

***trans*- μ -(2,5-Dioctyl-1,4-phenylene)diethynyl-bis[phenylbis(triethylphosphine)platinum(II)]**

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Key indicators

Single-crystal X-ray study

$T = 150\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.018\text{ \AA}$

R factor = 0.066

wR factor = 0.171

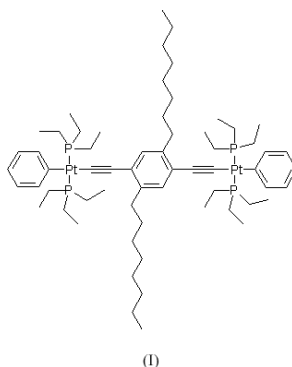
Data-to-parameter ratio = 18.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Pt}_2(\text{C}_6\text{H}_5)_2(\text{C}_{26}\text{H}_{36})(\text{C}_6\text{H}_{15}\text{P})_4]$, is a dinuclear Pt^{II} di-yne compound exhibiting π -conjugation along the molecular backbone. It is used as a model species for rigid-rod platinum poly-yne compounds of which it is a precursor. Such compounds are of interest due to the extended π -conjugation through the aromatic linker unit in the backbone. In this structure, the molecule lies on an inversion centre such that the asymmetric unit comprises half the formula unit.

Comment

In this paper, we report the structural characterization of the title compound, (I), which is a dinuclear platinum(II) di-yne species, *trans*-[(Ph)(PEt₃)₂Pt–C≡C–R–C≡C–Pt(PEt₃)₂–(Ph)] ($R = 2,5$ -dioctyl-1,4-benzenediyl). Such platinum-containing species form the building blocks for rigid-rod organometallic poly-ynes of general formula *trans*-[Pt(PX₃)₂–C≡C–R–C≡C–]_∞ ($X =$ tertiary phosphines and $R =$ aromatic linker unit). Platinum(II) poly-ynes are of immense current interest due to π -electron conjugation along the backbone, donor–acceptor metal–ligand interactions and novel photophysical properties (Wittmann *et al.*, 1994; Beljonne *et al.*, 1996; Younus *et al.*, 1998; Chawdhury *et al.*, 1998, 1999; Khan, Al-Mandhary, Al-Suti, Hisahm *et al.*, 2002; Khan, Al-Mandhary, Al-Suti, Feeder *et al.*, 2002; Khan, Al-Mandhary, Al-Suti, Corcoran *et al.*, 2003; Khan, Al-Suti *et al.*, 2003; Khan, Al-Mandhary, Al-Suti, Ahrens *et al.*, 2003). They possess interesting optoelectronic properties useful for application in light-emitting diodes and photocells (Wilson *et al.*, 2000; Wilson, Chawdhury *et al.*, 2001; Wilson, Dhoot *et al.*, 2001). Precursors to these species, such as the title compound, are utilized as models in the study of the molecular and electronic properties and structure–property relationships in metal poly-ynes.



(I)

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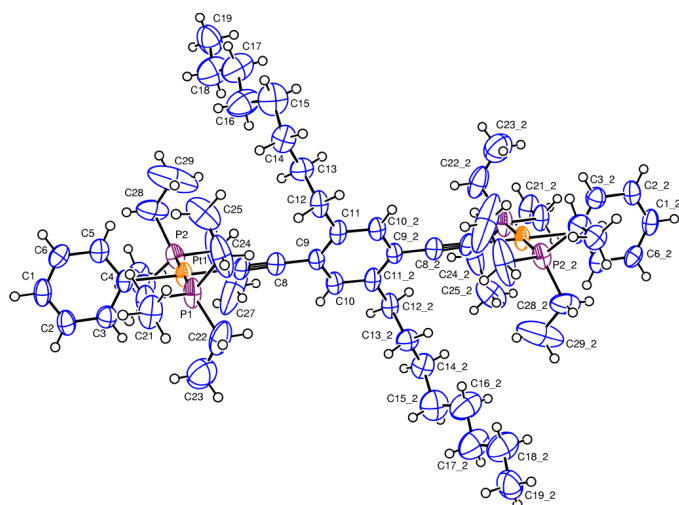


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was synthesized by the following procedure. To a stirred solution of *trans*-[(PEt₃)₂(Ph)PtCl] (0.543 g, 1.0 mmol) and 2,5-dioctyl-1,4-diethynylbenzene (0.175 g, 0.50 mmol) in CH₂Cl₂/Pr₂NH (50 ml, 1:1 *v/v*) under nitrogen was added a catalytic amount of CuI (5 mg). The yellow solution was stirred at room temperature for 20 h., after which all volatile components were removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and passed through a silica column by eluting with hexane/CH₂Cl₂ (1:1, *v/v*). Removal of the solvents under vacuo gave the title complex as a pale-yellow solid in 80% yield (0.546 g). Further purification was accomplished by triturating the complex in methanol.

Crystal data

[Pt ₂ (C ₆ H ₅) ₂ (C ₂₆ H ₃₆)(C ₆ H ₁₅ P) ₄]	<i>Z</i> = 1
<i>M_r</i> = 1365.53	<i>D_x</i> = 1.377 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 8.8760 (4) Å	Cell parameters from 26112 reflections
<i>b</i> = 13.7290 (9) Å	θ = 2.9–25.0°
<i>c</i> = 14.2320 (8) Å	μ = 4.37 mm ⁻¹
α = 81.892 (2)°	<i>T</i> = 150 (2) K
β = 74.610 (2)°	Plate, yellow
γ = 82.388 (2)°	0.32 × 0.20 × 0.08 mm
<i>V</i> = 1647.16 (16) Å ³	

Data collection

Bruker–Nonius KappaCCD diffractometer	5684 independent reflections
363 1° φ and 485 1° ω scans	4106 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	<i>R</i> _{int} = 0.109
<i>T</i> _{min} = 0.291, <i>T</i> _{max} = 0.705	θ _{max} = 25.0°
26112 measured reflections	<i>h</i> = –10 → 10
	<i>k</i> = –15 → 16
	<i>l</i> = –16 → 16

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.1002P)^2 + 1.5883P]$
$R[F^2 > 2\sigma(F^2)] = 0.066$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.172$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.07	$\Delta\rho$ _{max} = 2.29 e Å ⁻³
5684 reflections	$\Delta\rho$ _{min} = –2.59 e Å ⁻³
309 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

C4–Pt1	2.053 (10)	C24–P1	1.823 (15)
C7–C8	1.216 (13)	C26–P2	1.811 (15)
C7–Pt1	2.011 (10)	C28–P2	1.840 (13)
C8–C9	1.451 (13)	C30–P2	1.813 (11)
C20–P1	1.836 (11)	P1–Pt1	2.284 (3)
C22–P1	1.789 (14)	P2–Pt1	2.289 (2)
C8–C7–Pt1	178.6 (8)	C30–P2–C28	102.6 (6)
C7–C8–C9	178.2 (10)	C26–P2–Pt1	117.4 (5)
C22–P1–C24	102.7 (8)	C30–P2–Pt1	115.3 (4)
C22–P1–C20	105.5 (6)	C28–P2–Pt1	110.3 (5)
C24–P1–C20	104.6 (6)	C7–Pt1–C4	178.8 (4)
C22–P1–Pt1	114.7 (5)	C7–Pt1–P1	88.0 (3)
C24–P1–Pt1	112.2 (4)	C4–Pt1–P1	91.2 (3)
C20–P1–Pt1	115.8 (3)	C7–Pt1–P2	92.6 (3)
C26–P2–C30	106.3 (7)	C4–Pt1–P2	88.2 (3)
C26–P2–C28	103.3 (10)	P1–Pt1–P2	178.58 (11)
C8–C9–C10–C11 ⁱ	–179.8 (8)	C20–P1–Pt1–C7	172.7 (6)
C3–C4–Pt1–P1	–87.8 (8)	C26–P2–Pt1–C7	8.2 (9)
C3–C4–Pt1–P2	93.5 (8)	C30–P2–Pt1–C7	134.7 (6)
C22–P1–Pt1–C7	–63.9 (7)	C28–P2–Pt1–C7	–109.7 (6)
C24–P1–Pt1–C7	52.7 (7)		

Symmetry code: (i) 1 – *x*, 1 – *y*, 1 – *z*.

Aromatic, methylene and methyl H atoms were constrained as riding atoms fixed to the parent atoms at distances of 0.95, 0.99 and 0.98 Å, respectively. The isotropic displacement parameters were fixed at 120% of the *U*_{eq} values of the relevant parent atoms in the case of aromatic and methylene H atoms. Methyl H-atom isotropic displacement parameters were similarly treated but at a ratio of 1.5 relative to the appropriate parent atom. It will be noted that the anisotropic displacement parameters on certain phosphine C atoms are somewhat elongated. Attempts to model disorder in these regions resulted in negligible improvement in convergence. The solution and refinement of the crystal structure otherwise proceeded routinely. This observation can be readily explained by the fact that the sample chosen for X-ray analysis, while being the very best available after copious recrystallization attempts, was nevertheless a very thin plate of average quality. Hence, the data set obtained was not as ideal as those routinely collected on our diffractometers. The highest peak (2.29 e Å⁻³) and deepest hole (–2.59 e Å⁻³) are both associated with the metal atom, being located at distances of 1.04 and 0.97 Å, respectively, from Pt1.

Data collection: COLLECT (Nonius, 1997); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: DIRDIF99 (Beurskens *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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References

- Beljonne, D., Wittmann, H. F., Köhler, A., Graham, S., Younus, M., Lewis, J., Raithby, P. R., Khan, M. S., Friend, R. H. & Bredas, J. L. (1996). *J. Chem. Phys.* **105**, 3868–3877.

- Beurskens, P. T., Beurskens, G., de Gelder, R., Garcia-Granda, S., Israel, R., Gould, R. O. & Smits, J. M. M. (1999). *The DIRDIF99 Program System*. Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Chawdhury, N., Köhler, A., Friend, R. H., Wong, W.-Y., Lewis, J., Younus, M., Raithby, P. R., Corcoran, T. C., Al-Mandhary, M. R. A. & Khan, M. S. (1999). *J. Chem. Phys.* **110**, 4963–4970.
- Chawdhury, N., Köhler, A., Friend, R. H., Younus, M., Long, N. J., Raithby, P. R. & Lewis, J. (1998). *Macromolecules*, **31**, 722–727.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Khan, M. S., Al-Mandhary, M. R. A., Al-Suti, M. K., Ahrens, B., Mahon, M. F., Male, L., Raithby, P. R., Boothby, C. E. & Köhler, A. (2003). *J. Chem. Soc. Dalton Trans.* pp. 74–84.
- Khan, M. S., Al-Mandhary, M. R. A., Al-Suti, M. K., Corcoran, T. C., Al-Mahrooqi, Y., Attfield, J. P., Feeder, N., David, W. I. F., Shankland, K., Friend, R. H., Köhler, A., Marseglia, E. A., Tedesco, E., Tang, C. C., Raithby, P. R., Collings, J. C., Roscoe, K. P., Batsanov, A. S., Stimson, L. M. & Marder, T. B. (2003). *New J. Chem.* **27**, 140–149.
- Khan, M. S., Al-Mandhary, M. R. A., Al-Suti, M. K., Feeder, N., Nahar, S., Köhler, A., Friend, R. H., Wilson, P. J. & Raithby, P. R. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2441–2448.
- Khan, M. S., Al-Mandhary, M. R. A., Al-Suti, M. K., Hisahm, A. K., Raithby, P. R., Ahrens, B., Mahon, M. F., Male, L., Marseglia, E. A., Tedesco, E., Friend, R. H., Köhler, A., Feeder, N. & Teat, S. J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 1358–1368.
- Khan, M. S., Al-Suti, M. K., Al-Mandhary, M. R. A., Ahrens, B., Bjernemose, J. K., Mahon, M. F., Male, L., Raithby, P. R., Friend, R. H., Köhler, A. & Wilson, J. S. (2003). *J. Chem. Soc. Dalton Trans.* pp. 65–73.
- Nonius. (1997). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Wilson, J. S., Chawdhury, N., Al-Mandhary, M. R. A., Younus, M., Khan, M. S., Raithby, P. R., Köhler, A. & Friend, R. H. (2001). *J. Am. Chem. Soc.* **123**, 9412–9417.
- Wilson, J. S., Dhoot, A. S., Seeley, A. J. A. B., Khan, M. S., Köhler, A. & Friend, R. H. (2001). *Nature (London)*, **413**, 828–831.
- Wilson, J. S., Köhler, A., Friend, R. H., Al-Suti, M. K., Al-Mandhary, M. R. A., Khan, M. S. & Raithby, P. R. (2000). *J. Chem. Phys.* **113**, 7627–7634.
- Wittmann, H. F., Friend, R. H., Kahn, M. S. & Lewis, J. (1994). *J. Chem. Phys.* **101**, 2693–2698.
- Younus, M., Köhler, A., Cron, S., Chawdhury, N., Al-Mandhary, M. R. A., Khan, M. S., Lewis, J., Long, N. J., Friend, R. H. & Raithby, P. R. (1998). *Angew. Chem. Int. Ed.* **37**, 3036–3039.