$ = 4.0 Hz	45.6 47.0	−22.32 (m)	45.0	2892.6	4.36 (t of q's (CHP_2))[e] 1.84 (t of d's(CH_3CHP)$_2$))	$^2J_{P,H}$ = 13.8 Hz $^3J_{H,P}$ = 17.5 Hz
 **32**	−48.63[c]	90.7	48.1		33.0		2.26 (t)	$^3J_{H,P}$ = 18.0 Hz
	−60.66[c]	97.0	61.8	insoluble			1.67 (t)	$^3J_{H,P}$ = 19.1 Hz

[a] First-order doublet. [b] Two broad $X_3AA'X'_3$ "doublets". [c] $X_6AA'X'_6$ "doublets". [d] See text. [e] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [e] $^3J_{H,H}$ = 7.5 Hz.

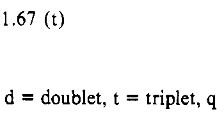
Methyl substitution of the bridging carbon has created nonequivalent terminal CF_3 environments on phosphorus.

The ^{19}F NMR signals of **2** are nontrivial second-order features consisting of a complex doublet and a 1:2:1 triplet of multiplets for the methyl and methylene fluorines, respectively (Figure 2). The doublet splitting of the $P(CF_3)_2$ resonance at highest frequency is assigned as $N_{CF_3} = \lvert ^2J_{P,F} + ^5J_{P,F} \rvert$ = 84.3 Hz of an $X_6AA'X'_6$[27] substructure. The $P(CF_3)_2$ fluorine resonance collapses to a "doublet" of this splitting, with other now smaller transitions clustered around the flanks of the main transitions, when themethylene fluorines are decoupled. The triplet splitting of the methylene fluorines, 77.6 Hz, is assigned to $N_{CF_2} = \lvert ^2J_{P,F} + ^3J_{P,F} \rvert$ for the X part of an $AXX'X''X'''A'$[26] spin system. The multiplet structure of each part of the triplet approximates to a septet, and we assign the splitting of 6.6 Hz to the fluorine–fluorine coupling constant between the terminal CF_3 and the bridging CF_2, $^4J_{F,F}$.

An estimate of 41.2 Hz is obtained for the phosphorus–phosphorus coupling constant, $\lvert ^3J_{P,P} \rvert$, of **1** from ^{19}F and ^{31}P NMR spectra.[25] $\lvert ^2J_{P,P} \rvert$ for **26** is estimated at ca. 150 Hz from the positions of the weak satellites of each signal in ^{19}F NMR spectra.[27]

Pt(II) Complexes of the Bis(phosphano)alkanes. Bis(phosphano)alkanes **1**, **2**, and **24**–**27** react completely within 10 min with $[PtCl_2(PhCN)_2]$ in chloroform solution at 70 °C. The products from the reactions of **2** and **25** are very soluble in chloroform and a wide range of other solvents; thus, analytical samples of the products of each reaction were not obtained. In all the other cases insoluble colorless crystalline precipitates were obtained in modest yields.

Microanalyses (C, H, Cl) of **28** and **30**–**32** are consistent with the formulation $[PtCl_2(L\frown L)]_x$ ($L\frown L$ = **1**, **24**, **26**, and **27**, respectively). Because **28**, **30**, and **32** were insufficiently soluble in $CDCl_3$, CD_2Cl_2, or other deuteriated solvents for ^{31}P NMR spectroscopy, a comprehensive NMR analysis of this series of compounds cannot be achieved (Table IV). The phosphorus shift in **31** (σ(P) −22.32, $^1J_{P,Pt}$ = 2892.6 Hz) is notable, occurring at 33 ppm lower frequency than the phosphorus shift in the free ligand. This unusual shielding effect on coordination is observed for the complexes $[MX_2(Ph_2PCHRPPh_2)]$ (M = Pt, X = Cl, R = H[28] or X = alkyl, aryl, R = H;[28] M = Pd, X = Cl[29] or I,[30] R = CH_3), wherein the bis(phosphano)alkanes form strained four-membered $\overline{MPCP}$ rings. The terminal CF_3 group inequivalence bestowed upon ligand **26** by virtue of the 1,1-ethane backbone is preserved in **31**. ^{19}F NMR spectra of **31** comprise similar independent $X_3AA'X'_3$[27] signals (the X parts) further split by a geminal fluorine–fluorine interaction ($^4J_{F,F}$ = 4.0 Hz). The signals approximate to doublets signifying that $\lvert ^2J_{P,P} \rvert$ is much lower in magnitude than that for the free ligand ($\lvert ^2J_{P,P} \rvert \sim$ 150 Hz). $\lvert ^2J_{P,P} \rvert$ for **31** is estimated to be 45.0 Hz from the ^{31}P NMR spectrum, which approximates to the A part of an $X_6AA'X'_6$ spin system. A ^{19}F NMR spectrum of compound **32** is indicative of an $X_6AA'X'_6$[27] nuclear spin system and an estimate of $\lvert ^2J_{P,P} \rvert$ from this spectrum is 33.0 Hz. Given all the NMR evidence, we assign a chelate monomeric structure to **31** and **32**.



R = H (**31**); R = CH_3 (**32**)

^{19}F NMR spectra of **28** and **30** are first-order doublets split by coupling to ^{195}Pt. Thus the magnitudes of phosphorus–

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(28) Hassan, F. S. M.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1501.

(29) Lee, C.-L.; Yang, Y.-P.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Organometallics* **1986**, *5*, 2220.

(30) Al-Jibori, S.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *74*, 235.

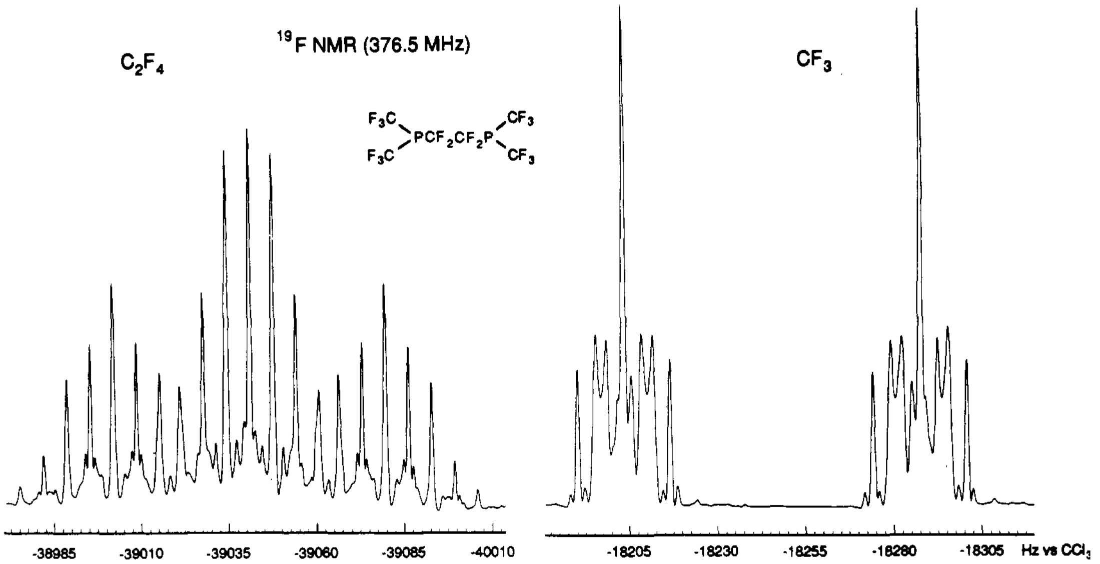


Figure 2. ^{19}F NMR spectrum of $(CF_3)_2PCF_2CF_2P(CF_3)_2$ (2) showing the C_2F_4 and $(CF_3)_2P$ parts of the spectrum.

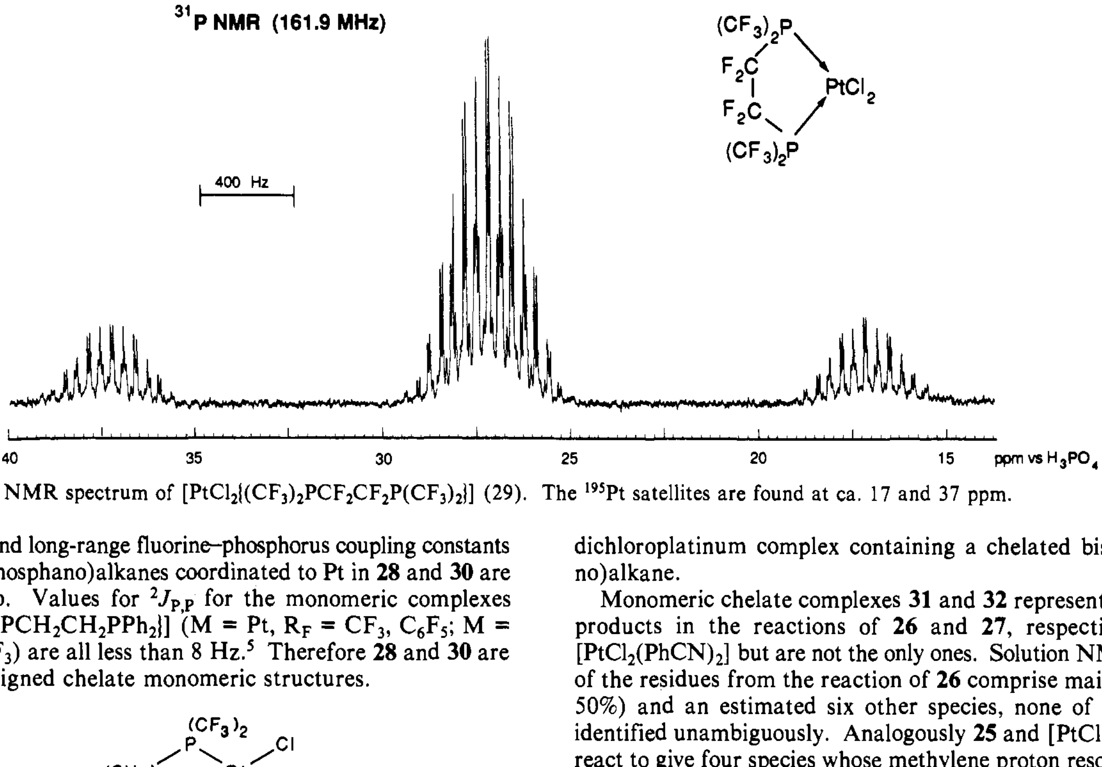
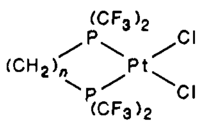


Figure 3. ^{31}P NMR spectrum of $[PtCl_2\{(CF_3)_2PCF_2CF_2P(CF_3)_2\}]$ (29). The ^{195}Pt satellites are found at ca. 17 and 37 ppm.

phosphorus and long-range fluorine–phosphorus coupling constants for the bis(phosphano)alkanes coordinated to Pt in **28** and **30** are close to zero. Values for $^2J_{P,P}$ for the monomeric complexes $[PtCl_2\{(R_F)_2PCH_2CH_2PPh_2\}]$ (M = Pt, R_F = CF_3, C_6F_5; M = Pd, R_F = CF_3) are all less than 8 Hz.[5] Therefore **28** and **30** are similarly assigned chelate monomeric structures.



n = 2 (**28**); *n* = 3 (**30**)

$[PtCl_2(PhCN)_2]$ and **2** reacted quantitatively to give a single species, **29** ^{31}P NMR spectra of **29** indicate that it contains a single phosphorus environment. The spectrum is a second-order multiplet split by coupling to ^{195}Pt, ($^1J_{P,Pt}$ = 3258.5 Hz) (Figure 3). The main peak and its satellites have identical P–F splitting patterns; therefore, the phosphorus nuclei are coordinated to a single Pt atom. Coordination has transformed the methylene fluorine ^{19}F NMR "triplet" signal of free **2** into a "doublet", which indicates a substantial drop in the magnitude of $|J_{P,P}|$.[27] Low values of $|^2J_{P,P}|$ are characteristic for coupling between cis-chelated tertiary bis(phosphano)alkanes coordinated to platinum, irrespective of the potential backbone contribution to $|J_{P,P}|$.[31] Therefore **29**, like **28** and **30**, appears to be a monomeric *cis*-dichloroplatinum complex containing a chelated bis(phosphano)alkane.

Monomeric chelate complexes **31** and **32** represent the major products in the reactions of **26** and **27**, respectively, with $[PtCl_2(PhCN)_2]$ but are not the only ones. Solution NMR spectra of the residues from the reaction of **26** comprise mainly **31** (ca. 50%) and an estimated six other species, none of which was identified unambiguously. Analogously **25** and $[PtCl_2(PhCN)_2]$ react to give four species whose methylene proton resonances are complex multiplets, thus indicating coupling to more than two phosphorus nuclei.[29] Clearly **25** does not form a monomeric chelate complex with $PtCl_2$. Instead dimeric or oligomeric products are suspected. Such products are known to predominate in the reactions of bis(phosphano)alkanes more suited to bridging than chelating interactions with transition metals, e.g., $Ph_2PCH_2PPh_2$ (dppm).[32] Recent evidence[33] suggests that bis(phosphano)methanes with more sterically encumbered phosphorus substituents favor the formation of small chelate rings by virtue of a Thorpe–Ingold effect.[34] We suggest that for our trifluoromethyl systems, in part at least, the same effect operates with successive methyl substitution on the backbone of **25** (to give **26** and **27**). At this stage we are in no position to gauge what influence the measurably weak trans influence of $(CF_3)_2P$[4,5] has on the preference of (trifluoromethyl)bis(phosphano)methane for formation of dimeric, oligomeric, or monomeric products.

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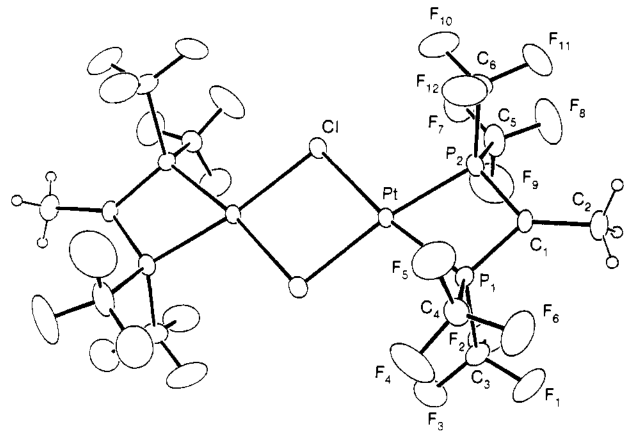


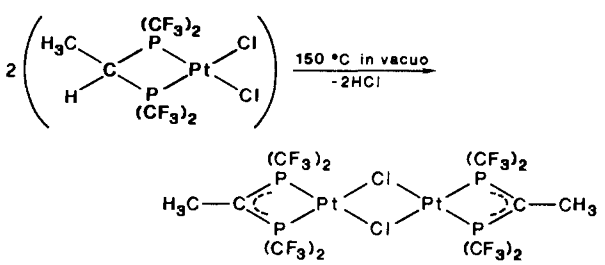
Figure 4. Molecular structure of **34** (ORTEP; thermal ellipsoids at 50% probability level).

Table V. Selected Interatomic Distances (Å) of **34**[a]

Pt–Cl	2.383 (2)	P1–C4	1.91 (1)
Pt–Cl′[b]	2.382 (2)	P2–C1	1.686 (8)
Pt–P1	2.202 (2)	P2–C5	1.88 (1)
Pt–P2	2.212 (2)	P2–C6	1.85 (1)
P1–C1	1.708 (8)	C1–C2	1.52 (1)
P1–C3	1.90 (1)	C–F	1.29 (4) av

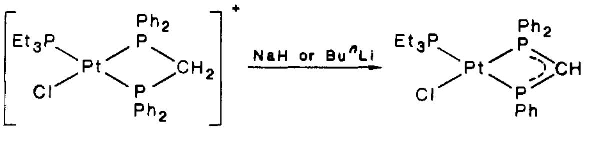
[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cl′ is the chloride atom trans to P2.

Pyrolysis of 32. Microanalytical data for **34**, the yellow sublimate prepared from heating **32** to 150 °C in vacuo, suggested that it was the product of a dehydrochlorination reaction. A ^{1}H NMR spectrum of **34** indicated the retention of the methyl group in an environment similar to that of **32** (δ(H) 1.84, $^3J_{H,P}$ = 17.5 Hz in **32**; δ(H) 1.67, $^3J_{H,P}$ = 19.1 Hz in **34**). Moreover only a single fluorine environment is observed for **34**, thus indicating loss of the inequivalence that was generated by the presence of the methyl group on the bridging carbon in the parent. An X-ray crystallographic determination of **34** showed it to be a chloride-bridged diplatinum(II) complex of the new bis(phosphano)methanide ligand $\{[(CF_3)_2P]_2CCH_3\}^-$ (Figure 4). Since the reaction proceeds readily almost 60 °C below the melting point of **34**, we suspect that loss of HCl occurs by an intermolecular process in the solid state summarized by eq 2.



(2)

Chelating bis(phosphano)methanides of many metals are known.[35-37] Typically they have been prepared from reaction of lithium bis(phosphano)methanides and a suitable metal chloride in THF or diethyl ether solution at low temperatures. Alternatively Bu^{n}Li and NaH have been shown to cleanly deprotonate chelated dppm on Pt(II)[38] (eq 3). **34** is the first structurally characterized example of a class of compound first prepared by Issleib and coworkers in 1970[37] that proved difficult to characerize fully because of solubility problems. Similarly **34** was insufficiently soluble for a ^{31}p NMR spectrum to be recorded.



(3)

Table VI. Selected Interatomic Angles (deg) of **34**[a]

Cl–Pt–P1	171.60 (8)	Pt–P2–C5	114.5 (4)
Cl′[b]–Pt–P1	103.22 (8)	Pt–P2–C6	116.4 (4)
Cl–Pt–P2	103.27 (8)	C1–P2–C5	114.7 (5)
Cl′[b]–Pt–P2	171.58 (8)	C1–P2–C6	112.9 (5)
P1–Pt–P2	68.36 (8)	C5–P2–C6	100.1 (7)
Pt–P1–C1	98.7 (3)	P1–C1–P2	93.9 (4)
Pt–P1–C3	115.8 (3)	P1–C1–C2	131.9 (8)
Pt–P1–C4	115.8 (3)	P2–C1–C2	134.2 (8)
C1–P1–C3	114.3 (5)	Cl–Pt–Cl′[b]	85.15 (7)
C1–P1–C4	113.5 (4)	Pt–Cl–Pt′[c]	94.85 (8)
C3–P1–C4	99.6 (5)	P–C–F	111.1 (29) av
Pt–P2–C1	99.0 (3)	F–C–F	107 (3) av

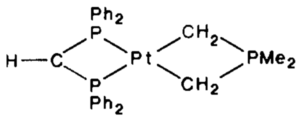
[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cl′ is the chloride trans to P2. [c] Pt′ is related to Pt by the center of symmetry.

Table VII. Intraannular Torsion Angles (deg) of **34**[a]

P2–Pt–P1–C1	−1.06 (0.57)
P1–Pt–P2–C1	1.07 (0.58)
Pt–P1–C1–P2	1.30 (0.70)
Pt–P2–C1–P1	−1.29 (0.69)

[a] Estimated standard deviations in parentheses.

Selected bond lengths and angles and intramolecular torsion angles of **34** are provided in Tables V–VII, respectively. Molecules of **34** are centrosymmetric (Figure 4), and the atoms of both chelate rings, the central Pt_2Cl_2 ring, and the terminal methyl carbons are virtually coplanar. The P(1)–C(1)–P(2) and P(1)–Pt–P(2) bond angles of 93.9 (4) and 68.36 (8)° differ little with respect to similar angles in $[Pt\{(Ph_2P)_2CH\}\{Me_2P(CH_2)_2\}]$ (**39**), 95 (1) and 69.6 (2)°,[36] $[PtCl(PEt_3)\{(Ph_2P)_2CH\}]$ (**40**), 98.6 (5) and 69.65 (8)°, [38] and $[Pt\{(Ph_2P)_2CH\}_2]$ (**41**), 99.4 (1) and 69.1 (1),[39] or for that matter in the dppm complex $[PtPh_2\{(Ph_2P)_2CH_2\}]$ (**42**), 95 and 73°.



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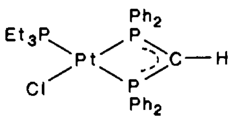

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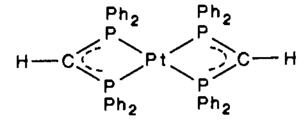

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The relative shortness of P(1)–C(1) (1.708 (8) Å) and P(2)–C(1) (1.686 (8) Å) when compared to other bis(phosphano)methanide chelate containing complexes, viz **39** (1.756 (17) Å),[36] **40** (1.72 Å)[38] and $[Sn\{(Me_2P)_3C\}_2]$ (**43**) (1.747 (2) Å),[35]

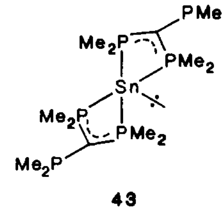

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Table VIII. NMR Spectroscopic Parameters of $\{Mo(CO)_4(L\frown L)\}$[a]

	σ_P[b]	$J_{P,P}$, Hz	$\delta_{C,F}$[c]	$\lvert{}^1J_{P,F} + {}^4J_{P,F}\rvert$, Hz	δ_H[d]
$[Mo(CO)_4(\mathbf{1})]$ (**35**)	+88.7[e]	13.1	−60.6	77.5[e]	2.39[h]
$[Mo(CO)_4(\mathbf{2})]$ (**36**)	+82.6 (m)	17.2	−55.4 ("d", CF_3)[f]	85.1	
			−124.4 ("d" of m, CF_2)[g]	49.3	
$[Mo(CO)_4(\mathbf{24})]$ (**37**)	+65.5[e]	19.6	−60.8	72.6[e]	2.50 (m, CH_2CH_2P) 2.12 (s, CH_2P)

[a] Recorded for $CDCl_3$ solutions at +25 °C. [b] Relative to 85% H_3PO_4(aq) at 161.9 MHz; positive shifts are to high frequency of the reference. [c] Relative to $CFCl_3$ at 376.5 MHz; negative shifts are to low frequency of the reference. [d] Relative to TMS at 300 MHz; positive shifts are to high frequency of standard. [e] These signals are the X(F) and A(P) parts respectively of $X_6AAX'_6$ spin systems (J(XX')0).[27] [f] This signals is a complex doublet reminiscent of the that of free ligand. [g] This is a second-order doublet of multiplets; estimated $^4J_{F,F}$ = 5.5 Hz. [h] $\lvert{}^2J_{P,H} + {}^3J_{P,H}\rvert$ = 15.0 Hz for an AXX′X″X‴A′ spin system.[26]

clearly indicates a marginally greater degree of ylidic character in the chelate P–C bonds of **34**. While the other P–C bonds within the molecule are much longer (average 1.89 (2) Å) they compare favorably with the $P-CF_3$ bond length of **22**, 1.869 (16) Å.[5] The multiple P–C bonds of $CF_3P{=}CF_2$ (1.690 (5) Å, gas-phase electron diffraction)[41] and (mesityl)$P{=}CPh_2$[42] (1.692 (3) Å) are only slightly shorter than the average length of the P–C(1) bonds of **34**.

The Pt–P bond lengths in **34** (2.212 (2) and 2.202 (2) Å), while much shorter than those in **39** (2.276 (5) Å)[36] or in **40** (2.317 (2) Å trans to PEt_3, 2.317 (2) Å trans to Cl)[38] are longer than the $(CF_3)_2P-Pt$ bond of **22** (2.168 (3) Å).[6] Clearly, in **34**, the Pt–P bonds are normal for single bonds with perfluoroalkyl-substituted phosphorus donors. The shortening arises from the enhancement of π-back-donation from Pt(II) to P by the CF_3 substituents, which has been recognized elsewhere.[5,6,43]

The Pt–Cl bond lengths of **34** (2.383 (2) and 2.382 (2) Å) though longer for Cl trans to Cl in *trans*-$[Pt_2Cl_2(\mu\text{-}Cl)_2L_2]$ (L = PR_3, AsR_3) (2.312 (5)–2.342 (5) Å)[44] are comparable to those measured for Cl trans to PR_3 in the same complexes (2.393 (1) to 2.425 (8) Å).[44]

Molybdenum Carbonyl Complexes of the Bis(phosphano)alkanes. Bis(phosphanes) **1**, **2**, and **24** react sluggishly with *cis*-$[Mo(CO)_4(piperidine)_2]$ in refluxing chloroform to give compounds **35**–**37**, which could only be isolated in indifferent yields on a small scale. Solution molecular weights and microanalyses for **35** and **37** are consistent with the formula $[Mo(CO)_4(L\frown L)]$ ($L\frown L$ = **1**, **24**). The carbonyl stretching frequencies of all three compounds are comparable with published data for *cis*-$[Mo(CO)_4\{RP(CF_3)_2\}]$ (R = H, halide, SCN, NMe_2).[45] We therefore assign monomeric chelate bis(phosphane) structures to **35**–**37**. Evidence of the direct increase in π-acidity of the bis(phosphano)alkane chelates with respect to increasing fluorine substitution is apparent in the relative CO stretching frequencies of compounds **35** and **36**. A more striking comparison can be made between the fully protonated analogues of **35** and **37**, $[Mo(CO)_4\{(CH_3)_2P(CH_2)_nP(CH_3)_2\}]$ (n = 2 (**44**), n = 3 (**45**),[46] whose CO stretching bands are between 40 and 60 cm^{-1} below the same bands in **35** and **37**, respectively. While **35** and **37** melt close to 100 °C, **26** (the perfluorinated analogue of **35**) melts at room temperature. A similar effect may be responsible for the increased solubility of **29** relative to **28**.

^{19}F NMR spectra of **35**–**37** consistently show a shift of ~5 ppm to low frequency with coordination of the $P(CF_3)_2$ fluorine resonances. The backbone ^1H and ^{19}F NMR resonances of **35** and **36**, respectively, more closely approximate doublet structures, thus indicating a decrease in the magnitude of $\lvert J_{P,P}\rvert$[27] with coordination as was similarly observed in **28** and **29**. Estimates of $J_{P,P}$ in **1** and **35** are respectively 41.2 and 13.1 Hz. Complexation of **24** to $Mo(CO)_4$ on the other hand leads to an increase in $J_{P,P}$ from ~2 to 19.6 Hz. As expected the shifts of phosphorus in ^{31}P NMR spectra of **35**–**37** are greatly deshielded with respect to those of the free ligands (Table VIII).[47]

During preliminary investigations of the reaction of **25** and **26** with *cis*-$[Mo(CO)_4(piperidine)_2]$ in refluxing chloroform, we observed incomplete reaction after 1 h. With prolonged reflux times, decomposition ensued to give the free ligands, CO, and the same unidentified Mo–piperidine complex. In neither case were the major products of incomplete reaction isolated or identified with confidence. The formation of *cis*- or *trans*-$[Mo(CO)_4(piperidine)\{\eta^1\text{-}(CF_3)_2PCHRP(CF_3)_2\}]$ (R = H or CH_3, respectively) is strongly suspected, but more work is needed to clarify the situation.

Further studies are planned to investigate the reactivities of the reported compounds and to expand the coordination chemistry of (trifluoromethyl)bis(phosphano)alkanes to other metal systems.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. **1**, 1535-30-4; **2**, 1991-44-2; **24**, 116531-60-3; **25**, 116531-61-4; **26**, 116531-62-5; **27**, 116531-63-6; **28**, 116564-27-3; **29**, 116564-28-4; **30**, 116564-29-5; **31**, 116564-30-8; **32**, 116564-31-9; **34**, 116595-88-1; **35**, 116564-32-0; **36**, 116564-33-1; **37**, 116564-34-2; $(CF_3)_2PP(CF_3)_2$, 2714-60-5; $CH(CH_3)I_2$, 594-02-5; $IC(CH_3)_2I$, 630-13-7; $[PtCl_2(PhCN)_2]$, 14873-63-3; *cis*-$[Mo(CO)_4(piperidine)_2]$, 65337-26-0; $I(CH_2)_4I$, 628-21-7; $(CF_3)_2P(CH_2)_4P(CF_3)_2$, 116531-64-7; $I(CH_2)_5I$, 55930-45-5; $(CF_3)_2P(CH_2)_5P(CF_3)_2$, 116531-65-8; $(CF_3)_2PCH(Ph)P(CF_3)_2$, 116531-66-9; $[(CF_3)_2P]_3CH$, 116531-67-0; CH_2I_2, 75-11-6; IC_2F_4I, 354-65-4; α,α-diiodotoluene, 28000-59-1; iodoform, 75-47-8.

Supplementary Material Available: Complete listing of crystallographic data (Table I-S), listings of anisotropic and equivalent isotropic thermal parameters (Table IX), rms amplitudes of thermal vibrations (Table X), and derived positional parameters of H atoms (Table XI), expanded lists of interatomic distances (Table XII) and angles (Table XIII), and a table of torsional angles (Table XIV) (6 pages); a list of calculated and observed structure factors (Table XV) (18 pages). Ordering information is given on any current masthead page.

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