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1,2-Bis{bis[4-(trifluoromethyl)phenyl]-phosphino}ethane

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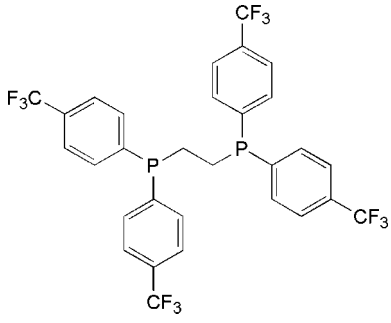
Key indicators: single-crystal X-ray study; T = 208 K; mean σ(C–C) = 0.004 Å; R factor = 0.061; wR factor = 0.162; data-to-parameter ratio = 15.5.

Crystals of the title compound, $C_{30}H_{20}F_{12}P_2$ or R_2PCH_2-CH_2PR_2 (R = 4-$C_6H_4CF_3$), were inadvertently prepared while attempting to recrystallize a crude sample of *trans*-$Re(Cl)(N_2)(R_2PCH_2CH_2PR_2)_2$ from diethyl ether. The molecule lies on a center of inversion. One of the rings lies approximately in the P—C—C—P plane; the dihedral angle is 174.53°.The other ring is not quite perpendicular; the dihedral angle is 71.1°. The compound is isostructural with the R = Ph, 4-$C_6H_4CH_3$ and 4-$C_6H_4CH_2CH_3$ analogues. It is well known that the basicity of phosphines and diphosphines can be altered by changing the electron-donating ability of R; however, the structural parameters for the title compound do not significantly differ from those of the aforementioned substituted-phenyl compounds.

Related literature

For the synthesis of the title compound, see: Chatt *et al.* (1985). For the crystal structures of similar 1,2-bis(diphenylphosphino)ethane structures, see: Tiekink (2001); Zeller *et al.* (2003); Zeller & Hunter (2004). For related literature, see: Allman & Goel (1982); Larson (1970); Nordwig *et al.* (2006); Streuli (1960); Tolman (1970).



Experimental

Crystal data

$C_{30}H_{20}F_{12}P_2$
M_r = 670.41
Monoclinic, $P2_1/n$
a = 15.188 (11) Å
b = 5.402 (4) Å
c = 18.123 (13) Å
β = 99.044 (9)°
V = 1468.3 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 208 K
0.40 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
T_{min} = 0.91, T_{max} = 0.98
9947 measured reflections
3240 independent reflections
2616 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.162
S = 0.95
3229 reflections
208 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2196).

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1,2-Bis{bis[4-(trifluoromethyl)phenyl]phosphino}ethane

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S1. Comment

1,2-Bis{bis[4-(trifluoromethyl)phenyl]phosphino}ethane was obtained accidently during the recrystallization of *trans*-Re(Cl)(N_2)($R_2PCH_2CH_2PR_2$)$_2$[*R* = 4-Ph—CF_3] from diethyl ether. We were interested in preparing this complex in order to measure its luminescent properties and then compare them to those for the analogous *R* = Ph, 4-Ph-OCH_3, and CH_2CH_3 complexes. Our preliminary results indicate that these complexes show simultaneous emission from two excited levels of different orbital parentage. Our intent is to investigate how changes in diphosphine basicity brought about by variations in *R* influence the bandshape and lifetimes of these emissions thereby allowing us to assign the excited states responsible for luminescence.

The title compound resides on a center of inversion. It is isostructural to its *R* = Ph, 4-Ph—CH_3, and 4-Ph—CH_2CH_3 analogues. It is well known that the basicity of phosphines and diphosphines can be altered by changing the electron donating ability of *R*; however, the structural parameters for the title compound do not significantly differ from the aforementioned phenyl substituted compounds.

A summary of the C—P bond distances, C—P—C bond angles, and sums of the C—P—C angles is given in Table 1 for this work and several related diphosphines that contain aromatic and aliphatic substituents. The title compound has nearly identical geoemtric parameters about phosphorus as the other phenyl diphosphines and there appears to be no experimentally significant trends that parallel the electron donating ability of the *para*-substituent, which follows the order CH_3CH_2> CH_3> H > CF_3 (Nordwig *et al.*, 2006; Allman & Goel, 1982; Tolman, 1970; Streuli, 1960). The aromatic diphosphines display Σ C—P—C values of about 303.5° which indicates a pyramidal arrangement of the bonds about phosphorus. The aliphatic diphosphines are more electron donating with the less sterically demanding *R* = CH_3 and CH_2CH_3 cases giving rise to lower ΣC—P—C values. The *R* = $CH(CH_3)_2$ and $C(CH_3)_3$ compounds display larger ΣC—P—C values and longer C—P bond distances due to increased space requirements for these bulkier substituents. Substituent effects for the alkyl substituted compounds have been discussed previously (Bruckmann & Kruger, 1997; Eisentrager *et al.*, 2003).

One of the rings lines approximately in the P—C—C—P plane; the dihedral angle is 174.53°.The other ring is not quite perpendicular; the dihedral angle is 71.1°.

S2. Experimental

A non-crystalline sample of $R_2PCH_2CH_2PR_2$ [*R* = 4-Ph—CF_3] and a crude sample of *trans*-Re(Cl)(N_2)($R_2PCH_2CH_2PR_2$)$_2$ [*R* = 4-Ph—CF_3] were prepared according to previously reported methods (Chatt, *et al.*, 1985). Crude *trans*-Re(Cl)(N_2)($R_2PCH_2CH_2PR_2$)$_2$ was dissolved in a minimum of diethyl ether at 20° C. The yellow-orange solution was filtered and ether was gradually evaporated by passing a slow stream of nitrogen gas through the flask. A mixture of microcrystalline orange solid and pale yellow-orange crystals formed over the course of 4 h. A pale crystal from this mixture was analyzed.

S3. Refinement

Reflections (11) in the vicinity of the beam stop, with [sin θ/λ] ^{2} < 0.01, were eliminated from the refinement.

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for aromatic H atoms and 0.96 Å for methylene H atoms, and with U_{iso}(H) = 1.2 U_{eq} (C). An extinction correction (Larson, 1970) was applied.

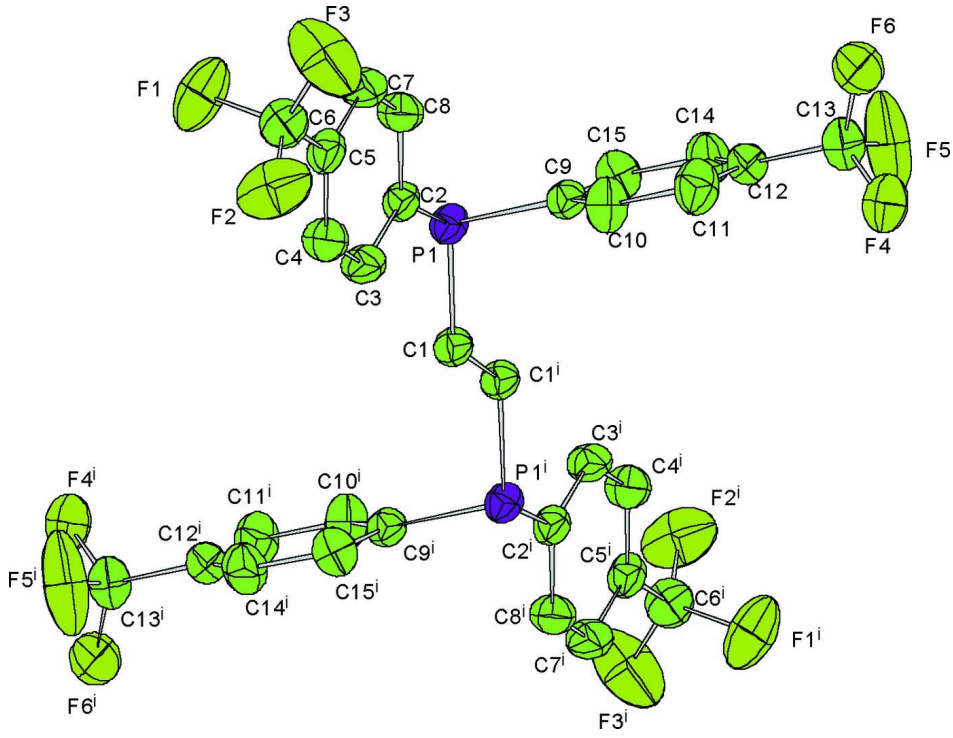

Figure 1

The title compound with displacement ellipsoids drawn at the 50% probability level. Symmetry code: i = -*x* + 2, -*y* + 2, -*z*.

1,2-Bis{bis[4-(trifluoromethyl)phenyl]phosphino}ethane

Crystal data

$C_{30}H_{20}F_{12}P_2$
M_r = 670.41
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 15.188 (11) Å
b = 5.402 (4) Å
c = 18.123 (13) Å
β = 99.044 (9)°
V = 1468.3 (19) Å^3
Z = 2
F(000) = 676
D_x = 1.516 Mg m^{-3}
Melting point: 471 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4592 reflections
θ = 2.3–27.2°
μ = 0.25 mm^{-1}
T = 208 K
Block, colorless
0.40 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
T_{min} = 0.91, T_{max} = 0.98
9947 measured reflections
3240 independent reflections

2616 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 27.2°$, $\theta_{min} = 1.6°$
$h = -19 \rightarrow 19$
$k = -4 \rightarrow 6$
$l = -23 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.162$
$S = 0.95$
3229 reflections
208 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.07P)^2 + 1.82P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: Larson (1970), Equation 22
Extinction coefficient: 100 (30)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	1.27583 (17)	0.8551 (5)	0.42720 (14)	0.0973
F2	1.22595 (19)	0.5004 (4)	0.40090 (12)	0.0933
F3	1.15394 (18)	0.7552 (7)	0.45867 (12)	0.1188
F4	0.58890 (16)	0.7965 (6)	0.11270 (19)	0.1126
F5	0.56328 (18)	1.1552 (8)	0.0760 (3)	0.1601
F6	0.59438 (18)	1.0822 (8)	0.19080 (19)	0.1525
C1	1.02538 (17)	0.9577 (5)	0.03782 (13)	0.0376
C2	1.06731 (16)	1.0281 (5)	0.19636 (13)	0.0366
C3	1.12029 (18)	0.8196 (5)	0.19746 (14)	0.0432
C4	1.16363 (19)	0.7219 (6)	0.26452 (15)	0.0474
C5	1.15250 (17)	0.8323 (5)	0.33151 (14)	0.0422
C6	1.1999 (2)	0.7337 (7)	0.40384 (16)	0.0566
C7	1.0996 (2)	1.0400 (6)	0.33167 (15)	0.0501
C8	1.05801 (19)	1.1393 (6)	0.26470 (15)	0.0466
C9	0.89383 (17)	1.1273 (5)	0.11969 (14)	0.0375
C10	0.8645 (2)	0.9282 (6)	0.15831 (18)	0.0531
C11	0.7744 (2)	0.8957 (7)	0.16050 (19)	0.0600
C12	0.71295 (19)	1.0603 (6)	0.12370 (17)	0.0530
C13	0.6158 (2)	1.0234 (9)	0.1269 (3)	0.0781
C14	0.7406 (2)	1.2566 (7)	0.08562 (19)	0.0587
C15	0.83094 (19)	1.2916 (6)	0.08420 (17)	0.0488
P1	1.01119 (4)	1.18369 (12)	0.11177 (3)	0.0363
H11	1.0876	0.9429	0.0344	0.0451*
H12	1.0028	0.7998	0.0503	0.0451*
H31	1.1270	0.7433	0.1527	0.0513*
H41	1.2006	0.5845	0.2647	0.0539*
H71	1.0918	1.1122	0.3768	0.0578*
H81	1.0232	1.2810	0.2648	0.0543*
H101	0.9059	0.8154	0.1819	0.0610*

H111	0.7548	0.7643	0.1868	0.0685*
H141	0.6989	1.3674	0.0614	0.0680*
H151	0.8499	1.4260	0.0587	0.0563*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0832 (16)	0.114 (2)	0.0773 (15)	−0.0152 (14)	−0.0410 (12)	0.0092 (14)
F2	0.135 (2)	0.0749 (15)	0.0578 (13)	0.0188 (14)	−0.0231 (13)	0.0109 (11)
F3	0.0998 (19)	0.211 (3)	0.0491 (12)	0.057 (2)	0.0224 (12)	0.0483 (17)
F4	0.0612 (14)	0.128 (2)	0.155 (3)	−0.0417 (15)	0.0383 (15)	−0.065 (2)
F5	0.0438 (14)	0.213 (4)	0.219 (4)	0.0033 (19)	0.0043 (19)	0.058 (3)
F6	0.0792 (17)	0.252 (4)	0.143 (3)	−0.069 (2)	0.0692 (18)	−0.128 (3)
C1	0.0375 (12)	0.0447 (14)	0.0301 (12)	−0.0025 (11)	0.0036 (9)	−0.0012 (10)
C2	0.0352 (12)	0.0416 (13)	0.0321 (11)	−0.0035 (10)	0.0022 (9)	−0.0015 (10)
C3	0.0476 (14)	0.0499 (15)	0.0306 (12)	0.0024 (12)	0.0015 (10)	−0.0059 (11)
C4	0.0480 (15)	0.0504 (16)	0.0419 (14)	0.0086 (12)	0.0012 (11)	−0.0001 (12)
C5	0.0368 (13)	0.0543 (16)	0.0338 (12)	−0.0062 (11)	0.0003 (10)	0.0016 (11)
C6	0.0545 (17)	0.076 (2)	0.0371 (14)	0.0052 (16)	−0.0006 (13)	0.0024 (14)
C7	0.0527 (16)	0.0644 (19)	0.0323 (13)	0.0042 (14)	0.0036 (11)	−0.0087 (12)
C8	0.0488 (15)	0.0506 (16)	0.0396 (14)	0.0089 (12)	0.0043 (11)	−0.0060 (12)
C9	0.0380 (12)	0.0408 (13)	0.0330 (12)	−0.0019 (10)	0.0041 (10)	−0.0020 (10)
C10	0.0447 (15)	0.0549 (18)	0.0584 (17)	−0.0033 (13)	0.0041 (13)	0.0165 (14)
C11	0.0525 (17)	0.066 (2)	0.0627 (19)	−0.0154 (15)	0.0142 (15)	0.0084 (16)
C12	0.0403 (14)	0.068 (2)	0.0514 (16)	−0.0054 (14)	0.0108 (12)	−0.0176 (15)
C13	0.0438 (18)	0.106 (3)	0.087 (3)	−0.011 (2)	0.0157 (18)	−0.029 (2)
C14	0.0437 (16)	0.067 (2)	0.0638 (19)	0.0105 (15)	0.0027 (14)	0.0007 (16)
C15	0.0469 (15)	0.0491 (16)	0.0507 (16)	0.0045 (13)	0.0090 (12)	0.0101 (13)
P1	0.0368 (4)	0.0389 (4)	0.0320 (3)	−0.0041 (3)	0.0022 (2)	0.0012 (2)

Geometric parameters (Å, º)

F1—C6	1.336 (4)	C2—C3	1.383 (4)
F2—C6	1.324 (4)	C2—C8	1.403 (4)
F3—C6	1.307 (4)	C2—P1	1.836 (3)
F4—C13	1.305 (5)	C3—C4	1.392 (4)
F5—C13	1.328 (6)	C3—H31	0.930
F6—C13	1.290 (5)	C4—C5	1.387 (4)
H101—C10	0.930	C5—C6	1.492 (4)
H111—C11	0.930	C5—C7	1.380 (4)
H141—C14	0.930	C7—C8	1.385 (4)
H151—C15	0.930	C9—C10	1.394 (4)
H41—C4	0.930	C9—C15	1.386 (4)
H71—C7	0.930	C9—P1	1.836 (3)
H81—C8	0.930	C10—C11	1.386 (4)
C1—C1^{i}	1.533 (5)	C11—C12	1.383 (5)
C1—P1	1.850 (3)	C12—C13	1.499 (5)
C1—H11	0.960	C12—C14	1.367 (5)

C1—H12	0.960	C14—C15	1.389 (4)
C1^{i}—C1—P1	110.6 (2)	C7—C8—H81	119.9
C1^{i}—C1—H11	109.3	C10—C9—C15	118.4 (3)
P1—C1—H11	109.2	C10—C9—P1	123.9 (2)
C1^{i}—C1—H12	109.1	C15—C9—P1	117.7 (2)
P1—C1—H12	109.2	C9—C10—H101	119.3
H11—C1—H12	109.5	C9—C10—C11	120.5 (3)
C3—C2—C8	118.3 (2)	H101—C10—C11	120.2
C3—C2—P1	125.28 (19)	C10—C11—H111	120.6
C8—C2—P1	116.3 (2)	C10—C11—C12	120.0 (3)
C2—C3—C4	121.0 (2)	H111—C11—C12	119.4
C2—C3—H31	119.5	C11—C12—C13	119.3 (3)
C4—C3—H31	119.5	C11—C12—C14	120.3 (3)
C3—C4—H41	120.6	C13—C12—C14	120.4 (3)
C3—C4—C5	119.7 (3)	C12—C13—F5	112.9 (4)
H41—C4—C5	119.7	C12—C13—F4	113.4 (3)
C4—C5—C6	120.5 (3)	F5—C13—F4	103.3 (4)
C4—C5—C7	120.2 (2)	C12—C13—F6	113.0 (3)
C6—C5—C7	119.3 (3)	F5—C13—F6	106.4 (4)
C5—C6—F1	112.1 (3)	F4—C13—F6	107.0 (4)
C5—C6—F2	114.2 (3)	H141—C14—C12	119.8
F1—C6—F2	103.4 (3)	H141—C14—C15	120.4
C5—C6—F3	113.2 (3)	C12—C14—C15	119.8 (3)
F1—C6—F3	104.7 (3)	C14—C15—C9	121.0 (3)
F2—C6—F3	108.3 (3)	C14—C15—H151	119.9
C5—C7—H71	119.8	C9—C15—H151	119.1
C5—C7—C8	119.9 (3)	C1—P1—C2	102.20 (13)
H71—C7—C8	120.3	C1—P1—C9	99.93 (12)
C2—C8—C7	120.8 (3)	C2—P1—C9	100.83 (13)
C2—C8—H81	119.3		
C2—P1—C1—C1^{i}	174.53 (18)	C7—C5—C6—F2	160.7 (3)
C9—P1—C1—C1^{i}	71.1 (2)	C4—C5—C6—F3	−146.1 (3)
C2—P1—C9—C10	−25.8 (3)	C7—C5—C6—F1	−82.2 (3)
C1—P1—C2—C3	11.2 (3)	C7—C5—C6—F3	36.0 (4)
C9—P1—C2—C3	113.9 (2)	C5—C7—C8—C2	1.4 (5)
C1—P1—C2—C8	−171.8 (2)	P1—C9—C10—C11	−178.7 (2)
C9—P1—C2—C8	−69.1 (2)	C15—C9—C10—C11	0.4 (4)
C1—P1—C9—C15	−100.4 (2)	P1—C9—C15—C14	177.9 (2)
C1—P1—C9—C10	78.8 (3)	C10—C9—C15—C14	−1.3 (4)
C2—P1—C9—C15	155.1 (2)	C9—C10—C11—C12	0.5 (5)
P1—C1—C1^{i}—P1^{i}	179.98 (16)	C10—C11—C12—C13	−179.7 (4)
P1—C2—C3—C4	176.8 (2)	C10—C11—C12—C14	−0.6 (5)
C3—C2—C8—C7	−1.1 (4)	C11—C12—C13—F4	−47.9 (5)
C8—C2—C3—C4	−0.1 (4)	C11—C12—C13—F5	−165.0 (4)
P1—C2—C8—C7	−178.4 (2)	C11—C12—C13—F6	74.1 (5)
C2—C3—C4—C5	1.1 (4)	C14—C12—C13—F4	133.0 (4)

C3—C4—C5—C7	−0.8 (4)	C14—C12—C13—F5	15.8 (6)
C3—C4—C5—C6	−178.7 (3)	C14—C12—C13—F6	−105.0 (5)
C4—C5—C6—F1	95.7 (4)	C11—C12—C14—C15	−0.3 (5)
C4—C5—C6—F2	−21.5 (4)	C13—C12—C14—C15	178.8 (3)
C4—C5—C7—C8	−0.4 (4)	C12—C14—C15—C9	1.3 (5)
C6—C5—C7—C8	177.5 (3)		

Symmetry code: (i) −*x*+2, −*y*+2, −*z*.