

Structure of *cis*-Diacetylido-bis(triethylphosphine)platinum(II)

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Abstract. $[\text{Pt}(\text{C}_2\text{H})_2(\text{C}_6\text{H}_{15}\text{P})_2]$, $M_r = 481.5$, monoclinic, $P2_1/n$, $a = 10.410$ (2), $b = 13.689$ (2), $c = 14.985$ (1) Å, $\beta = 109.27$ (10)°, $V = 2015.8$ (4) Å³, $Z = 4$, $D_x = 1.59$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 71.8$ cm⁻¹, $T = 298$ K, $F(000) = 944$, $R = 0.0476$ for 1731 reflections with $I > 3.0\sigma(I)$ (3253 unique reflections). The acetylide ligands are bound to Pt in a *cis* configuration, with the C—Pt—C angle 86.0 (6)° and the P—Pt—P angle 105.3 (1)°. The two Pt—C [1.987 (15)–1.949 (16) Å] bonds and the two Pt—P [2.308 (5)–2.312 (4) Å] bonds form a square plane with a mean deviation of 0.013 Å from planarity.

Introduction. Acetylide derivatives are known for most of the transition metals (Nast, 1982). A variety of platinum acetylide complexes have been reported (Chatt & Shaw, 1959; Bell, Chisholm, Couch & Rankell, 1977; Sonogashira, Yatake, Tohda, Takahashi & Hagihara, 1977; Sonogashira, Fujikura, Yatake, Toyoshima, Takahashi & Hagihara, 1978), but very few have been structurally characterized (e.g., Furlani, Licoccia, Russo, Villa & Guastini, 1984; Sebald, Stader, Wrackmeyer & Bensch, 1986; and references therein). Further, those structurally characterized examples do not include complexes of the parent non-substituted acetylene. Here we report that the non-substituted acetylide experiences little change in the C≡C bond length when bound to Pt.

Experimental. Synthesis of *cis*-Pt(C≡CH)₂(PEt₃)₂ was based on the method of Sonogashira (Sonogashira, Yatake, Tohda, Takahashi & Hagihara, 1977) with the following modifications. After dissolution of the product into benzene and extraction with water, the solvent was removed from the yellow benzene solution *in vacuo*. The residue was washed with pentane, then redissolved in toluene. After slow cooling to 233 K, yellow crystals of the product were obtained. ¹H NMR (C₆D₆): δ 2.51 [³J(Pt—H) = 48 Hz, ⁴J(P—H) = 3.5 Hz]. ³¹P{¹H} NMR (C₆D₆): δ 5.36 [¹J(Pt—P) = 2224 Hz]. (Proton chemical shifts are relative to Me₄Si at 0.00 ppm; phosphorus chemical shifts are relative to 85% H₃PO₄ at 0.00 ppm.)

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The X-ray data were collected using a Nicolet R3m/V automated diffractometer, an Mo X-ray source, and a graphite crystal monochromator. Table 1 gives the crystal and intensity data. An empirical absorption correction from ψ -scan data was applied. The space group $P2_1/n$ was indicated by the systematic absences $h0l$: $h + l = 2n + 1$ and $0k0$: $k = 2n + 1$.

The structure was solved by direct methods, followed by full-matrix least-squares refinement on F^2 using $\sum w(F_o - F_c)^2$ as the weighting scheme, where $w = [\sigma^2(F_o) + g(F_c)^2]^{-1}$. After initial use of isotropic temperature factors, anisotropic factors were employed for all non-H atoms. H atoms were placed in fixed idealized positions riding on carbon for the final cycles of refinement. Refinement converged with $R = 0.0476$ and $wR = 0.0643$. Calculations were performed on a MicroVAX II computer using the *SHELXTL-Plus* program package (Sheldrick, 1987) with atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 2 contains final atomic coordinates, Table 3 contains bond distances and angles, and Fig. 1 shows the molecular structure with the atomic numbering scheme.† The arrangement about the Pt atom is essentially square planar, with P(1), P(2), C(1) and C(3) exhibiting a mean deviation from an idealized plane of 0.013 Å. The P—Pt—P angle of 105.3 (1)° and the C—Pt—C angle of 86.0 (6)° are distorted from the ideal value of 90°, reflecting the relative steric bulk of PEt₃ with respect to the acetylide. The Pt—P distances, 2.308 (5)–2.312 (4) Å, and the Pt—C distances, 1.987 (14)–1.949 (14) Å, resemble those reported for *cis*-Pt[C≡CC(OH)Me₂]₂(PPh₃)₂ (Furlani, Licoccia, Russo, Villa & Guastini, 1984), where Pt—P = 2.307 (5)–2.331 (5) and Pt—C = 1.99 (2)–2.02 (2) Å. They are elongated and short-

† Fractional atomic coordinates for H atoms, anisotropic temperature factors for non-H atoms, least-squares-planes information and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52876 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. X-ray data collection and structure refinement for *cis*-Pt(C≡CH)₂(PEt₃)₂

Crystal size (mm)	0.40 × 0.40 × 0.15
Scan type	ω -2 θ
Scan speed (° min ⁻¹)	1.50–26.04
2 θ range (machine-centered reflections) (°)	15–30
No. of machine-centered reflections	50
2 θ range (data collection) (°)	3–55
Range of <i>hkl</i>	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 18, -20 ≤ <i>l</i> ≤ 20
Check reflections (<i>hkl</i>)*	610, 191, 117
No. of independent reflections measured	3253
No. of reflections with <i>I</i> > 3 σ (<i>I</i>)	1731
No. of parameters refined	172
<i>T</i> _{max} for absorption correction	1.00
<i>T</i> _{min} for absorption correction	0.446
<i>g</i>	0.003701
Max. Δ/σ	0.006
Max., min. in $\Delta\rho$ (e Å ⁻³)	1.97, 2.03
<i>S</i> (goodness of fit)	0.9215
<i>R</i>	0.0476
<i>wR</i>	0.0643

* Check reflections monitored for changes in intensities every 100 reflections.

Table 2. Atomic coordinates (× 10⁴) and equivalent displacement parameters (Å² × 10³) in *cis*-Pt(C≡CH)₂(PEt₃)₂

*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Pt(1)	3876 (1)	2425 (1)	6701 (1)	49 (1)
P(1)	6115 (5)	1960 (3)	7399 (3)	59 (2)
P(2)	3657 (5)	3872 (3)	7435 (3)	54 (2)
C(1)	3723 (16)	1250 (11)	5894 (10)	60 (7)
C(2)	3639 (22)	548 (13)	5393 (14)	85 (9)
C(3)	1970 (18)	2659 (11)	5975 (11)	60 (6)
C(4)	757 (27)	2832 (15)	5528 (16)	99 (11)
C(11)	7294 (20)	2619 (15)	8410 (13)	86 (9)
C(12)	8686 (25)	2235 (16)	8803 (16)	118 (12)
C(13)	7003 (21)	1933 (15)	6539 (13)	89 (9)
C(14)	7207 (32)	2963 (18)	6165 (18)	140 (17)
C(15)	6307 (21)	688 (12)	7779 (15)	93 (9)
C(16)	5645 (23)	524 (16)	8604 (14)	107 (12)
C(21)	2287 (18)	3809 (12)	7940 (12)	77 (8)
C(22)	2518 (21)	3061 (16)	8697 (13)	99 (10)
C(23)	3126 (23)	4822 (12)	6554 (13)	90 (10)
C(24)	4069 (24)	5016 (16)	6001 (17)	126 (13)
C(25)	5074 (20)	4418 (12)	8355 (13)	83 (9)
C(26)	4802 (22)	5422 (13)	8740 (14)	99 (10)

ened, respectively, with respect to those reported for *trans*-Pt(C≡CMe)₂(PEt₃)₂ (Sebald, Stader, Wrackmeyer & Bensch, 1986), where Pt—P = 2.284 (2) and Pt—C = 2.062 (8) Å. This lengthening of the Pt—P bonds *trans* to the acetylide ligands illustrates the strong *trans* effect of the acetylide ligands. The C≡C bond lengths of 1.205 (25) and 1.241 (30) Å are not significantly longer than the C≡C bond length of 1.2033 (2) Å for free acetylene (Fast & Welsh, 1972). This suggests that a minimum amount of Pt→acetylide (π^*) backbonding occurs on coordination of the acetylide to Pt.

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Table 3. Bond distances (Å) and bond angles (°) in *cis*-Pt(C≡CH)₂(PEt₃)₂

Pt(1)—P(1)	2.308 (5)	Pt(1)—P(2)	2.312 (4)
Pt(1)—C(1)	1.987 (15)	Pt(1)—C(3)	1.949 (16)
P(1)—C(11)	1.841 (18)	P(1)—C(13)	1.816 (24)
P(1)—C(15)	1.822 (17)	P(2)—C(21)	1.825 (21)
P(2)—C(23)	1.804 (18)	P(2)—C(25)	1.815 (17)
C(1)—C(2)	1.205 (25)	C(3)—C(4)	1.241 (30)
C(11)—C(12)	1.470 (30)	C(13)—C(14)	1.558 (34)
C(15)—C(16)	1.617 (35)	C(21)—C(22)	1.487 (27)
C(23)—C(24)	1.503 (38)	C(25)—C(26)	1.552 (27)
P(1)—Pt(1)—P(2)	105.3 (1)	P(1)—Pt(1)—C(1)	85.3 (4)
P(2)—Pt(1)—C(1)	169.1 (4)	P(1)—Pt(1)—C(3)	171.2 (5)
P(2)—Pt(1)—C(3)	83.3 (5)	C(1)—Pt(1)—C(3)	86.0 (6)
Pt(1)—P(1)—C(11)	122.4 (7)	Pt(1)—P(1)—C(13)	111.0 (6)
C(11)—P(1)—C(13)	103.7 (10)	Pt(1)—P(1)—C(15)	113.3 (7)
C(11)—P(1)—C(15)	103.7 (9)	C(13)—P(1)—C(15)	100.0 (10)
Pt(1)—P(2)—C(21)	111.7 (5)	Pt(1)—P(2)—C(23)	108.9 (6)
C(21)—P(2)—C(23)	104.2 (10)	Pt(1)—P(2)—C(25)	122.1 (7)
C(21)—P(2)—C(25)	104.8 (9)	C(23)—P(2)—C(25)	103.6 (8)
Pt(1)—C(1)—C(2)	178.7 (17)	Pt(1)—C(3)—C(4)	178.1 (16)
P(1)—C(11)—C(12)	117.1 (15)	P(1)—C(13)—C(14)	113.5 (17)
P(1)—C(15)—C(16)	110.0 (14)	P(2)—C(21)—C(22)	113.4 (14)
P(2)—C(23)—C(24)	115.6 (15)	P(2)—C(25)—C(26)	116.4 (13)

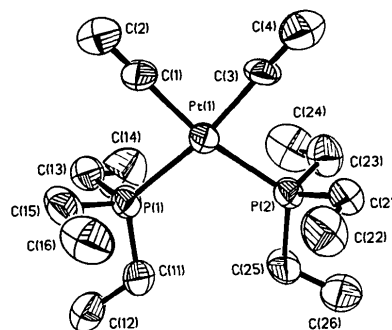


Fig. 1. ORTEP (Johnson, 1965) drawing of *cis*-Pt(C≡CH)₂(PEt₃)₂ showing the atomic labeling scheme and 50% probability thermal ellipsoids.

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Structure of Bis[(4,5- η)-3,3,6,6-tetramethyl-1-thiacyclohept-4-yne]-bis(μ -thiophenolato)-dicopper(I)

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Abstract. $[\text{Cu}_2(\text{C}_6\text{H}_5\text{S})_2(\text{C}_{10}\text{H}_{16}\text{S})_2]$, $M_r = 682.04$, monoclinic, $P2_1/n$, $a = 11.644$ (2), $b = 12.138$ (1), $c = 24.124$ (2) Å, $\beta = 102.31$ (1)°, $V = 3331.2$ (7) Å³, $Z = 4$, $D_x = 1.36$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54051$ Å, $\mu = 3.85$ mm⁻¹, $F(000) = 1424$, $T = 298$ K, $R = 0.053$ for 6140 observed reflexions. The molecule is a cyclic dimer containing two Cu atoms and two bridging thiophenolato ligands in its center. In addition each Cu atom is η^2 -coordinated via the C \equiv C group of the thiacycloheptyne ligands. The high stability of the Cu^I complex is a consequence of the large strain energy in 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne, which is significantly reduced during the process of complex formation.

Introduction. The study of the title compound was undertaken as part of an investigation of Cu^I compounds with different anionic and neutral ligands. The alkyne 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne represents a highly strained cycloalkyne with a low-lying LUMO (lowest unoccupied molecular orbital) and is, therefore, an interesting ligand for Cu^I (Bennet & Schwemlein, 1989).

Experimental. The complex was prepared from equimolar amounts of copper(I) thiophenolate and 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne in tetrahydrofuran at 195 K. After hydrolysis and extraction

with *n*-hexane the product was recrystallized from *n*-hexane. Light-green crystals were obtained, stable to air and X-rays. A crystal of size 0.7 × 0.3 × 0.1 mm was used for all measurements. An Enraf-Nonius CAD-4 diffractometer was used with graphite-monochromated Cu $K\alpha$ radiation. The cell parameters were determined by least-squares refinement of the setting angles of 25 reflexions with 2θ from 76.6 to 97.0°. Intensity data were measured by $\theta/2\theta$ scans ($4.5 \leq 2\theta \leq 153^\circ$, $0 \leq h \leq 14$, $0 \leq k \leq 15$, $-30 \leq l \leq 30$). There was no significant decay for three standard reflexions monitored after every 2 h. 7836 data were measured of which 6715 were symmetry independent ($R_{\text{int}} = 0.0283$). 6140 reflexions with $|F_o| > 3\sigma(F_o)$ were considered observed and were used in all calculations. The data were corrected for Lorentz and polarization but not for absorption effects.

The structure was solved by the heavy-atom method. All H atoms were localized in theoretical positions (sp^2 hybridization for benzene-type C atoms and sp^3 hybridization and 'staggered' conformation for all other C atoms). The structure was refined by full-matrix least-squares procedures on F assigning anisotropic thermal displacement parameters to Cu, S and C, and one common isotropic thermal parameter for all H atoms. The refinement converged at $R = 0.053$ and $wR = 0.055$ with $w = 1/[\sigma^2(F_o) + 0.0009F_o^2]$. 411 parameters were refined and the ratio of reflexions to the number of variables

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