The Crystal and Molecular Structures of *trans*-Bis(trimethylphosphine)-[1,2-bis(methoxycarbonyl)vinyl](phenylethynyl)palladium(II)

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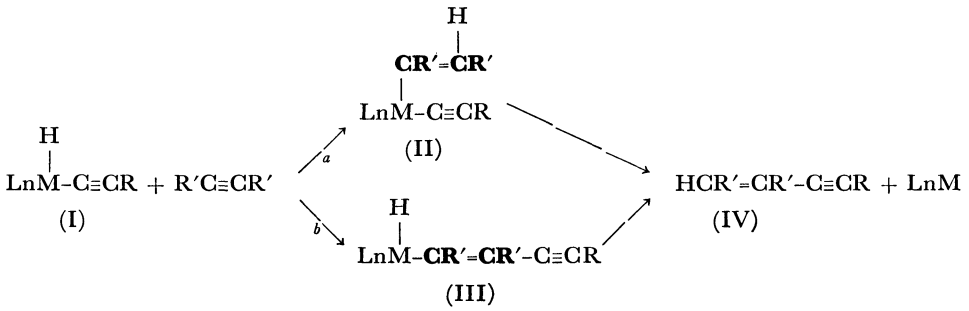
The X-ray molecular structure of the addition product of *trans*-$HPd(PEt_3)_2(C{\equiv}CPh)$ with dimethyl acetylenedicarboxylate has been determined to be [*trans*-{$(MeO_2C)HC{=}C(CO_2Me)$}$Pd(PEt_3)_2(C{\equiv}CPh)$]. The crystal belongs to the monoclinic system, space group $P2_1/c$, with eight formula units in a cell with dimensions of $a=17.844(3)$, $b=9.476(3)$, $c=36.061(4)$ Å, $\beta=98.18(1)°$. Two independent molecules have similar structures except for the conformation of the phenylethynyl groups and one of the triethylphosphine groups. The 1,2-bis(methoxycarbonyl)vinyl and phenylethynyl groups are σ-bonded to the palladium atom. No significant difference is observed between the Pd-C(sp)[2.04(2) and 2.03(2) Å] and Pd-C(sp^2)[2.05(2) and 2.06(2) Å] bond lengths. The environment of the palladium atom is approximately square-planar: Pd-P=2.321(5), 2.312(5), and 2.305(5), 2.311(5) Å.

It has been reported that a hydridoalkynylmetal complex (I), which is formed by the oxidative addition of a terminal acetylene group to the metal, can be considered to be an intermediate in the oligomerization of terminal acetylenes catalyzed by low-valent transition-metal complexes,[1] and that the hydrido or alkynyl groups of such an intermediate may add to acetylenes to form an alkynylalkenyl (II) or a hydridoalkenyl (III) complex,[2] which can subsequently undergo reductive elimination to the dimer and reform the starting low-valent complex (Scheme).



Spectroscopic studies of the reaction products of dimethyl acetylenedicarboxylate with hydridoalkynyl complexes of palladium(II) and platinum(II) suggest that the addition may produce alkenylalkynyl derivatives[3] (Path *a* in the scheme). In order to establish the molecular structure and clarify the reaction mechanism, an X-ray structure analysis of the addition product of *trans*-$HPd(PEt_3)_2(C{\equiv}CPh)$ with dimethyl acetylenedicarboxylate has now been carried out.

Experimental

Yellow needle crystals of the addition product mentioned above were supplied by Professor N. Hagihara and his coworkers. The unit-cell parameters were determined by the least-squares fit, using 35 2θ values of high-angle reflections.

Crystal Data: [*trans*-{$(MeO_2C)HC{=}C(CO_2Me)$}$Pd(PEt_3)_2$-$(C{\equiv}CPh)$], $C_{26}H_{42}O_4P_2Pd$, F. W. 591.0, monoclinic, $P2_1/c$, $a=17.844(3)$, $b=9.476(3)$, $c=36.061(4)$ Å, $\beta=98.18(1)°$, $U=6036(2)$ Å^3, $\lambda(MoK\alpha)=0.71069$ Å, $D_m=1.29$ g·cm^{-3}, $Z=8$, $D_c=1.29$ g·cm^{-3}, $\mu(MoK\alpha)=7.59$ cm^{-1}.

The intensity data were collected on a Rigaku automated, four-circle diffractometer using the θ-2θ scan technique. The graphite-monochromatized Mo$K\alpha$ radiation was used. The crystal used had dimensions of *ca.* $0.3\times0.3\times0.2$ mm. The integrated intensity was determined by scanning over a peak at a rate of 4° min^{-1} and by subtracting the background obtained by averaging the two values measured for 5 s at both ends of a scan. The scan width in 2θ was $(1.6+0.70\theta_c)°$, where θ_c is the calculated Bragg angle for Mo$K\alpha_1$. A total of 4920 reflections was measured ($\sin\theta/\lambda\leqq0.46$), of which 954 were less than $\sigma(F)$ and were classed "unobserved". Five standard reflections measured after every 60 reflections showed no significant change in intensity throughout the data collection. The Lorentz and polarization corrections were made in the usual way.

Structure Solution and Refinement

Two independent molecules are contained in an asymmetric unit. The palladium atoms were located from the Patterson map. The non-hydrogen atoms were then located from the subsequent Fourier synthesis. The structure was refined anisotropically by the block-diagonal least-squares procedure, using the HBLS V program.[4] The function minimized was $\Sigma w(\Delta F)^2$, where w was taken as unity. The final refinement reduced the R to 0.075 for 3966 non-zero reflections($\sin\theta/\lambda\leqq0.46$). Hydrogen atoms were not included in the refinement. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography, Vol. IV.[5] The positional and thermal parameters are given in Table 1.**

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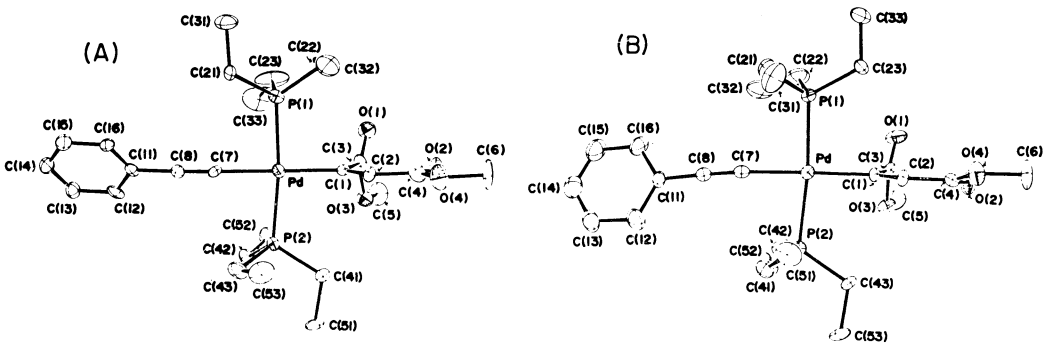
** The table of observed and calculated structure factors is kept as Document No. 7720 at the Chimical Society of Japan.

TABLE 1. ATOMIC PARAMETERS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES
Positional parameters in fraction of cell edges and thermal parameters in the form of
$\exp[-\{B(11)h^2+B(22)k^2+B(33)l^2+B(12)hk+B(13)hl+B(23)kl\}]$.

ATOM	X	Y	Z	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
PDA	.19373(7)	.60404(13)	.40338(4)	.00304(5)	.00857(16)	.000850(13)	.00051(4)	.00033(8)	.00049(0)
P(1A)	.16916(26)	.4262 (5)	.35907(14)	.00340(19)	.0104 (6)	.00106 (5)	-.0006 (6)	.00078(15)	-.00101(30)
P(2A)	.20826(26)	.7964 (5)	.44322(13)	.00402(20)	.0084 (6)	.00078 (5)	.0001 (6)	-.00008(15)	.00052(28)
O(1A)	.1550 (7)	.2767 (13)	.45029(34)	.0059 (6)	.0149 (19)	.00114 (14)	-.0060 (18)	.00090(15)	.0003 (8)
O(2A)	.3118 (7)	.2642 (14)	.5000 (4)	.0046 (6)	.0215 (23)	.00133 (15)	.0046 (19)	-.0001 (4)	.0047 (10)
O(3A)	.1674 (7)	.4556 (12)	.49188(32)	.0072 (6)	.0139 (18)	.00090 (13)	-.0001 (18)	.0022 (5)	.0000 (8)
O(4A)	.4733 (7)	.3255 (16)	.4849 (4)	.0043 (6)	.0241 (26)	.00199 (20)	.0038 (20)	.0008 (5)	.0030 (12)
C(1A)	.2435 (9)	.4646 (16)	.4429 (4)	.0036 (7)	.0086 (21)	.00056 (15)	-.0012 (20)	-.0001 (5)	-.0008 (9)
C(2A)	.3187 (9)	.4393 (17)	.4522 (4)	.0033 (7)	.0124 (25)	.00073 (17)	.0013 (21)	-.0008 (5)	.0006 (10)
C(3A)	.1851 (9)	.3841 (17)	.4614 (5)	.0030 (7)	.0101 (24)	.00135 (21)	.0003 (21)	-.0001 (6)	.0018 (12)
C(4A)	.3489 (11)	.3351 (21)	.4806 (6)	.0060 (9)	.0140 (31)	.00148 (26)	.0020 (27)	.0013 (8)	.0009 (15)
C(5A)	.1080 (12)	.3882 (26)	.5103 (6)	.0058 (10)	.029 (4)	.00169 (29)	-.002 (4)	.0033 (9)	.0037 (19)
C(6A)	.4596 (12)	.2234 (27)	.5112 (7)	.0058 (11)	.030 (5)	.00216 (35)	.012 (4)	-.0023 (10)	.0078 (21)
C(7A)	.1437 (9)	.7422 (17)	.3642 (4)	.0037 (7)	.0113 (24)	.00045 (15)	-.0012 (21)	-.0001 (5)	-.0010 (10)
C(8A)	.1124 (8)	.8218 (16)	.3412 (4)	.0027 (6)	.0090 (21)	.00074 (16)	-.0006 (19)	.0007 (5)	.0000 (10)
C(11A)	.0790 (8)	.9181 (16)	.3113 (5)	.0026 (6)	.0070 (21)	.00112 (19)	-.0018 (19)	-.0015 (5)	-.0004 (11)
C(12A)	.0183 (9)	1.0045 (17)	.3192 (5)	.0029 (7)	.0072 (22)	.00170 (24)	-.0019 (21)	-.0012 (6)	-.0018 (12)
C(13A)	-.0147 (9)	1.0944 (19)	.2901 (5)	.0036 (7)	.0134 (26)	.00110 (20)	.0007 (23)	-.0001 (6)	.0009 (12)
C(14A)	.0120 (10)	1.0922 (20)	.2547 (5)	.0049 (8)	.0139 (28)	.00103 (20)	-.0005 (26)	-.0013 (6)	.0004 (13)
C(15A)	.0713 (10)	1.0017 (20)	.2485 (5)	.0048 (8)	.0144 (28)	.00101 (20)	-.0055 (26)	-.0006 (6)	.0002 (13)
C(16A)	.1038 (9)	.9146 (17)	.2769 (4)	.0035 (7)	.0113 (23)	.00061 (16)	.0009 (21)	.0008 (5)	-.0009 (10)
C(21A)	.1792 (12)	.4815 (19)	.3113 (5)	.0094 (12)	.0114 (26)	.00060 (17)	.0060 (30)	.0008 (7)	.0012 (11)
C(22A)	.2269 (15)	.2623 (19)	.3656 (6)	.0113 (15)	.0065 (24)	.00177 (30)	.0061 (31)	.0022 (10)	-.0008 (13)
C(23A)	.0709 (14)	.3579 (33)	.3568 (8)	.0066 (12)	.044 (7)	.0028 (4)	-.021 (5)	.0037 (12)	-.0134 (29)
C(31A)	.1588 (13)	.3653 (24)	.2805 (6)	.0084 (12)	.021 (4)	.00134 (25)	.000 (4)	.002 (9)	-.0045 (16)
C(32A)	.3087 (14)	.2867 (28)	.3591 (7)	.0082 (13)	.029 (5)	.00200 (35)	.016 (4)	.0017 (10)	-.0034 (21)
C(33A)	.0150 (11)	.4276 (33)	.3657 (10)	.0030 (9)	.039 (6)	.0041 (6)	.000 (4)	.0014 (12)	-.0081 (32)
C(41A)	.2511 (11)	.7667 (19)	.4928 (5)	.0066 (10)	.0137 (28)	.00072 (19)	.0013 (27)	-.0007 (7)	-.0011 (12)
C(42A)	.1119 (10)	.8757 (18)	.4474 (5)	.005 (8)	.0116 (26)	.00139 (23)	.0057 (24)	.0022 (7)	-.0001 (13)
C(43A)	.2602 (11)	.9458 (19)	.4251 (6)	.0067 (10)	.0120 (28)	.00157 (27)	-.0076 (27)	.0013 (8)	.0001 (14)
C(51A)	.2547 (13)	.9062 (21)	.5175 (5)	.0102 (13)	.0160 (31)	.00064 (19)	-.0045 (34)	.0000 (8)	.0034 (13)
C(52A)	.0573 (11)	.7675 (23)	.4595 (6)	.0046 (9)	.0193 (35)	.00183 (29)	.0037 (29)	.0014 (8)	.0022 (16)
C(53A)	.3463 (11)	.9110 (27)	.4290 (6)	.0038 (8)	.031 (5)	.0018 (29)	-.0082 (33)	.0018 (8)	-.0019 (19)
PDB	.46689(7)	.49196(14)	.35631(4)	.00322(5)	.00957(17)	.001110(14)	.00050(16)	.00061(4)	.00075(9)
P(1B)	.74866(26)	.6721 (5)	.34650(14)	.00333(19)	.0093 (6)	.00122 (6)	-.0012 (6)	.00032(16)	.00058(31)
P(2B)	.57581(26)	.3308 (5)	.36795(14)	.00321(19)	.0123 (7)	.00113 (6)	-.0013 (6)	.00037(16)	.00142(32)
O(1B)	.8165 (8)	.3458 (13)	.3091 (4)	.0073 (7)	.0123 (18)	.00175 (17)	-.0062 (18)	.0041 (6)	-.0014 (9)
O(2B)	.8713 (7)	.1309 (13)	.3732 (4)	.0052 (6)	.0168 (20)	.00156 (16)	.0079 (18)	.0007 (5)	-.0019 (9)
O(3B)	.7253 (7)	.1885 (12)	.3126 (4)	.0059 (6)	.0101 (17)	.00169 (17)	-.0029 (17)	.0009 (5)	-.0002 (9)
O(4B)	.8971 (7)	.2064 (15)	.4329 (4)	.0045 (5)	.0231 (24)	.00147 (16)	.0059 (19)	-.0003 (5)	.0001 (10)
C(1B)	.7533 (9)	.3461 (16)	.3618 (5)	.0027 (6)	.0084 (23)	.00142 (22)	.0027 (20)	.0016 (6)	.0006 (11)
C(2B)	.7936 (9)	.3110 (18)	.3971 (5)	.0032 (7)	.0105 (24)	.00140 (23)	.0044 (22)	.0005 (6)	.0022 (12)
C(3B)	.7718 (10)	.2933 (16)	.3766 (6)	.0042 (8)	.0060 (21)	.00178 (27)	.0023 (21)	.001 (7)	.0010 (12)
C(4B)	.8557 (9)	.2034 (19)	.3989 (5)	.0025 (7)	.0123 (28)	.00164 (23)	-.0011 (23)	.0010 (6)	.0019 (13)
C(5B)	.7347 (15)	.1465 (29)	.2753 (7)	.0103 (15)	.018 (4)	.00170 (30)	-.005 (4)	.0021 (11)	-.0061 (17)
C(6B)	.9598 (12)	.1064 (25)	.4390 (7)	.0054 (10)	.027 (4)	.00183 (30)	.017 (4)	-.0011 (8)	.0001 (19)
C(7B)	.5784 (10)	.6279 (19)	.3474 (7)	.0032 (7)	.0100 (27)	.00255 (33)	-.0033 (23)	.0009 (8)	.0007 (15)
C(8B)	.5219 (9)	.6977 (18)	.3380 (5)	.0034 (7)	.0099 (24)	.00162 (25)	-.0017 (22)	.0010 (7)	.0001 (13)
C(11B)	.4546 (9)	.7755 (17)	.3285 (5)	.0032 (7)	.0108 (25)	.00115 (21)	.0029 (21)	.0002 (6)	.0001 (12)
C(12B)	.3851 (12)	.7316 (25)	.3406 (7)	.0055 (10)	.023 (4)	.0025 (4)	.0009 (34)	.0032 (10)	-.0037 (20)
C(13B)	.3181 (11)	.8165 (26)	.3278 (7)	.0041 (9)	.023 (4)	.00240 (34)	.0016 (31)	.0013 (9)	-.0048 (20)
C(14B)	.3226 (12)	.9303 (23)	.3067 (7)	.0061 (10)	.019 (4)	.00197 (31)	.0021 (31)	-.0006 (9)	-.0038 (17)
C(15B)	.3885 (13)	.9686 (25)	.2935 (7)	.0069 (12)	.020 (4)	.0023 (4)	.0035 (35)	-.0016 (10)	.0029 (19)
C(16B)	.4556 (11)	.8902 (21)	.3050 (6)	.0052 (9)	.0151 (31)	.00198 (30)	-.0002 (29)	-.0023 (8)	.0026 (16)
C(21B)	.7283 (11)	.8365 (20)	.3681 (6)	.0053 (9)	.0120 (28)	.00185 (28)	.0016 (26)	.0012 (8)	-.0044 (14)
C(22B)	.7454 (14)	.7112 (26)	.2943 (7)	.0078 (12)	.024 (4)	.0022 (4)	-.006 (4)	.0010 (10)	.0071 (21)
C(23B)	.8512 (9)	.6407 (19)	.3615 (7)	.0023 (7)	.0115 (27)	.0027 (4)	-.0003 (22)	.0011 (8)	-.0022 (15)
C(31B)	.7367 (16)	.8211 (27)	.4097 (7)	.0121 (17)	.024 (4)	.00131 (28)	.008 (5)	.0010 (11)	-.0027 (19)
C(32B)	.6743 (14)	.7524 (30)	.2754 (7)	.0084 (14)	.035 (6)	.00152 (30)	-.012 (5)	-.0002 (10)	.0052 (21)
C(33B)	.9037 (11)	.7626 (24)	.3533 (8)	.0039 (9)	.019 (4)	.0030 (4)	-.0050 (29)	.0018 (9)	-.0023 (20)
C(41B)	.4981 (10)	.3109 (22)	.3793 (5)	.0046 (8)	.0200 (34)	.00112 (22)	-.0029 (28)	-.0006 (7)	.0018 (14)
C(42B)	.6063 (10)	.1479 (17)	.3802 (6)	.0047 (8)	.0074 (24)	.00209 (29)	.0004 (23)	.0021 (8)	.0030 (13)
C(43B)	.5256 (10)	.3893 (21)	.4071 (5)	.0042 (8)	.0191 (32)	.00126 (23)	.0010 (27)	.0020 (7)	.0005 (14)
C(51B)	.5286 (14)	.2856 (29)	.2924 (6)	.0090 (14)	.034 (5)	.00110 (25)	-.016 (5)	-.0002 (9)	-.0024 (19)
C(52B)	.5447 (12)	.0559 (20)	.3965 (6)	.0066 (10)	.0141 (31)	.00159 (27)	-.0050 (28)	.0017 (8)	.0048 (15)
C(53B)	.5846 (13)	.4101 (26)	.4430 (6)	.0073 (11)	.029 (4)	.00102 (23)	-.005 (4)	.0016 (8)	-.0037 (17)



Results and Discussion

Figure 1 shows a stereoscopic view of the two independent molecules in an asymmetric unit. The two molecules (A and B) have similar structures except for the conformation of the phenylethynyl groups and one of the triethylphosphine groups. Selected bond lengths and bond angles are given in Fig. 2.

The main feature of the structure is that the 1,2-bis(methoxycarbonyl)vinyl and phenylethynyl groups are σ-bonded to the palladium atom, and that they are

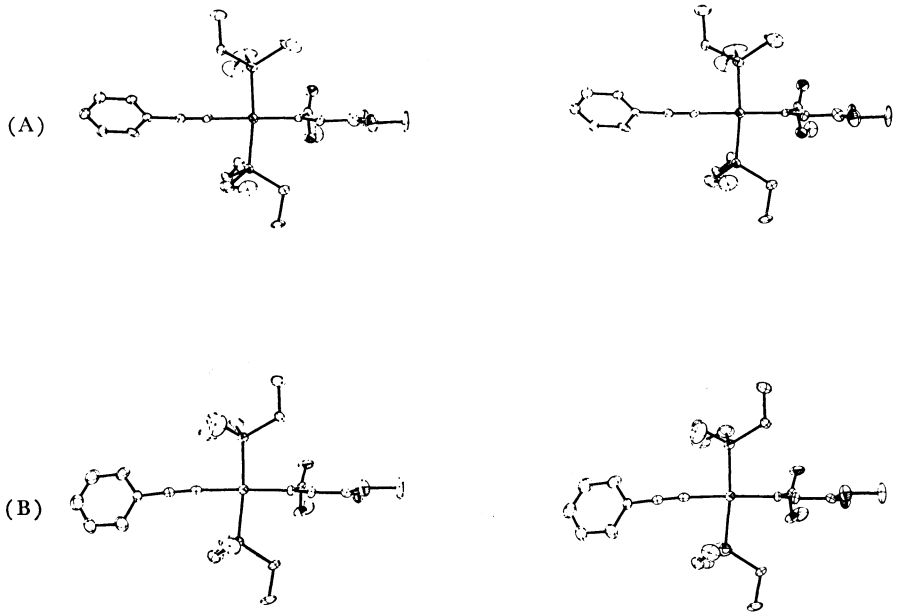


Fig. 1. Stereoscopic drawing of two independent molecules of [*trans*-{$(MeO_2C)HC{=}C(CO_2Me)$}$Pd(PEt_3)_2(C{\equiv}CPh)$].

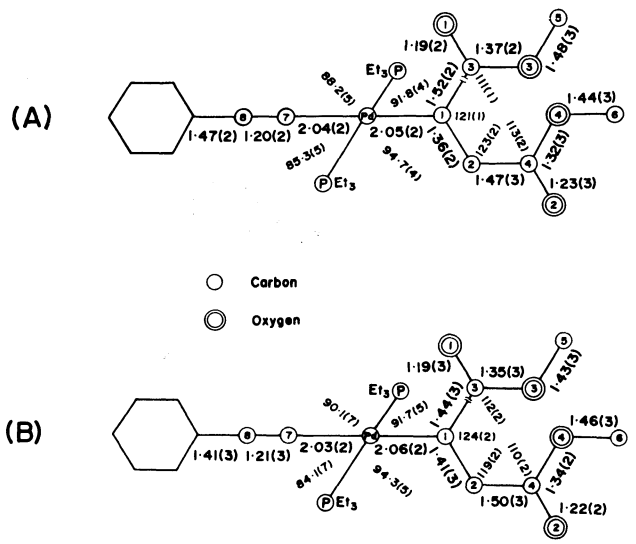
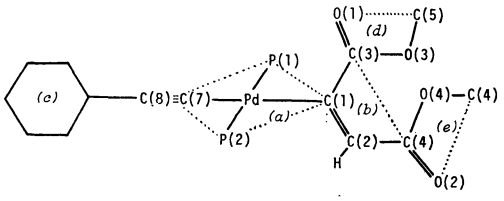


Fig. 2. Selected bond lengths and bond angles. E.s.d.'s in parentheses.

both in the *trans* position. This indicates that, of the two possible reaction paths in the scheme, the terminal acetylene reacted with the hydridoalkynylmetal complex to give the alkenylalkynyl derivative (Path *a* in the scheme). A third feature is that two methoxycarbonyl groups are mutually *cis*, the insertion of dimethyl acetylenedicarboxylate into the palladium atom being found to be a *cis*-insertion. This may be caused by the electronic repulsion between the methoxycarbonyl group and the palladium atom.

The environment of the palladium atom is approximately square-planar: the Pd, P(1), P(2), C(1), and C(7) atoms lie on a plane within 0.13 Å. The two Pd–P lengths are equal [2.321(5), 2.312(5) and 2.305(5), 2.311(5) Å], and no significant difference is found between the Pd–C(sp) [2.04(2) and 2.03(2) Å] and Pd–C(sp^2) lengths [2.05(2) and 2.06(2) Å].

TABLE 2. DIHEDRAL ANGLES



Molecule	Dihedral angles [°] between				
	(*a*) & (*b*)	(*a*) & (*c*)	(*a*) & C(7)≡C(8)	(*b*) & (*d*)	(*b*) & (*e*)
A	82.6	51.2	1.8	89.0	2.7
B	83.2	24.3	9.9	95.5	13.3

The alkenyl group, or, more exactly, the vinyl plane ((*b*) in Table 2), is roughly perpendicular to the co-ordination plane (*a*). The bulkiness of the alkenyl group probably causes the P(1)–Pd–C(1) and P(2)–Pd–C(1) bond angles to be larger than 90°. One of the methoxycarbonyl groups (*d*) is approximately perpendicular to, whereas the other one (*e*) is nearly parallel to, the vinyl plane (*b*). It seems that the C(4)=O(2) double bond lengths [1.23(3) and 1.22(2) Å] are slightly longer than the C(3)=O(1) lengths [1.19(2) and 1.19(3) Å], though this is not really significant; it can be explained by the conjugation of the C(4)=O(2) bond with the vinylic π-system.

The phenylethynyl groups in two molecules have rather different conformations: the C(7)–C(8) bonds make different angles of 1.8 and 9.9° with the co-ordination plane. The dihedral angles between the phenyl ring and the co-ordination plane also have different values [51.2 and 24.3°]. This is probably the result of the difference in the conformations of the triethylphosphine groups (Fig. 1). The bond lengths

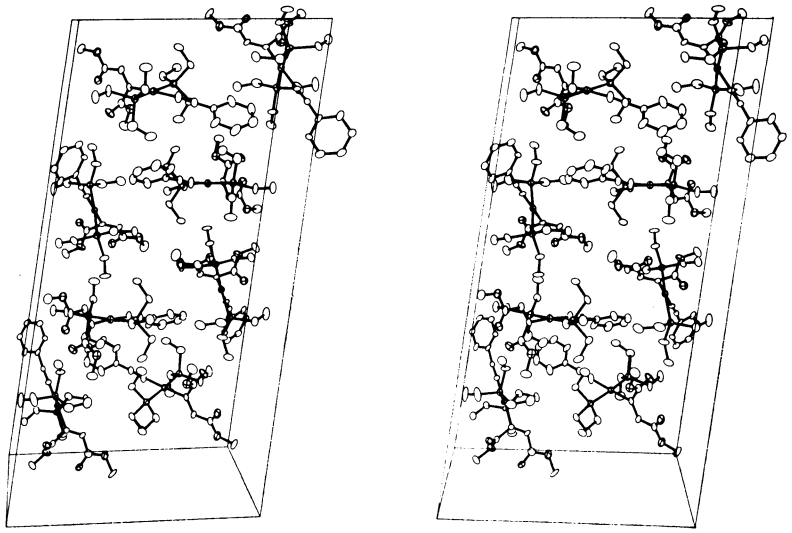


Fig. 3. Stereoscopic view of the crystal structure projected along the b axis. Non-hydrogen atoms are represented by thermal ellipsoid at 50% probability level.

(av. 1.40 and 1.40 Å) and bond angles (av. 120 and 120°) in the phenyl groups are normal.

As has been mentioned before, the triethylphosphine groups, including the P(1) atom have different conformations in two independent molecules: the PEt_3 group in Molecule B is rotated about 120° from that in A (Fig. 1). The exceptionally large thermal parameters of C(23) and C(33) atoms in A and the unusually short C(23A)–C(33A) bond length [1.28(5) Å] suggest disorder in these atoms. The other C–C bond lengths in ethyl groups have normal values (av. 1.55 Å).

The crystal structure is shown in Fig. 3. No close intermolecular atomic contacts less than the usual van der Waals distances can be observed.

All the computations in the present study were carried out on a NEAC 2200-700 computer at Osaka University. Figures 1 and 3 were drawn on a NUMERICON 7000 system at Osaka University, with a local version of ORTEP.[6]

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