C11—N1—C12	114.4 (3)	C1—C10—C5	118.6 (4)
C2—C1—C10	119.9 (3)	C1—C10—C9	124.5 (4)
C2—C1—C11	118.9 (3)	C5—C10—C9	116.9 (4)
C10—C1—C11	121.2 (3)	P1—C11—N1	112.8 (2)
O1—C2—C1	118.2 (3)	P1—C11—C1	112.5 (3)
O1—C2—C3	120.7 (4)	N1—C11—C1	112.3 (3)
C1—C2—C3	121.1 (4)	N1—C12—C13	110.7 (3)
C2—C3—C4	119.7 (4)	O2—C13—C12	107.8 (4)
C3—C4—C5	121.8 (4)	O5—C14—C15	111.1 (4)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H12···O3^{i}	0.810	1.998	2.761 (4)	157.06
O1—H1···O4^{ii}	0.819	1.716	2.529 (3)	171.63
O2—H2···O3^{iii}	0.830	1.996	2.789 (5)	160.83

Symmetry codes: (i) $2-x, -y, 2-z$; (ii) $x-1, y, z$; (iii) $1-x, -y, 2-z$.

All non-H atoms were refined with anisotropic displacement parameters. The H atoms of the naphthyl group were placed geometrically 0.95 Å from their corresponding C atoms, while other H atoms were taken from a $\Delta\rho$ map. For all H atoms a riding model was used with $U_{\rm iso}(\rm H) = 1.3U_{\rm eq}(\rm C, N, O)$.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1384). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Aguilar, M., Miralles, N. & Sastre, M. A. (1989). *Rev. Inorg. Chem.* **10**, 93–119.

Assche, I. van, Soroka, M., Haemers, A., Hooper, M., Blanot, D. & van Heijenoort, J. (1991). *Eur. J. Med. Chem.* **26**, 505–515.

Cameron, D. G., Hudson, H. R. & Pianka, M. (1993). *Phosphorus Sulfur Silicon*, **83**, 21–37.

Choi, N., Failla, S., Finocchiaro, P., McPartlin, M. & Scowen, I. J. (1994). *J. Chem. Res.* (*S*), pp. 340–341.

Enraf–Nonius (1993). *CAD*-4 *Express Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Gibson, D. & Karaman, R. (1989). *Inorg. Chem.* **28**, 1928–1932.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lavielle, G., Hautefaye, P., Schaeffer, C., Boutin, J. A., Cudennec, C. A. & Pierré, A. (1991). *J. Med. Chem.* **34**, 1998–2003.

Toroš, Z. R., Prodić, B. K. & Šljukić, M. (1978). *Acta Cryst.* B**34**, 3110–3113.

Acta Cryst. (1996). C**52**, 3135–3138

1-Diphenylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12)

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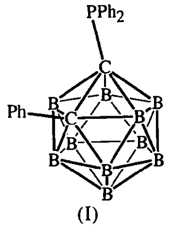
Abstract

The two crystallographically independent molecules of the title compound, 1-[$(C_6H_5)_2P$]-2-C_6H_5-1,2-$C_2B_{10}H_{10}$ ($C_{20}H_{25}B_{10}P$), in the asymmetric fraction of the unit cell are highly congruent. The conformation of the cage phenyl groups is defined by θ = 1.15° and the average C1—C2 distance is 1.744 (8) Å, which is significantly longer than that usually found for 1,2-$C_2B_{10}H_{10}$ compounds. The PPh_2 substituent is tilted away from an idealized radial position on C1 as a result of intramolecular crowding.

Comment

1-Diphenylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12), (I), is an exceptionally stable compound with the potential for extensive derivatization of both the phosphine moiety and the carborane polyhedron. It was synthesized and characterized in order to extend the series of structural determinations of carboryl phosphines (Kivekäs, Sillanpää, Teixidor, Viñas & Nuñez, 1994; Kivekäs, Teixidor, Viñas & Nuñez, 1995) and also to establish a structural basis for its subsequent use as a carborane-containing ligand (Reid, 1992).



(I)

There are two crystallographically independent molecules in the asymmetric fraction of the unit cell. A perspective view of one molecule (atom labels unprimed) is shown in Fig. 1 and Table 2 lists selected geometric parameters. There is a high degree of congruence between the two independent molecules, with no equivalent parameters differing by greater than 3σ. Consequently, average values are quoted hereafter.

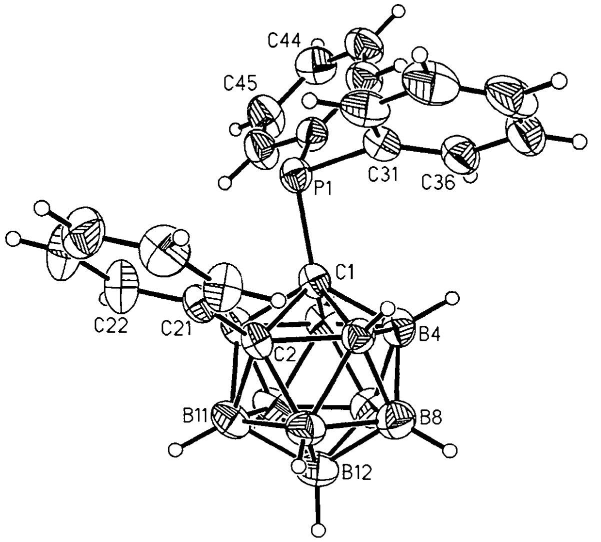


Fig. 1. The molecular structure of (I) shown with 40% probability displacement ellipsoids for non-H atoms. The cage numbering scheme can be seen in this and Fig. 2. The phenyl ring C atoms are numbered in sequence.

The C_2B_{10} cage has the expected near icosahedral geometry. The conformation of the phenyl substituent at C2 is described by a θ value of 1.15° (θ is defined as the modulus of the average $C_{Ph}—C_{Ph}—C_{cage}—C_{cage}$ torsion angle; Cowie, Reid, Watmough & Welch, 1994) and thus the phenyl ring is face-on to the phosphine substituent in order to minimize interactions arising from the bulky PPh_2 substituent at C1. We have shown previously (Brain *et al.*, 1996) that the C1—C2 distance in icosahedral carboranes is sensitive to θ, with low θ values contributing to weak C1—C2 bonding (Lewis & Welch, 1993). In the present compound, C1—C2 is 1.744 (8) Å, which is 0.042 (10) Å longer than the corresponding value in $1\text{-}PPh_2\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10}$ (Kivekäs *et al.*, 1994) and 0.078 (12) Å longer than in $1\text{-}PPh_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ (Kivekäs *et al.*, 1995). Normally in undistorted 1,2-dicarboranes $C—C < C—B < B—B$ (Thomas, Rosair & Welch, 1996). In the title compound, the average C1—C2 bond is extended beyond the limit of C—B distances [1.692 (7)–1.739 (7) Å], while remaining below the range of B—B distances [1.753 (8)–1.801 (9) Å].

The P—C1 distance [1.876 (7) Å] compares well with that found in $1\text{-}PPh_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ [1.871 (6) Å; Kivekäs *et al.*, 1995] and that in $1\text{-}PPh_2\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10}$ [1.888 (4) Å; Kivekäs *et al.*, 1994]. Moreover, the similarity between these three compounds extends to a pronounced deformation of the PPh_2 substituent away from an ideal radial position on C1, resulting in a wide range of $P1—C1—C_{cage}$ angles, from 111.6 (6) (P1—C1—C2) to 130.0 (5)° (P1—C1—B4). Previously, this deformation has been ascribed to intramolecular steric congestion between cage and PPh_2 fragments (Kivekäs *et al.*, 1994). The title molecule as viewed along the C1···B12 vector is shown in Fig. 2 and it is clear that the H5 and H3 atoms lie under the phosphine-bound phenyl rings. Ring plane-to-H atom distances are 2.72 and 2.79 Å, and are at the limit of the sum of the van der Waals radii for hydrogen and an aromatic ring, even using the lowest accepted value (1.0 Å) of the former.

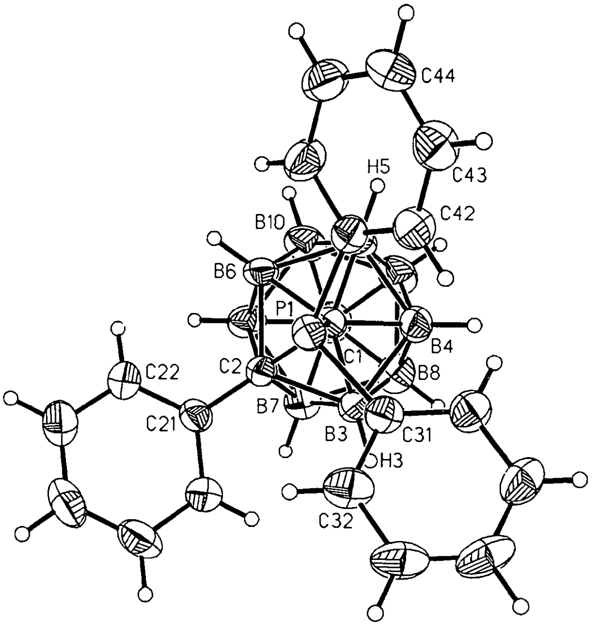


Fig. 2. A view down the C1···B12 vector showing the distortion of the phosphine away from the radial position at C1.

Inspection of Fig. 2 also suggests that the lone pair of electrons on the P atom lies above the B6—C2 connectivity, displaced towards the latter. The stereochemical consequences of utilizing this lone pair of electrons in coordination to metal fragments will be the subject of future contributions.

Experimental

For the preparation of (I), 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ (Brain *et al.*, 1996) (1.00 g, 4.54 mmol) was dissolved in diethyl ether (20 ml) under a dry nitrogen atmosphere and cooled to 273 K. MeLi (5 mmol, 3.6 ml of a 1.4 *M* solution in diethyl ether) was added dropwise and the resulting solution allowed to warm to room temperature with stirring over a period of 30 min. PPh_2Cl (1.10 g, 0.89 ml, 5 mmol) was added dropwise to the stirred mixture, resulting in the formation of a white precipitate. The mixture was stirred for a further 30 min, then filtered through silica (2 cm). Volatiles were removed *in vacuo*, affording a white adhesive solid. This was triturated with *n*-pentane and dried *in vacuo*, resulting in a dry white powder (1.54 g, 84%). Crystals were grown by slow evaporation of an *n*-pentane solution at room temperature. Analysis calculated for $C_{20}H_{25}B_{10}P$: C 59.4, H 6.23%; found: C 59.4, H 6.62%. FTIR (CH_2Cl_2): ν = 2605 cm^{-1} (B—H). ^{1}H FTNMR (400.1 MHz, $CDCl_3$, 293 K, TMS): δ (p.p.m.) 7.85–7.15 (*m*, Ar—H). ^{11}B-{^{1}H} FTNMR (128.4 MHz, $CDCl_3$, 293 K, $BF_3.Et_2O$): δ (p.p.m.) 3.04 (1B), 0.36 (1B), −5.81 (8B). ^{31}P-{^{1}H} FTNMR (162.0 MHz, $CDCl_3$, 293 K, H_3PO_4): δ (p.p.m.) 12.66 (*s*). MS (FAB, Noba) parent ion: 407. NMR spectra were recorded on a Brüker DPX400 spectrometer, the IR spectrum on a Nicolet Impact 400 spectrophotometer and the mass spectrum on a VG/MS9 spectrometer.

Crystal data

$C_{20}H_{25}B_{10}P$
M_r = 404.47
Monoclinic
$P2_1/c$
a = 23.896 (2) Å
b = 10.608 (4) Å
c = 20.173 (3) Å
β = 114.218 (6)°
V = 4663.7 (17) Å^3
Z = 8
D_x = 1.152 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 5.56–23.13°
μ = 0.124 mm^{-1}
T = 293 (2) K
Block
0.30 × 0.25 × 0.20 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scans (*SHELXTL*; Sheldrick, 1994)
T_{min} = 0.823, T_{max} = 0.872
9893 measured reflections
8127 independent reflections
3636 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.059
θ_{max} = 25°
$h = -28 \rightarrow 26$
$k = -12 \rightarrow 1$
$l = -1 \rightarrow 23$
3 standard reflections monitored every 97 reflections intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0689
$wR(F^2)$ = 0.1810
S = 0.988
8122 reflections
559 parameters
H atoms riding with C—H 0.93, B—H 1.10 Å and U(H) = 1.2U_{eq}(C/B)

$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.278 e Å^{-3}
$\Delta\rho_{min}$ = −0.233 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P1	0.82304 (6)	0.65246 (14)	0.22525 (7)	0.0436 (3)
C1	0.8837 (2)	0.7729 (5)	0.2748 (3)	0.0404 (11)
C2	0.9351 (2)	0.7150 (5)	0.3594 (3)	0.0420 (12)
B3	0.8835 (2)	0.8331 (6)	0.3545 (3)	0.0438 (13)
B4	0.8778 (3)	0.9326 (6)	0.2811 (4)	0.052 (2)
B5	0.9233 (3)	0.8674 (6)	0.2395 (3)	0.053 (2)
B6	0.9561 (3)	0.7263 (7)	0.2869 (3)	0.0467 (14)
B7	0.9618 (3)	0.8352 (7)	0.4201 (3)	0.0531 (15)
B8	0.9269 (3)	0.9739 (7)	0.3719 (4)	0.062 (2)
B9	0.9522 (3)	0.9941 (7)	0.3005 (4)	0.066 (2)
B10	1.0004 (3)	0.8662 (8)	0.3039 (4)	0.063 (2)
B11	1.0071 (3)	0.7697 (7)	0.3781 (3)	0.054 (2)
B12	1.0032 (3)	0.9350 (8)	0.3854 (4)	0.067 (2)
C21	0.9255 (2)	0.5853 (5)	0.3828 (3)	0.0443 (12)
C22	0.9538 (3)	0.4819 (6)	0.3688 (3)	0.067 (2)
C23	0.9452 (3)	0.3632 (7)	0.3909 (4)	0.081 (2)
C24	0.9102 (3)	0.3468 (7)	0.4291 (3)	0.075 (2)
C25	0.8824 (3)	0.4474 (6)	0.4444 (3)	0.072 (2)
C26	0.8902 (3)	0.5678 (6)	0.4216 (3)	0.0586 (15)
C31	0.7567 (2)	0.7094 (5)	0.2406 (3)	0.0473 (12)
C32	0.7342 (2)	0.6259 (6)	0.2761 (3)	0.062 (2)
C33	0.6861 (3)	0.6602 (8)	0.2944 (3)	0.075 (2)
C34	0.6623 (3)	0.7769 (8)	0.2793 (3)	0.077 (2)
C35	0.6838 (2)	0.8634 (7)	0.2435 (3)	0.069 (2)
C36	0.7308 (2)	0.8294 (6)	0.2234 (3)	0.0583 (14)
C41	0.8042 (2)	0.6847 (5)	0.1291 (3)	0.0451 (12)
C42	0.7463 (2)	0.7164 (6)	0.0794 (3)	0.0560 (14)
C43	0.7329 (3)	0.7207 (6)	0.0056 (3)	0.066 (2)
C44	0.7764 (3)	0.6944 (6)	−0.0196 (3)	0.064 (2)
C45	0.8344 (3)	0.6614 (7)	0.0294 (3)	0.072 (2)
C46	0.8478 (2)	0.6537 (7)	0.1021 (3)	0.064 (2)
P1′	0.66505 (5)	0.33925 (13)	0.38240 (6)	0.0393 (3)
C1′	0.6125 (2)	0.2099 (4)	0.3839 (2)	0.0352 (10)
C2′	0.5590 (2)	0.2613 (4)	0.4153 (2)	0.0358 (11)
B3′	0.6168 (2)	0.1571 (6)	0.4664 (3)	0.0402 (12)
B4′	0.6275 (3)	0.0529 (6)	0.4043 (3)	0.0450 (14)
B5′	0.5781 (3)	0.1005 (6)	0.3162 (3)	0.0450 (14)
B6′	0.5375 (2)	0.2366 (6)	0.3236 (3)	0.0405 (13)
B7′	0.5403 (2)	0.1422 (6)	0.4582 (3)	0.0431 (13)
B8′	0.5816 (3)	0.0087 (6)	0.4513 (3)	0.052 (2)
B9′	0.5567 (3)	−0.0256 (6)	0.3570 (3)	0.053 (2)
B10′	0.5011 (3)	0.0863 (6)	0.3064 (3)	0.052 (2)
B11′	0.4901 (2)	0.1911 (6)	0.3689 (3)	0.0452 (14)
B12′	0.5031 (3)	0.0287 (6)	0.3896 (4)	0.055 (2)
C21′	0.5625 (2)	0.3949 (5)	0.4412 (3)	0.0400 (11)
C22′	0.5983 (3)	0.4271 (6)	0.5123 (3)	0.063 (2)
C23′	0.5988 (3)	0.5509 (7)	0.5352 (4)	0.084 (2)
C24′	0.5663 (4)	0.6414 (7)	0.4886 (5)	0.085 (2)
C25′	0.5295 (4)	0.6105 (7)	0.4174 (5)	0.090 (2)
C26′	0.5277 (3)	0.4876 (6)	0.3944 (3)	0.068 (2)
C31′	0.7327 (2)	0.3216 (5)	0.4682 (3)	0.0449 (12)
C32′	0.7680 (2)	0.2141 (6)	0.4961 (3)	0.0602 (15)
C33′	0.8173 (3)	0.2198 (8)	0.5640 (3)	0.074 (2)
C34′	0.8316 (3)	0.3302 (9)	0.6030 (3)	0.083 (2)
C35′	0.7975 (3)	0.4360 (8)	0.5756 (3)	0.078 (2)
C36′	0.7486 (3)	0.4320 (6)	0.5091 (3)	0.060 (2)
C41′	0.6882 (2)	0.2889 (5)	0.3101 (3)	0.0431 (11)
C42′	0.7443 (3)	0.2397 (7)	0.3212 (3)	0.070 (2)
C43′	0.7594 (3)	0.2247 (8)	0.2610 (4)	0.092 (2)
C44′	0.7196 (3)	0.2539 (8)	0.1933 (3)	0.087 (2)
C45′	0.6638 (3)	0.3034 (8)	0.1823 (3)	0.083 (2)
C46′	0.6485 (2)	0.3231 (6)	0.2407 (3)	0.063 (2)

Table 2. *Selected geometric parameters (Å, °)*

P1—C1	1.883 (5)	P1′—C1′	1.869 (5)
P1—C31	1.837 (5)	P1′—C31′	1.829 (5)
P1—C41	1.835 (5)	P1′—C41′	1.838 (5)
C1—B3	1.733 (7)	C1′—B3′	1.719 (7)
C1—B4	1.709 (8)	C1′—B5′	1.722 (7)
C1—B5	1.720 (7)	C1′—B4′	1.717 (7)
C1—B6	1.717 (7)	C1′—B6′	1.727 (7)
C1—C2	1.755 (6)	C1′—C2′	1.732 (6)
C2—C21	1.503 (7)	C2′—C21′	1.500 (7)
C2—B3	1.732 (7)	C2′—B3′	1.739 (7)
C2—B6	1.735 (7)	C2′—B6′	1.725 (6)
C2—B7	1.700 (8)	C2′—B7′	1.692 (7)
C2—B11	1.705 (7)	C2′—B11′	1.698 (7)
B3—B4	1.777 (8)	B3′—B4′	1.766 (8)
B3—B7	1.794 (8)	B3′—B7′	1.775 (7)

B3—B8	1.768 (9)	B3′—B8′	1.753 (8)
B4—B5	1.765 (9)	B4′—B5′	1.755 (8)
B4—B8	1.778 (10)	B4′—B8′	1.782 (8)
B4—B9	1.779 (9)	B4′—B9′	1.772 (8)
B5—B6	1.776 (9)	B5′—B6′	1.779 (8)
B5—B9	1.761 (10)	B5′—B9′	1.753 (9)
B5—B10	1.767 (8)	B5′—B10′	1.774 (8)
B6—B10	1.772 (10)	B6′—B10′	1.781 (9)
B6—B11	1.801 (9)	B6′—B11′	1.789 (8)
B7—B8	1.772 (10)	B7′—B8′	1.764 (9)
B7—B11	1.768 (9)	B7′—B11′	1.783 (7)
B7—B12	1.777 (10)	B7′—B12′	1.773 (9)
B8—B9	1.789 (10)	B8′—B9′	1.782 (9)
B8—B12	1.779 (10)	B8′—B12′	1.787 (9)
B9—B10	1.764 (11)	B9′—B10′	1.761 (9)
B9—B12	1.760 (10)	B9′—B12′	1.760 (9)
B10—B11	1.765 (9)	B10′—B11′	1.780 (8)
B10—B12	1.775 (11)	B10′—B12′	1.769 (9)
B11—B12	1.766 (10)	B11′—B12′	1.771 (9)
C41—P1—C31	105.2 (2)	C41′—P1′—C31′	106.5 (2)
C31—P1—C1	102.6 (2)	C31′—P1′—C1′	104.4 (2)
C41—P1—C1	103.6 (2)	C41′—P1′—C1′	102.8 (2)
B4—C1—P1	130.0 (4)	B4′—C1′—P1′	129.9 (3)
B6—C1—P1	113.1 (4)	B3′—C1′—P1′	118.7 (3)
B5—C1—P1	127.6 (3)	B5′—C1′—P1′	126.0 (3)
B3—C1—P1	116.6 (3)	B6′—C1′—P1′	112.2 (3)
C2—C1—P1	111.0 (3)	C2′—C1′—P1′	112.1 (3)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Brain, P. T., Cowie, J., Donohoe, D. J., Hnyk, D., Rankin, D. W. H., Reed, D., Reid, B. D., Robertson, H. E., Welch, A. J., Hofmann, M. & von R. Schleyer, P. (1996). *Inorg. Chem.* **35**, 1701–1708.

Cowie, J., Reid, B. D., Watmough, J. M. S. & Welch, A. J. (1994). *J. Organomet. Chem.* **481**, 283–293.

Kivekäs, R., Sillanpää, R., Teixidor, F., Viñas, C. & Nuñez, R. (1994). *Acta Cryst.* **C50**, 2027–2030.

Kivekäs, R., Teixidor, F., Viñas, C. & Nuñez, R. (1995). *Acta Cryst.* **C51**, 1868–1870.

Lewis, Z. G. & Welch, A. J. (1993). *Acta Cryst.* **C49**, 705–708.

Reid, B. D. (1992). PhD thesis, University of Edinburgh, Scotland.

Sheldrick, G. M. (1994). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Thomas, R. Ll., Rosair, G. M. & Welch, A. J. (1996). *Acta Cryst.* **C52**, 1024–1026, and references therein.

Acta Cryst. (1996). **C52**, 3138–3140

Tetraethyl (1Z,3Z)-Buta-1,3-diene-1,2,3,4-tetracarboxylate

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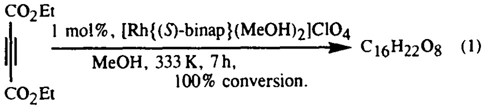
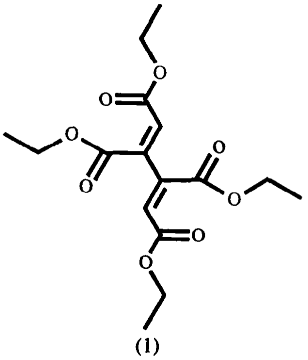
Abstract

The title compound, $C_{16}H_{22}O_8$, was obtained as the product of a cationic Rh^I-catalyzed hydridodimerization of diethyl acetylenedicarboxylate in methanol. The molecule lies on a crystallographic inversion centre. The diene moiety of the molecule possesses *s-trans* and *Z,Z* geometry.

Comment

The title compound, (1), has been synthesized by non-catalytic reactions (Bruce, Koutsantonis, Tiekink & Nicholson, 1991; Ryu, Kusumoto, Ogawa, Kambe & Sonoda, 1989; Neunhoeffer, Lehmann & Ewald, 1977); the Z,Z geometry, however, has been reported without X-ray analysis. We found an excellent cationic rhodium(I) catalyst containing the (*S*)-(−)-2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl [(*S*)-binap] ligand which exhibited high catalytic activity for the hydridodimerization of acetylenic compounds. The synthetic details will be published elsewhere. The title compound was prepared according to the scheme shown below.





(1)

The reaction product was purified by distillation using a Kuhrgelrohr apparatus and subsequent recrystalliza-

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