[2,2'-(1,3'-Bicyclohexenyl)]bis(triphenylphosphine)platinum(0) Tetrahydrofuran Solvate

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Abstract

The Pt atom has square-planar coordination in the title complex, $[Pt(C_{12}H_{16})(C_{18}H_{15}P)_2].0.85C_4H_8O$. The bidentate ligand is not in the plane of coordination, but forms an angle of $162.6(3)°$ with it. The PPh_3 ligands are in a *cis* conformation. The Pt—P lengths are different [2.311(1) and 2.348(1) Å] and the P—Pt—P angle is 94.77(5)°.

Comment

For some years we have been interested in the preparation and characterization of transition metal complexes of strained cyclic allenes (Omrcen, Conti & Jones, 1991; Abboud, Lu & Jones, 1992; Lu, Jones & Winchester, 1993; Lu, Abboud & Jones, 1993). Prior to 1993, the smallest complexes that had been isolated were iron (Manganiello, Oon, Radcliffe & Jones, 1985; Winchester & Jones, 1985; Oon, Koziol, Palenik & Jones, 1987; Oon & Jones, 1988) and platinum complexes of 1,2-cycloheptadiene (Visser & Ramakers, 1972) and 1,2,4,6-cycloheptatetraene. The former was prepared by generating the allene moiety from a previously complexed ligand and the latter by ligand displacement involving previously generated allenes. In 1993, we reported the preparation of the first recorded six-membered allene complex, a zirconocene complex of 1-methyl-1,2-cyclohexadiene (Yin, Abboud & Jones, 1993). As in the preparation of the Fe complex of 1,2-cycloheptadiene, this was synthesized by generating the allene from a previously complexed ligand. The purpose of this work was to determine whether a transition metal complex of 1,2-cyclohexadiene could be prepared by a ligand displacement reaction.

Tris(triphenylphosphine)platinum was selected as the metal system for this study because platinum has a vacant coordination site to which the highly unstable allene could complex and because Visser had successfully trapped 1,2-cycloheptadiene with this reagent (Visser & Ramakers, 1972). Although Visser had failed to prepare a complex of 1,2-cyclohexadiene by this reaction, it oc-

curred to us that use of a different base for generating the six-membered allene might lead to more positive results (Lu, Abboud & Jones, 1993). After confirming both Visser's success (preparation of the 1,2-cycloheptadiene complex) and failure (no trace of a 1,2-cyclohexadiene complex) using KO^tBu as the base, the reaction was repeated using lithium diethylamide (LDA). To our surprise, this reaction gave two products in a ratio of about 10:1, the major one being the platinum–cyclohexyne complex (1) and the minor one being the title structure (3).
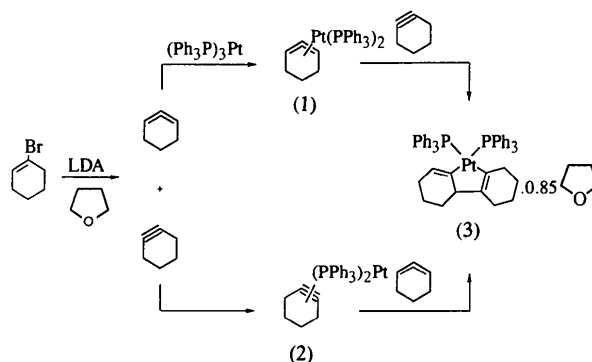
The two most likely origins of complex (3) are reaction of 1,2-cyclohexadiene with (2) or coupling of cyclohexyne with the desired platinum complex of 1,2-cyclohexadiene, (1). The former possibility was eliminated by treating 1-bromocyclohexene with LDA in the presence of only complex (2). No trace of (3) was detected. This is consistent with the alternative possibility, *i.e* reaction of cyclohexyne with the allene complex of interest. Less obvious mechanisms for formation of (3) are, of course, also possible.

The five-membered ring of (3) containing the Pt atom exhibits an envelope conformation, with the Pt atom occupying the flap position (Fig. 1). The plane of the flap (containing atoms Pt, C1 and C1') forms an angle of $151.1(3)°$ with the plane of the envelope (containing atoms C1, C1', C2 and C2'). The Pt atom lies at a distance of $0.77(1)$ Å from the envelope plane. Although atoms C1 and C1' have similar electronic environments, they have different bond lengths with the Pt atom, Pt—C1 being the shorter. This shortening of the Pt—C1 bond and the lengthening of the opposite Pt—P2 bond is similar to a *trans* effect if there were differences in the electronic environments of C1 and C1', though it is not clear why C1 would have a stronger *trans* effect (if any) than C1'. It is worthy of note that the C1=C6 and C1'=C2' double bonds have different orientations with respect to the opposite Pt—P bonds; Pt—C1=C6 is $126.4(5)$ and Pt—C1'=C2' is $113.4(4)°$. This asymmetric bonding between Pt and P is observed in many Pt complexes found in the Cambridge Structural Database (Spring 1995 release; Allen, Kennard & Taylor, 1983). The closest example

is the structure of [7,7'-di(cyclohepta-1,3,5-trien-1-yl)]-bis(triphenylphosphine)platinum (Winchester, Gawron, Palenik & Jones, 1985), where the Pt—P distances are 2.300 and 2.335 Å, and the Pt—C distances are 1.923 and 2.096 Å.
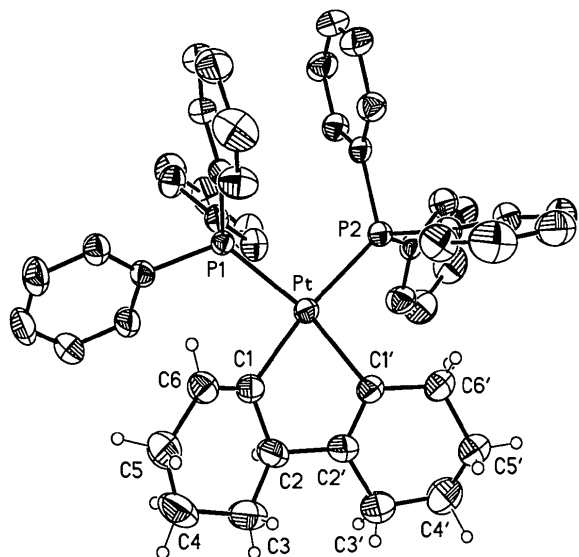

Fig. 1. The molecular structure of (3) showing the atom-numbering scheme and ellipsoids at 50% probability. Phenyl H atoms have been removed for clarity.

Experimental

The title compound, (3), was synthesized by dissolving tris(triphenylphosphine)platinum (0.5 g, 0.51 mmol) and LDA (lithium diethylamide; 0.2 g, 1.0 mmol) in tetrahydrofuran (10 ml). To this solution, 1-bromocyclohexene (0.1 g, 0.62 mmol) in tetrahydrofuran (2 ml) was added dropwise at room temperature. After 2 h, the solution was filtered through silica gel. The products, (2) and (3), were collected by adding excess hexane to induce crystallization. The products were further purified by recrystallization from tetrahydrofuran/hexane solution. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.1–7.5 (m), 4.9 (m, $^3J_{PtH}$ = 60.2 Hz), 3.2 (m), 1.0–1.8 (m). ^{31}P NMR (121 MHz, CDCl$_3$): δ 23.8 (d, $^1J_{PtP}$ = 1792 Hz, $^2J_{PP}$ = 7 Hz), 28.1 (d, $^2J_{PP}$ = 7 Hz). Analysis for C$_{48}$H$_{46}$P$_2$Pt.0.85C$_4$H$_8$O: calculated C 65.62, H 5.68; found C 65.63; H 5.64%. A single crystal of (3) was grown from hexane/tetrahydrofuran solution and its structure established by X-ray diffraction.

Crystal data

[Pt(C$_{12}$H$_{16}$)(C$_{18}$H$_{15}$P)$_2$].-
0.85C$_4$H$_8$O
M_r = 941.17
Triclinic
$P\bar{1}$
a = 9.711 (1) Å
b = 10.907 (2) Å
c = 20.669 (3) Å
α = 89.58 (1)°
β = 84.04 (1)°
γ = 85.54 (1)°
V = 2170.8 (6) Å^3
Z = 2
D_x = 1.44 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32
reflections
θ = 10–11°
μ = 3.34 mm^{-1}
T = 293 (2) K
Needle
0.34 × 0.15 × 0.12 mm
Pale yellow

Data collection

Siemens P3/mV diffractometer
ω scans
Absorption correction:
from measured crystal
faces (SHELXTL-Plus;
Sheldrick, 1991)
T_{min} = 0.328, T_{max} = 0.669
8112 measured reflections
7619 independent reflections

6233 observed reflections
[$I > 2\sigma(I)$]
R_{int} = 0.0176
θ_{max} = 25.00°
h = 0 → 11
k = −12 → 12
l = −24 → 24
4 standard reflections
monitored every 96
reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R(F)$ = 0.0367
$wR(F^2)$ = 0.0786
S = 1.052
7619 reflections
460 parameters
H atoms riding with C—H = 0.96 Å
$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.014
$\Delta\rho_{max}$ = 1.098 e Å^{-3}
$\Delta\rho_{min}$ = −1.060 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}
Pt	0.24217 (2)	0.13824 (2)	0.26017 (1)	0.03605 (8)
P1	0.35558 (13)	0.09881 (12)	0.35189 (6)	0.0346 (3)
P2	0.33357 (15)	−0.04364 (13)	0.20643 (6)	0.0390 (3)
C1	0.1374 (5)	0.2960 (5)	0.2989 (3)	0.0430 (13)
C1′	0.1443 (6)	0.2114 (5)	0.1812 (3)	0.0500 (14)
C2	0.1245 (7)	0.3974 (5)	0.2489 (3)	0.059 (2)
C2′	0.1140 (8)	0.3350 (6)	0.1852 (3)	0.065 (2)
C3	0.0071 (9)	0.4949 (7)	0.2687 (4)	0.084 (2)
C3′	0.0785 (11)	0.4118 (7)	0.1293 (4)	0.103 (3)
C4	0.0016 (9)	0.5310 (7)	0.3377 (4)	0.088 (2)
C4′	0.0894 (14)	0.3439 (8)	0.0657 (4)	0.130 (4)
C5	−0.0218 (8)	0.4208 (7)	0.3820 (3)	0.075 (2)
C5′	0.0466 (9)	0.2230 (7)	0.0722 (4)	0.085 (2)
C6	0.0663 (6)	0.3078 (6)	0.3576 (3)	0.0527 (15)
C6′	0.1242 (8)	0.1483 (6)	0.1198 (3)	0.071 (2)
C11	0.3342 (5)	0.2129 (5)	0.4185 (2)	0.0388 (12)
C12	0.2794 (6)	0.1887 (5)	0.4809 (3)	0.0493 (14)
C13	0.2674 (7)	0.2802 (7)	0.5280 (3)	0.065 (2)
C14	0.3094 (7)	0.3949 (6)	0.5133 (3)	0.067 (2)
C15	0.3664 (8)	0.4189 (6)	0.4512 (3)	0.067 (2)
C16	0.3793 (7)	0.3284 (5)	0.4042 (3)	0.057 (2)
C21	0.5449 (5)	0.0943 (5)	0.3366 (3)	0.0418 (12)
C22	0.6317 (6)	0.0741 (6)	0.3854 (3)	0.055 (2)
C23	0.7738 (7)	0.0804 (7)	0.3701 (4)	0.074 (2)
C24	0.8295 (7)	0.1112 (7)	0.3091 (4)	0.076 (2)

C25	0.7422 (7)	0.1352 (7)	0.2620 (4)	0.072 (2)
C26	0.6015 (6)	0.1274 (6)	0.2750 (3)	0.055 (2)
C31	0.3038 (6)	−0.0400 (5)	0.3950 (2)	0.0406 (12)
C32	0.3903 (7)	−0.1238 (5)	0.4260 (3)	0.0500 (14)
C33	0.3343 (9)	−0.2210 (6)	0.4605 (3)	0.067 (2)
C34	0.1965 (10)	−0.2363 (6)	0.4640 (3)	0.078 (2)
C35	0.1099 (8)	−0.1549 (7)	0.4320 (4)	0.082 (2)
C36	0.1636 (6)	−0.0580 (6)	0.3980 (3)	0.062 (2)
C41	0.4172 (6)	−0.1721 (5)	0.2504 (2)	0.0403 (12)
C42	0.5572 (6)	−0.1767 (5)	0.2591 (3)	0.0490 (14)
C43	0.6207 (7)	−0.2735 (6)	0.2910 (3)	0.063 (2)
C44	0.5442 (8)	−0.3674 (6)	0.3151 (3)	0.070 (2)
C45	0.4046 (8)	−0.3648 (6)	0.3084 (3)	0.065 (2)
C46	0.3423 (6)	−0.2680 (5)	0.2754 (3)	0.0520 (14)
C51	0.1986 (6)	−0.1242 (5)	0.1722 (3)	0.0476 (14)
C52	0.0679 (7)	−0.1161 (7)	0.2054 (4)	0.072 (2)
C53	−0.0398 (8)	−0.1739 (8)	0.1817 (5)	0.093 (3)
C54	−0.0161 (10)	−0.2387 (7)	0.1253 (5)	0.092 (3)
C55	0.1113 (10)	−0.2486 (7)	0.0926 (4)	0.087 (3)
C56	0.2194 (7)	−0.1912 (5)	0.1163 (3)	0.060 (2)
C61	0.4665 (6)	−0.0231 (5)	0.1385 (2)	0.0439 (13)
C62	0.4890 (7)	0.0944 (6)	0.1159 (3)	0.057 (2)
C63	0.5922 (8)	0.1127 (7)	0.0664 (3)	0.079 (2)
C64	0.6729 (8)	0.0146 (8)	0.0384 (4)	0.083 (2)
C65	0.6527 (7)	−0.1017 (8)	0.0600 (3)	0.075 (2)
C66	0.5496 (7)	−0.1215 (6)	0.1095 (3)	0.059 (2)

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

Pt—C1	2.053 (5)	P1—C11	1.846 (5)
Pt—C1'	2.095 (5)	P2—C61	1.831 (5)
Pt—P1	2.311 (1)	P2—C51	1.836 (6)
Pt—P2	2.348 (1)	P2—C41	1.845 (5)
P1—C21	1.829 (5)	C1—C6	1.334 (7)
P1—C31	1.828 (5)	C1'—C2'	1.358 (8)

C1—Pt—C1'	77.7 (2)	C61—P2—C51	105.6 (3)
C1—Pt—P1	92.99 (15)	C61—P2—C41	101.1 (2)
C1'—Pt—P1	168.4 (2)	C51—P2—C41	99.7 (2)
C1—Pt—P2	171.33 (15)	C61—P2—Pt	115.0 (2)
C1'—Pt—P2	95.1 (2)	C51—P2—Pt	111.9 (2)
P1—Pt—P2	94.77 (5)	C41—P2—Pt	121.4 (2)
C21—P1—C31	110.2 (2)	C6—C1—C2	120.2 (5)
C21—P1—C11	97.4 (2)	C6—C1—Pt	126.4 (4)
C31—P1—C11	101.5 (2)	C2—C1—Pt	112.5 (4)
C21—P1—Pt	113.8 (2)	C2'—C1'—C6'	118.2 (5)
C31—P1—Pt	113.0 (2)	C2'—C1'—Pt	113.4 (4)
C11—P1—Pt	119.3 (2)	C6'—C1'—Pt	127.8 (4)

The intensity contribution of the disordered tetrahydrofuran molecule was calculated with *PLATON/SQUEEZE* (Spek, 1994) and subtracted from the full data set; ratio of complex to tetrahydrofuran was found to be 1:0.85. The new data set, with the solvent contribution removed, was used in the final refinement.

Data collection: *SHELXTL-Plus* (Sheldrick, 1991). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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(Diethyl ether-*O*)[*N*-(2,6-diisopropyl-phenyl)-*N*-(trimethylsilyl)amido-*N*]-(pyridine-*N*)lithium

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Abstract

The title compound, [Li($C_{15}H_{26}NSi$)($C_4H_{10}O$)(C_5H_5N)], contains an Li atom with approximately trigonal-planar coordination, whose principal coordination sphere consists of one *N*-(2,6-diisopropylphenyl)-*N*-(trimethylsilyl)amido, one pyridine and one diethyl ether ligand. There is a further possible bonding contact between the Li atom and the N-*ipso* C atom of the 2,6-diisopropylphenyl group.