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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(C-C) = 0.005 \text{ \AA}$
R factor = 0.035
wR factor = 0.094
Data-to-parameter ratio = 16.2

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

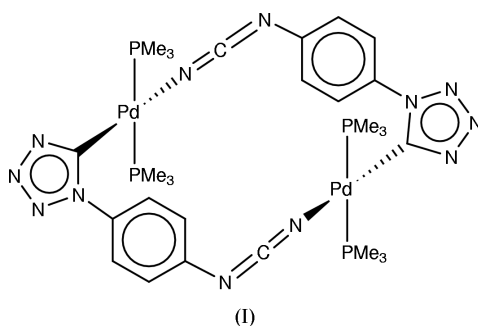
A cyclic dipalladium compound formed by concomitant N–C coupling and [2+3]-cycloaddition: bis[μ -1-[4-(carbodiimido)phenyl]tetrazolato- $\kappa^2 N:C^5$]-bis[bis(trimethylphosphine- κP)palladium(II)]

The title compound, $[\text{Pd}_2(\text{C}_8\text{H}_4\text{N}_6)_2(\text{C}_3\text{H}_9\text{P})_4]$, was prepared by treating $\text{Pd}(\text{PMe}_3)_2(\text{N}_3)_2$ with 1,4-phenylene diisocyanide $[\text{C}_6\text{H}_4(\text{NC})_2]$. This compound, a cyclic dimer, was formed by concomitant N–C coupling and [2 + 3]-cycloaddition. Around the square-planar Pd atom, the carbodiimide moiety and the tetrazolate ring are mutually *trans*. The N atom of the carbodiimide moiety is bonded to the Pd center, and the five-membered tetrazolate ring is coordinated to the Pd atoms through the C atom. The molecule is located on a center of symmetry.

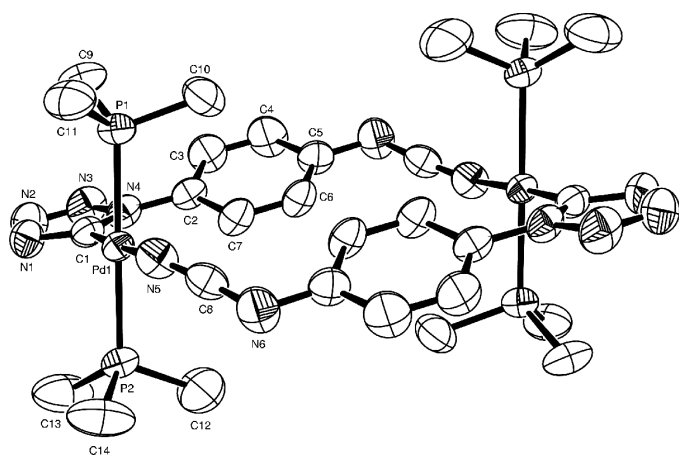
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Comment

Transition-metal complexes containing a carbodiimide or bis(carbodiimide) ligand, in which the nitrogen of a linear $\text{N}=\text{C}=\text{N}$ fragment is directly bonded to the metal, have received a great deal of attention due to their potential applications as catalysts for polymerization, precursors for metal nitrides and metal carbonitrides, and intermediates for organic cyanamides (Veneziani *et al.*, 1998; Kamijo *et al.*, 2001). Although many studies on the preparation and structures of metal–carbodiimide ($M-\text{N}=\text{C}=\text{N}-R$) and metal–tetrazolate [$M-\text{CN}_4(R)$] complexes have been reported, their chemical properties remain relatively unexplored. Furthermore, there have been only a few reports on the formation of complexes containing both carbodiimido and C-tetrazolate ligands, formed by concomitant N–C coupling with N_2 elimination (for the carbodiimide ligand) and [2 + 3]-cycloaddition (for the C-tetrazolato ligand) (Kim, Kwak *et al.*, 2002; Kim, Joo *et al.*, 2002). We have prepared a novel dipalladium cyclic complex, (I), containing both the above-mentioned ligands, by treating $\text{Pd}(\text{PMe}_3)_2(\text{N}_3)_2$ with 1,4-phenylene diisocyanide $[\text{C}_6\text{H}_4(\text{NC})_2]$.



The asymmetric unit of (I) consists of only half the formula unit with the other half generated by crystallographic inversion. The Pd atom is coordinated by two trimethylphosphines, a carbodiimide group, and a tetrazolate ring. The geometry of


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the crystallographic inversion.

the Pd atom can be described as slightly distorted square-planar. The carbodiimide ligand and tetrazolate ring are mutually *trans*. The molecular structure clearly shows that an N atom of the carbodiimide ligand is bonded to the Pd center and that the five-membered tetrazolate ring is coordinated to Pd through the C atom. The tetrazolate ligand is essentially planar, and the benzene ring attached to the tetrazolate ring is twisted out of that ring plane, with a dihedral angle of 23.9 (2)°. The carbodiimide group is approximately linear [$\text{N}=\text{C}=\text{N} = 173.9(4)^\circ$]. The Pd···Pd separation is 8.157 (3) Å. The Pd–N(carbodiimide) and the Pd–C(tetrazolate) bond lengths are 2.058 (3) and 1.980 (3) Å, respectively, which are similar to those found in the closely related compounds, *trans*-Pd[CN₄(R)](N=C=N–R)L₂ (R = 2,6-Me₂C₆H₃, L = PMe₃ or PMe₂Ph) (Kim, Kwak *et al.*, 2002).

Experimental

A solution of Pd(PMe₃)₂(N₃)₂ (100 mg, 0.29 mmol) and 1,4-phenylene diisocyanide (37 mg, 0.36 mmol) in nitromethane (30 ml) was stirred for 3 h, and the solvent was removed under vacuum. The resulting solids were washed with diethyl ether (2 × 20 ml) to give the title compound. Recrystallization from dichloromethane–diethyl ether gave orange crystals, 96 mg, 74.6%; m.p. 535–537 K (decomposition). IR (KBr, ν, cm⁻¹): 2154, 2117 (NCN); ¹H NMR (CDCl₃, p.p.m.): 1.19 (s, 36 H, PMe₃), 7.07–8.17 (m, C₆H₄); ¹³C{¹H} NMR (CDCl₃, p.p.m.): 13.73 (s, PMe₃), 120.6–128.6 (C₆H₄ or CN₄), 151.7 (s, NCN); ³¹P{¹H} NMR (CDCl₃, p.p.m.): –11.70 (s, PMe₃); analysis calculated for C₂₈H₄₄N₁₂P₄Pd₂: C 37.98, H 5.01, N 18.98%; found: C 36.99, H 4.96, N 19.14%.

Crystal data

[Pd₂(C₈H₄N₆)₂(C₃H₉P)₄]
M_r = 885.43
 Triclinic, P $\bar{1}$
a = 8.842 (3) Å
b = 9.519 (3) Å
c = 11.996 (3) Å
 α = 99.095 (19)°
 β = 103.42 (2)°
 γ = 90.85 (2)°
V = 968.5 (5) Å³

Z = 1
D_x = 1.518 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 26 reflections
 θ = 5.1–12.5°
 μ = 1.13 mm⁻¹
T = 293 (2) K
 Block, orange
 0.50 × 0.42 × 0.20 mm

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
T_{min} = 0.574, *T_{max}* = 0.798
 3615 measured reflections
 3374 independent reflections
 3039 reflections with *I* > 2σ(*I*)

R_{int} = 0.021
 θ_{max} = 25.0°
h = 0 → 10
k = –11 → 11
l = –14 → 13
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.035
wR(*F*²) = 0.094
S = 1.03
 3374 reflections
 208 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.2618P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|-------------|-----------|------------|
| Pd1–C1 | 1.980 (3) | N2–N3 | 1.308 (5) |
| Pd1–N5 | 2.058 (3) | N3–N4 | 1.375 (4) |
| Pd1–P1 | 2.3219 (11) | N4–C1 | 1.362 (4) |
| Pd1–P2 | 2.3318 (11) | N5–C8 | 1.166 (5) |
| N1–C1 | 1.336 (5) | N6–C8 | 1.272 (5) |
| N1–N2 | 1.361 (5) | | |
| C1–Pd1–N5 | 176.78 (13) | N5–Pd1–P2 | 91.35 (10) |
| C1–Pd1–P1 | 89.50 (10) | P1–Pd1–P2 | 179.48 (3) |
| N5–Pd1–P1 | 88.28 (10) | N5–C8–N6 | 173.9 (4) |
| C1–Pd1–P2 | 90.86 (10) | | |

All H atoms were placed in ideal positions (C–H = 0.93–0.93 Å) and refined using a riding model, with *U_{iso}*(H) = 1.2*U_{eq}*(C). One trimethylphosphine ligand is probably slightly disordered, but the disorder was not resolved. Anisotropic refinement applying several possible site occupation factors was unstable and that is why the displacement parameters of the C atoms (C12–C14) in that phosphine ligand are relatively large compared to those in the other phosphine ligand.

Data collection: XSCANS (Siemens, 1995); cell refinement: XSCANS; data reduction: SHELXTL (Siemens, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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