

gefunden, wenn das Zahlenverhältnis von Kationen zu Anionen 2:1 beträgt (Müller, Klingelhöfer, Eicher & Bohrer, 1984; Conradi, Bohrer, Weber & Müller, 1987).

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Literatur

- CONRADI, E., BOHRER, R., WEBER, R. & MÜLLER, U. (1987). *Z. Kristallogr.* **181**, 187–198. Dort weitere Literatur.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1897.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- FELTZ, A. (1963). *Z. Anorg. Allg. Chem.* **323**, 35–43.
- HAASE, W. & HOPPE, H. (1968). *Acta Cryst.* **B24**, 282–283.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- JOHNSON, C. K. (1965). *ORTEP*. Bericht ORNL-3794. Oak Ridge National Laboratory, Tennessee, VSta.
- KRUG, V. (1988). Dissertation, Univ. Marburg, Bundesrepublik Deutschland.
- KRUG, V., KOELLNER, G. & MÜLLER, U. (1988). *Z. Naturforsch. Teil B*, **43**, 1501–1509.
- MÜLLER, U. (1971). *CADLP*. Programm zur Auswertung und Lp-Korrektur von Diffraktometerdaten. Univ. Marburg, Bundesrepublik Deutschland.
- MÜLLER, U., KLINGELHÖFER, P., EICHER, J. & BOHRER, R. (1984). *Z. Kristallogr.* **168**, 121–131.
- SHELDRIK, G. M. (1976). *SHELX76*. Program für die Kristallstrukturbestimmung. Univ. Cambridge, England.
- STOECKLI-EVANS, H. (1974). *Helv. Chim. Acta*, **57**, 684–689.
- THEWALT, U. & KEBBEL, B. (1978). *J. Organomet. Chem.* **150**, 59–66.
- THEWALT, U. & SCHOMBURG, D. (1977). *J. Organomet. Chem.* **127**, 169–174.
- WATENPAUGH, K. & CAUGHLAN, C. N. (1967). *Inorg. Chem.* **6**, 963–967.

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A Seven-Membered Platinum–Amino–Amidine Metallacycle. X-ray Structure of *cis*-[Pt(NH=CPhNBu'CH₂CH₂NHBu')Cl₂]_{1/2}Me₂CO

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Abstract. *cis*-Dichloro{*N*¹-*tert*-butyl-*N*¹-[2-(*tert*-butylamino)ethyl]benzamidine-*N*²,*N*}platinum, [PtCl₂(C₁₇H₂₉N₃)_{1/2}C₃H₆O, *M*_r = 570.47, monoclinic, *C2/c*, *a* = 27.426 (17), *b* = 9.843 (7), *c* = 16.542 (12) Å, β = 99.69 (6)°, *V* = 4402 (5) Å³, *Z* = 8, *D*_x = 1.722 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 6.695 mm⁻¹, *F*(000) = 2240, room temperature, *R* = 0.0398, *wR* = 0.0490 for 1402 independent observed reflections. In the complex the coordination of platinum is roughly planar and involves two Cl atoms [Pt—Cl = 2.286 (6) and 2.291 (7) Å] and two N atoms from the chelating aminoamidine ligand [Pt—N = 2.015 (15) and 1.961 (15) Å].

Introduction. The synthetic and structural chemistry of coordinated nitriles which are susceptible to nucleophilic attack by water, alcohols and amines to yield the corresponding amides, imidic esters, and amidines has already been broadly established (Storhoff & Lewis, 1977; Braunstein, Matt, Dusausoy & Protas, 1979; Braunstein, Matt,

Dusausoy & Fischer, 1983; Uchiyama, Takagi, Matsumoto, Ooi, Nakamura & Kawaguchi, 1979, 1981). We found that [PtCl₂(NCPh)₂], which is widely used as a starting material for the preparation of organoplatinum(II) complexes, reacts readily with weak nucleophiles such as *N,N'*-di-*tert*-butylethylenediamine and also with hydroxide ion to give amidine and amidate platinum(II) species. The structures of two such products, [Pt(NH=CPhNBu'CH₂CH₂NHBu')Cl(NHCOPh)] and *cis*-[Pt(NH=CPhNBu'CH₂CH₂NHBu')Cl₂(NCPh)], have already been determined by X-ray diffraction methods (Maresca, Natile, Intini, Gasparini, Tiripicchio & Tiripicchio Camellini, 1986). We now report the X-ray structure of *cis*-[Pt(NH=CPhNBu'CH₂CH₂NHBu')Cl₂], (1), which is the ultimate product in the reaction of *cis*-[PtCl₂(NCPh)₂] with the diamine.

Experimental. The compound (1) is obtained from *cis*-[Pt(NH=CPhNBu'CH₂CH₂NHBu')Cl₂(NCPh)]

(2) by release of a benzonitrile molecule. From a solution of (2), on standing at room temperature, compound (1) is formed and precipitates out owing to its low solubility in common organic solvents. The rate of transformation depends very much upon the nature of the solvent. This transformation occurs also in the solid state and can be followed by running from time to time the IR spectrum of the compound in a KBr pellet. A prismatic pale yellow crystal approximately 0.05 × 0.14 × 0.20 mm, Siemens AED diffractometer, Nb-filtered Mo K α radiation, 24 reflections ($9.5 < \theta < 13.5^\circ$) for accurate unit-cell parameters; $\theta/2\theta$ scan mode, 3067 independent reflections with $3 < \theta < 23^\circ$, $-30 \leq h \leq 28$, $0 \leq k \leq 10$, $0 \leq l \leq 18$, 1402 reflections with $I \geq 2\sigma(I)$ considered observed, no significant intensity deterioration of the standard reflection (413). Lp corrections. Correction for absorption effects was applied (maximum and minimum transmission factors 1.1976 and 0.8522 respectively; Walker & Stuart, 1983; Uguzzoli, 1987). Patterson and Fourier methods; full-matrix least-squares refinement on F , anisotropic thermal parameters for non-H atoms excepting those of the acetone molecule; all the H atoms at their geometrically calculated positions with fixed isotropic thermal parameters ($U = 0.09 \text{ \AA}^2$ except for the H atoms of acetone for which $U = 0.20 \text{ \AA}^2$) (SHELX76; Sheldrick, 1976). Final $R = 0.0398$, $wR = 0.0490$; $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.7077$ and $g = 0.0052$ at convergence; $(\Delta/\sigma)_{\max} = 0.69$, final $\Delta\rho$ values $< |0.6| \text{ e \AA}^{-3}$; atomic scattering factors (anomalous dispersion of Pt and Cl atoms) from *International Tables for X-ray Crystallography* (1974); calculations performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord Orientale, Casalecchio (Bologna) with financial support from the University of Parma.*

Discussion. Final atomic coordinates for the non-H atoms are listed in Table 1 and relevant distances and angles in Table 2.

The structure consists of platinum complexes and of molecules of acetone of crystallization (which straddle crystallographic diad axes). The coordination of the Pt atom (Fig. 1) is roughly planar and involves two Cl atoms and two N atoms from the chelating aminoamidine ligand. Pt, Cl(1), Cl(2), N(1) and N(2) are displaced from the mean plane passing through them by 0.012 (9), 0.020 (11), -0.030 (11),

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for the non-H atoms, with e.s.d.'s in parentheses

$B_{\text{eq}} = \frac{1}{3}\text{trace } U$ except for O, C(18) and C(19) for which B_{eq} is the refined isotropic displacement parameter.

	x	y	z	B_{eq} (\AA^2)
Pt	2687 (1)	-246 (1)	2571 (1)	2.8
Cl(1)	2110 (2)	654 (5)	1554 (3)	4.2
Cl(2)	3112 (2)	-1171 (6)	1625 (4)	4.8
N(1)	2368 (5)	644 (16)	3447 (8)	2.2
N(2)	3167 (6)	-1100 (20)	3434 (9)	3.0
N(3)	3614 (7)	811 (22)	4006 (11)	3.6
C(1)	2744 (7)	1214 (24)	4140 (12)	3.9
C(2)	3205 (7)	1709 (24)	3835 (13)	3.6
C(3)	3539 (8)	-572 (23)	3924 (12)	3.2
C(4)	1964 (8)	-74 (27)	3817 (12)	5.0
C(5)	2148 (11)	-1465 (21)	4148 (18)	6.0
C(6)	1530 (8)	-349 (30)	3103 (13)	5.1
C(7)	1778 (8)	683 (24)	4466 (12)	4.2
C(8)	4124 (9)	1379 (24)	4018 (15)	4.0
C(9)	4081 (10)	2439 (35)	3367 (23)	10.9
C(10)	4501 (9)	345 (32)	3925 (24)	8.5
C(11)	4288 (11)	2097 (42)	4855 (21)	9.9
C(12)	3857 (8)	-1515 (28)	4503 (16)	4.7
C(13)	3959 (10)	-1298 (47)	5307 (16)	6.2
C(14)	4221 (14)	-2188 (49)	5852 (27)	9.7
C(15)	4395 (16)	-3270 (64)	5490 (32)	10.9
C(16)	4343 (13)	-3613 (38)	4730 (33)	10.1
C(17)	4027 (8)	-2662 (29)	4188 (18)	5.1
O	0	180 (67)	2500	22 (2)
C(18)	0	1353 (145)	2500	22 (4)
C(19)	347 (15)	2064 (45)	3108 (24)	18 (2)

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

Pt—Cl(1)	2.286 (6)	C(2)—N(3)	1.42 (3)
Pt—Cl(2)	2.291 (7)	N(2)—C(3)	1.30 (3)
Pt—N(1)	2.015 (15)	N(3)—C(3)	1.38 (3)
Pt—N(2)	1.961 (15)	C(3)—C(12)	1.50 (3)
N(1)—C(1)	1.52 (2)	N(3)—C(8)	1.50 (3)
C(1)—C(2)	1.52 (3)	N(1)—C(4)	1.53 (3)
Cl(1)—Pt—Cl(2)	91.2 (4)	N(3)—C(2)—C(1)	114 (2)
Cl(1)—Pt—N(1)	91.7 (6)	C(2)—N(3)—C(3)	120 (2)
N(1)—Pt—N(2)	89.0 (7)	C(2)—N(3)—C(8)	118 (2)
Cl(2)—Pt—N(2)	88.3 (7)	C(3)—N(3)—C(8)	119 (2)
Pt—N(1)—C(1)	113 (1)	N(3)—C(3)—C(12)	119 (2)
Pt—N(1)—C(4)	121 (1)	N(2)—C(3)—C(12)	117 (2)
C(1)—N(1)—C(4)	108 (2)	N(2)—C(3)—N(3)	123 (2)
N(1)—C(1)—C(2)	111 (2)	Pt—N(2)—C(3)	130 (2)

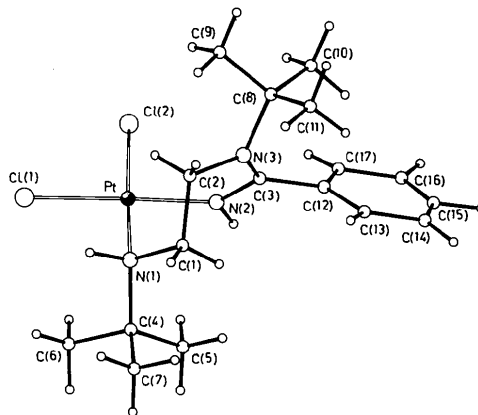


Fig. 1. View of the complex *cis*-[Pt(NH=CPhNBu'CH₂CH₂-NHBu')Cl₂] with the atomic numbering scheme.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52371 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

–0.092 (18) and 0.094 (21) Å, respectively. The Pt—N(1) bond, 2.015 (15) Å, is slightly longer than Pt—N(2), 1.961 (15) Å, reflecting the different hybridization of the donor atoms. The 'bite' angle of the chelating ligand is 89.0 (7)°. In square-planar platinum(II) complexes the bite angle of the chelate ring takes up the theoretical value of 90° only in the case of seven-membered metallacycles (Maresca, Natile, Intini, Gasparri, Tiripicchio & Tiripicchio Camellini, 1986), while much smaller values are found for five- and six-membered rings (Geue & Snow, 1971; Gollogly & Hawkins, 1972; Corey & Bailar, 1959; Fanizzi, Maresca, Natile, Lanfranchi, Manotti Lanfredi & Tiripicchio, 1988). This indicates that increasing the ring size decreases the steric strain within it and therefore the low occurrence of hepta-atomic rings is due to thermodynamic rather than steric factors.

The rather short N(3)—C(3) bond, 1.38 (3) Å, and the rough planarity of the aminic group at N(3) suggest extensive electron delocalization within the amidine moiety. Consequently, the N(2)C(3)N(3)C(2) torsion angle is only 26 (4)° although this causes some steric repulsion between the adjacent phenyl and *tert*-butyl groups. This situation is quite comparable to that found in (2), in which the ligand is monodentate, and in [Pt(NH=CPhN⁺Bu⁺CH₂CH₂NHBu⁺)Cl(NHCOPh)], in which the ligand participates in a chelate ring

(Maresca, Natile, Intini, Gasparri, Tiripicchio & Tiripicchio Camellini, 1986).

References

- BRAUNSTEIN, P., MATT, D., DUSAUSOY, Y. & FISCHER, J. (1983). *Organometallics*, **2**, 1410–1417.
 BRAUNSTEIN, P., MATT, D., DUSAUSOY, Y. & PROTAS, J. (1979). *J. Chem. Soc. Chem. Commun.* pp. 763–764.
 COREY, E. J. & BAILAR, J. C. (1959). *J. Am. Chem. Soc.* **81**, 2620–2629.
 FANIZZI, F. P., MARESCA, L., NATILE, G., LANFRANCHI, M., MANOTTI LANFREDI, A. M. & TIRIPICCHIO, A. (1988). *Inorg. Chem.* **27**, 2422–2431.
 GEUE, R. J. & SNOW, M. R. (1971). *J. Chem. Soc. A*, pp. 2981–2987.
 GOLLOGLY, J. R. & HAWKINS, C. J. (1972). *Inorg. Chem.* **11**, 156–161.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–101, 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 MARESCA, L., NATILE, G., INTINI, F. P., GASPARRINI, F., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1986). *J. Am. Chem. Soc.* **108**, 1180–1185.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 STORHOFF, B. N. & LEWIS, H. C. JR (1977). *Coord. Chem. Rev.* **23**, 1–29.
 UCHIYAMA, T., TAKAGI, K., MATSUMOTO, K., OOI, S., NAKAMURA, Y. & KAWAGUCHI, S. (1979). *Chem. Lett.* pp. 1197–1198.
 UCHIYAMA, T., TAKAGI, K., MATSUMOTO, K., OOI, S., NAKAMURA, Y. & KAWAGUCHI, S. (1981). *Bull. Chem. Soc. Jpn*, **54**, 1077–1084.
 UGOZZOLI, F. (1987). *Comput. Chem.* **11**, 109–120.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

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Structure of Benzyltrimethylammonium 7,7,7-Tricarbonyldodecahydro-7-cobalta-*nido*-undecaborate(1–)

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Abstract. [PhCH₂NMe₃][7,7,7-(CO)₃-7-CoB₁₀H₁₂], C₁₀H₁₆N⁺.B₁₀C₃CoH₁₂O₃⁻, *M_r* = 413.39, monoclinic, *P*2₁/*c*, *a* = 10.634 (5), *b* = 14.118 (5), *c* = 14.168 (4) Å, β = 91.81 (3)°, *V* = 2126.0 Å³, *Z* = 4, *D_x* = 1.291 Mg m⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.82 mm⁻¹, *F*(000) = 856, *T* = 185 (1) K, *R* = 0.0985 for 1967 independent observed reflections. The anion has effective *C*₃ molecular symmetry, with one carbonyl ligand lying *endo* to the open face of the cage. R.m.s. misfit calculations suggest that the B₁₀H₁₂ moiety is better described as the *arachno* fragment {B₁₀H₁₂}⁴⁻, and hence that the formal metal oxidation state is +3, the overall geometry of

the cobaltaborane approximating to that of the *nido* fragment of an icosahedron.

Introduction. At their simplest level metallaboranes and metallaheteroboranes can be viewed in two ways, either as complexes between a metal and a (hetero)borane ligand, or as heteroboranes in which the metal atom occupies a polyhedral vertex. In many cases these two views are entirely complementary and semantical.

Recent studies (Wynd, Welch & Parish, 1989; Wynd, 1988) from this laboratory, however, suggest that in some systems a distinction can be made