The solution was concentrated, and yellow crystals of *trans*-[Pd(SPh)$_2$(PMe$_3$)$_2$] precipitated: yield 0.16 g (86%); mp 101 °C dec; ^{1}H NMR (CDCl$_3$) δ 7.70–7.47, 7.20–6.87 (SPh), 1.77 (t, $J_{P,H}$ = 7.4, PMe); ^{31}P NMR (CDCl$_3$) δ −13.07 (s). Anal. Calcd for $C_{14}H_{16}P_2S_2Pd$: C, 45.33; H, 5.92. Found: C, 44.47; H, 6.44.

(IV) With [Pd(η^3-2-MeC$_3$H$_4$)(η^5-C$_5$H$_5$)]. A −40 °C solution of 17 (2.10 g, 4.40 mmol) in pentane (10 mL) was added at −40 °C to a pentane solution (10 mL) of [Pd(η^3-2-MeC$_3$H$_4$)(η^5-C$_5$H$_5$)] (1.00 g, 4.40 mmol). The solution was allowed to reach room temperature under continuous stirring. After 4 h the yellow solution was concentrated, cooled to −78 °C, and left for several days. The resulting yellow precipitate was collected, washed several times with cold pentane, and dried under high vacuum to give [Pd$_2$(PEt$_3$)$_2$(μ-2-MeC$_3$H$_4$)(μ-C$_5$H$_5$)] (21). yield 1.80 g (72%); mp 62 °C. Anal. Calcd for $C_{21}H_{42}P_2Pd_2$: C, 44.31; H, 7.44; P, 37.38. Found: C, 44.48; H, 7.99; P, 36.55.

An analagous reaction between 17 and [Pd(η^3-2-*t*-BuC$_3$H$_4$)(η^5-C$_5$H$_5$)] led to the formation of [Pd$_2$(PEt$_3$)$_2$(μ-2-*t*-BuC$_3$H$_4$) (μ-C$_5$H$_5$)] (23) as yellow crystals in 65% yield; mp 58 °C dec. Anal. Calcd for $C_{24}H_{48}P_2Pd_2$: C, 47.15; H, 7.91; P, 34.81. Found: C, 47.50; H, 8.52; P, 33.97.

[Pd$_2$(PMe$_3$)$_2$(μ-2-MeC$_3$H$_4$)(μ-C$_5$H$_5$)] (20) and [Pd$_2${P(OMe)$_3$}$_2$-(μ-2-MeC$_3$H$_4$)(μ-C$_5$H$_5$)] (22) were prepared in related reactions between 14 and 18 with [Pd(η^3-2-MeC$_3$H$_5$)(η^5-C$_5$H$_5$)] and identified by comparison of their NMR spectra with those of authentic samples. MS (23, $C_{24}H_{48}P_2Pd_2$ (611.4), 50 °C), *m/e* (rel intensity, assignt) 342 (3, L$_2$Pd$^+$), 313 (1, (Et$_2$P)LPd$^+$), 268 (69, (C$_7$H$_{13}$)(C$_5$H$_5$)Pd$^+$), 203 (100, C$_7$H$_{13}$Pd$^+$) (L = PEt$_3$).

(V) With [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$. Pentane solutions of 17 (0.48 g, 1.00 mmol) and [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ (0.20 g, 0.50 mmol) were cooled to −40 °C, mixed, and stirred at room temperature for ca. 4 h. On cooling to −78 °C, yellow crystals of [Pd$_2$(PEt$_3$)$_2$(μ-Cl)(μ-2-MeC$_3$H$_4$)] (24) were precipitated: yield 0.38 g (69%); mp 82 °C dec; MS ($C_{16}H_{37}ClP_2Pd_2$ (539.7), 100 °C), *m/e* rel intensity, assignt) 538 (6, M$^+$), 416 (5, (EtP)(Et$_2$P)(C$_4$H$_7$)Pd$_2$$^+$), 390 (3, (Et$_2$P)$_2Pd_2$$^+$), 342 (21, L$_2Pd^+$), 314 (89, (C$_4H_7$)ClLPd$^+$), 279 (27, (C$_4H_7$)LPd$^+$), 224 (100, LPd$^+$) (L = PEt$_3$). Anal. Calcd for $C_{16}H_{37}ClP_2Pd_2$: C, 35.61; H, 6.91; P, 39.43. Found: C, 36.32; H, 6.82; P, 39.03.

Crystal Structure of [Pd(PMe$_3$)$_2$(η^2-CH$_2$═C$_5$Me$_4$)] (14). Bright yellow needles were obtained by cooling a pentane solution of 14 to −78 °C. A suitable crystal was sealed in a glass capillary under argon and mounted on an Enraf-Nonius CAD-4 diffractometer and subjected to Mo Kα radiation at −173 °C. Relevant crystal data have been brought together in Table XI. The final atomic coordinates are shown in Table XII. The structure was solved by the standard Patterson (Pd, P) and Fourier (C) methods. The structure was refined by using full-matrix techniques[24] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were located in a final difference Fourier synthesis and were included in the final refinement cycles,[25] and their isotropic temperature factors were refined, converging at R = 0.0260 (R_w = 0.0313) for 5565 independently observed reflections. A total of 300 parameters were included in the refinement.

Bond lengths and angles are shown in Tables VII and VIII, and the structure is shown in Figure 1. The contents of a unit cell are shown in Figure 2: as can be seen, the molecules of 14 are stacked perpendicular to the *ac* plane. There are no unusual molecular contacts.

Acknowledgment. We are indebted to Dr. R. Benn and Dr. R. Mynott for the measurement and interpretation of the numerous NMR spectra. Part of this work was supported financially by the Deutsche Forschungsgemeinschaft. G.T.C. thanks The Alexander von Humboldt Foundation for the award of a stipend.

Registry No. 3, 86422-37-9; 4, 83463-65-4; 5, 86422-38-0; 6, 86422-39-1; 7, 83463-66-5; 8, 86422-40-4; 9, 86422-41-5; 10, 86422-42-6; 11, 86422-43-7; 12, 86422-44-8; 13, 86422-45-9; 14, 83463-67-6; 15, 86422-46-0; 16, 86422-47-1; 17, 86422-48-2; 18, 83463-68-7; 19, 86422-49-3; 20, 86422-52-8; 21, 86436-12-6; 22, 54497-81-3; 23, 86422-51-7; 24, 86422-53-9; [PdCl(η^3-C$_3$H$_5$)]$_2$, 12012-95-2; [PdCl(η^3-1-MeC$_3$H$_4$)]$_2$, 86422-54-0; [PdCl(η^3-1,3-Me$_2$C$_3$H$_3$)]$_2$, 67463-14-3; [PdCl(η^3-2-*t*-BuC$_3$H$_4$)]$_2$, 73769-66-1; LiC$_5$Me$_4$Et, 71237-30-4; LiC$_5$Me$_5$, 51905-34-1; PdI(Me)(PMe$_3$)$_2$, 68146-10-1; PdI(Me)(PEt$_3$)$_2$, 18974-13-5; *trans*-[Pd(SPh)$_2$(PMe$_3$)$_2$], 86422-50-6; Pd(η^3-2-MeC$_3$H$_4$)(η^5-C$_5$H$_5$), 33593-95-2; Pd(η^3-2-*t*-BuC$_3$H$_4$)(η^5-C$_5$H$_5$), 58496-57-4; [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$, 12081-18-4; methyl iodide, 74-88-4; dimethyl acetylenedicarboxylate, 762-42-5; tetramethylfulvene, 76089-59-3; thiophenol, 108-98-5.

Supplementary Material Available: Tables of thermal parameters and structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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(24) Scattering factors used were those given in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(25) Computer programs used in this investigation have been summarized in ref 26.

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A Seven-Platinum Cluster Containing a Trigonal-Bipyramidal Unit as the Main Framework, $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$[1]

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A seven-platinum cluster, 1, $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$, was prepared by the reduction of dichloro(2,6-xylyl isocyanide)platinum(II) with sodium amalgam. The cluster 1 was characterized by single-crystal X-ray diffraction. Crystal data: space group $P2_1/a$, a = 28.565 (6) Å, b = 26.694 (25) Å, c = 15.278 (3) Å, β = 119.66 (2)°, V = 10123 Å^3. The molecule contains a metal atom cluster derived from a distorted trigonal-bipyramidal unit to which two extra platinum atoms have been attached in bridging positions between one equatorial and each apical Pt atom. One of the isocyanide groups coordinates in an unusual fashion: through the C═N– group to three platinum atoms by four electrons, in such a way as to form a planar cyclic CNPt$_3$ unit.

Metal clusters are of interest as a potential bridge between homogeneous and heterogeneous catalytic reactions.[2] Many carbonyl clusters are prepared and characterized by spectroscopic and X-ray crystallographic analyses.[3]

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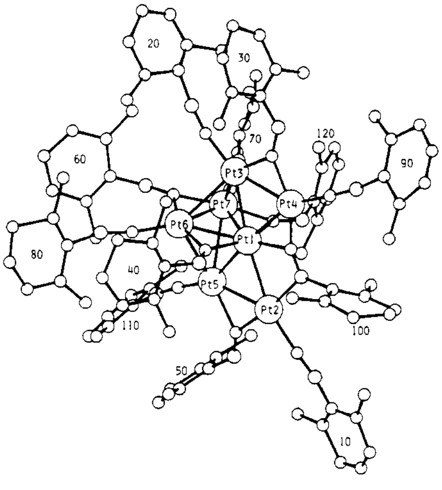

Figure 1. Molecular structure of $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$.

However, there are only few examples of isocyanide clusters. Metal clusters containing only isocyanide ligands have been limited to nickel,[4] palladium,[5] and platinum.[6] These cluster skeletons consist of three or four metals: $Ni_4(t\text{-}BuNC)_7$, $Pd_3(RNC)_6$,[7] and $Pt_3(t\text{-}BuNC)_6$. We report here the preparation and crystallographic structural analysis of a high nuclearity isocyanide cluster containing seven platinum atoms, which was obtained from the reduction of dichlorobis(2,6-xylyl isocyanide)platinum(II) with sodium amalgam. To our knowledge, this cluster has the highest nuclearity of any isocyanide cluster isolated to date. A preliminary account of this work has been appeared previously.[8]

Results and Discussion

Preparation. Treatment of dichlorobis(2,6-xylyl isocyanide)platinum(II) with sodium amalgam in THF at room temperature gave dark brown compound **1** formulated as $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$, as well as **2** and **3** formulated as $Pt(2,6\text{-}Me_2C_6H_3NC)_3(2,6\text{-}Me_2C_6H_3NC)$[9] and $Pt(2,6\text{-}Me_2C_6H_3NC)_4(2,6\text{-}Me_2C_6H_3N)$,[9] respectively. The infrared spectrum of **1** showed the presence of terminal and bridging isocyanide groups. The ^1H NMR spectrum showed a very complicate pattern, and no structural information was obtained from it. A crystallographic study of **1** provided a definitive structural assignment.

Description of the Crystal Structure. The molecular geometry of **1** is shown in Figures 1 and 2. Bond distances and angles are given in Tables I and II. The molecule contains a metal atom cluster derived from a distorted trigonal-bipyramidal unit to which extra atoms [Pt(2) and Pt(4)] have been attached in the edge-bridging positions between one equatorial platinum atom [Pt(1)] and each apical one [Pt(3) and Pt(5)].

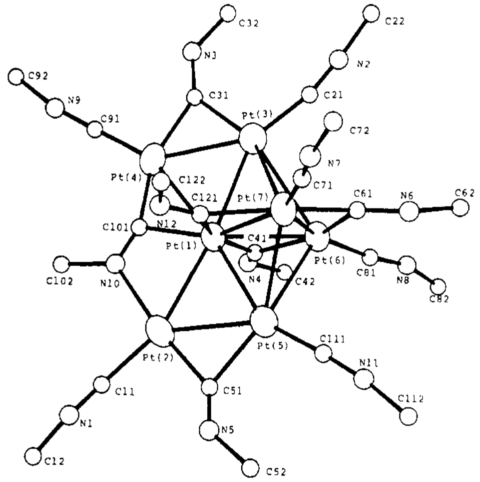

Figure 2. The central core of $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$. The 2,6-xylyl groups are omitted for clarity.

Table I. Bond Distances (Å) in $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$

Pt(1)-Pt(2)	2.765 (4)	Pt(4)-C(91)	1.83 (5)
Pt(1)-Pt(3)	2.734 (4)	Pt(4)-C(101)	1.99 (8)
Pt(1)-Pt(4)	2.725 (3)	Pt(5)-C(51)	2.05 (7)
Pt(1)-Pt(5)	2.686 (3)	Pt(5)-C(111)	1.83 (5)
Pt(1)-Pt(6)	2.714 (2)	Pt(6)-C(41)	2.18 (5)
Pt(1)-Pt(7)	2.720 (3)	Pt(6)-C(61)	2.05 (5)
Pt(2)-Pt(5)	2.766 (3)	Pt(6)-C(81)	1.86 (5)
Pt(3)-Pt(4)	2.723 (3)	Pt(7)-C(61)	1.99 (4)
Pt(3)-Pt(6)	3.018 (3)	Pt(7)-C(121)	2.03 (5)
Pt(3)-Pt(7)	3.020 (3)	C(11)-N(1)	1.18 (10)
Pt(5)-Pt(6)	2.918 (3)	C(21)-N(2)	1.18 (8)
Pt(5)-Pt(7)	2.983 (4)	C(31)-N(3)	1.29 (8)
Pt(6)-Pt(7)	2.625 (3)	C(41)-N(4)	1.16 (7)
Pt(1)-C(41)	2.08 (4)	C(51)-N(5)	1.17 (9)
Pt(1)-C(101)	2.13 (5)	C(61)-N(6)	1.22 (6)
Pt(1)-C(121)	2.03 (5)	C(71)-N(7)	1.17 (7)
Pt(2)-N(10)	2.02 (5)	C(81)-N(8)	1.20 (6)
Pt(2)-C(11)	1.97 (9)	C(91)-N(9)	1.27 (7)
Pt(3)-C(51)	1.94 (6)	C(101)-N(10)	1.20 (10)
Pt(3)-C(21)	1.80 (6)	C(111)-N(11)	1.23 (7)
Pt(3)-C(31)	2.02 (5)	C(121)-N(12)	1.26 (5)
Pt(4)-C(31)	1.93 (6)		

The dihedral angle between the equatorial Pt(1)Pt(6)-Pt(7) plane and the Pt(1)Pt(2)Pt(4) plane containing the two edge-bridging Pt atoms is ca. 92°. The Pt(2) and Pt(4) atoms are located −2.31 and +2.26 Å from the equatorial plane, respectively. These results show that the seven-platinum core has a pseudo C_{2v} symmetry. It is interesting to note that the Pt(1) atom has a particularly high formal coordination number, involving six metal–metal bonds as well as three metal-bridging isocyanide ligands.

The mean distance between the equatorial atoms [Pt(1), Pt(6), and Pt(7)], 2.686 Å, is approximately equal to the sum (2.62 Å) of the covalent radii of two platinum atoms. They can be regarded as normal single Pt–Pt bonds, in good agreement with those found in other diplatinum and platinum cluster complexes.[10] The mean distance between each apical platinum [Pt(3) or Pt(5)] and two equatorial

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(1) Studies on interaction of isocyanide with transition-metal complexes. 23. For the preceeding paper, see: Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chim. Acta* **1982**, *68*, 75.

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(7) Muetterties and his co-workers proposed a structure having a *triangulo*-tripalladium skeleton.[4] A crystallographic study has not been reported to date.

(8) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Chem. Lett.* **1979**, 391.

(9) Compound **2**: IR (Nujol) 2163 ($N{\equiv}C$), 1654 ($C{=}N$) cm^{-1}; NMR (CD_2Cl_2) δ 1.85 (s, 2 CH_3), 2.32 (s, 2 CH_3), 2.45 (s, 2 CH_3), 6.2–7.5 (aromatic protons). The structure is tentatively assigned as *cis*-bis(2,6-xylyl isocyanide)(η^2-*C,N*-*N,N′*-di-2,6-xylylcarbodiimide)platinum. By an x-ray crystallographic study of **3**, the structure is confirmed to be *cis*-bis(2,6-xylyl isocyanide)(1,3-bis(2,6-xylylimino)-2-*N*-2,6-xylylamino)platina-2-*N*-cyclobutane). The details will be reported elsewhere.

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Table II. Bond Angles (deg) in $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$

Pt(2)-Pt(1)-Pt(3)	172.5 (1)	Pt(6)-Pt(5)-Pt(7)	52.8 (1)	Pt(3)-Pt(7)-Pt(6)	64.2 (1)
Pt(2)-Pt(1)-Pt(4)	112.7 (1)	Pt(3)-C(31)-Pt(4)	87 (3)	Pt(5)-Pt(7)-Pt(6)	62.3 (1)
Pt(2)-Pt(1)-Pt(5)	61.0 (1)	Pt(5)-C(51)-Pt(5)	88 (3)	Pt(2)-C(11)-N(1)	170 (6)
Pt(3)-Pt(1)-Pt(4)	59.8 (1)	Pt(1)-C(101)-Pt(4)	87 (2)	Pt(3)-C(21)-N(2)	168 (4)
Pt(3)-Pt(1)-Pt(6)	67.3 (1)	Pt(4)-C(101)-N(10)	167 (5)	Pt(4)-C(91)-N(9)	176 (5)
Pt(3)-Pt(1)-Pt(7)	67.3 (1)	Pt(1)-C(121)-Pt(7)	84 (2)	Pt(5)-C(111)-N(11)	173 (6)
Pt(4)-Pt(1)-Pt(5)	172.4 (1)	Pt(1)-Pt(6)-Pt(3)	56.7 (1)	Pt(6)-C(81)-N(8)	171 (7)
Pt(6)-Pt(1)-Pt(7)	57.8 (1)	Pt(1)-Pt(6)-Pt(5)	56.8 (1)	Pt(7)-C(71)-N(7)	176 (6)
Pt(1)-Pt(2)-Pt(5)	58.1 (1)	Pt(1)-Pt(6)-Pt(7)	61.2 (1)	Pt(1)-C(41)-Pt(6)	79 (2)
Pt(1)-Pt(3)-Pt(7)	56.2 (1)	Pt(3)-Pt(6)-Pt(7)	64.3 (1)	Pt(6)-C(61)-Pt(7)	81 (2)
Pt(1)-Pt(4)-Pt(3)	60.2 (1)	Pt(1)-Pt(7)-Pt(5)	56.0 (1)	Pt(1)-C(101)-N(10)	110 (4)
Pt(1)-Pt(5)-Pt(2)	60.9 (1)	Pt(1)-Pt(7)-Pt(6)	61.0 (1)	Pt(2)-N(10)-C(101)	114 (4)
Pt(1)-Pt(5)-Pt(6)	57.7 (1)				

atoms [Pt(6) and Pt(7)] is 2.985 Å, longer than sum of the covalent radii, and is comparable with the intertriangular Pt–Pt distances (3.055 Å) of $[Pt_3(CO)_6]_n^{2-}$ (n = 2, 3, 5).[11] These long bond distances may be caused by minimizing steric hindrance of the bulky isocyanide groups. Two other apical–equatorial distances [Pt(1)–Pt(3) and Pt(1)–Pt(5)] and four Pt–Pt distances containing edge-bridging atoms [Pt(1)–Pt(2), Pt(1)–Pt(4), Pt(2)–Pt(5), and Pt(3)–Pt(4)] give a mean value of 2.723 Å. The mean distance (2.800 Å) of 13 Pt–Pt bonds formed from the seven platinum atoms is longer by ca. 0.16 Å than those found in $Pt_3(t\text{-}BuNC)_6$[6] and $Hg[Pt_3(2,6\text{-}Me_2C_6H_3NC)_6]_2$,[12] the increase probably due to the highly crowded environment of the Pt_7 cluster.

In two triangles Pt(3)Pt(6)Pt(7) and Pt(5)Pt(6)Pt(7), the angles Pt(6)–Pt(3)–Pt(7) and Pt(6)–Pt(5)–Pt(7) are smaller by 12° than the other four angles, resulting in a smaller distances for Pt(6)–Pt(7) as compared to the other four Pt–Pt distances.

The average Pt–C(terminal) and Pt–C(bridging) distances are 1.86 and 2.30 Å, respectively, comparable with those found in the other isocyanide complexes. The mean values of the Pt–C–N and C–N–C bond angles in the terminal isocyanide ligands are ca. 172 and 169°, respectively. The Pt–C–Pt angles in the bridging isocyanide ligands range from 88 to 79°, being larger than those (mean value 78°) found in $Pt_3(t\text{-}BuNC)_6$.

The most remarkable bonding mode found in this complex involves a four-electron coordination of a C=N– group to three different platinum atoms [Pt(1), Pt(2), and Pt(4)]: this isocyanide ligand coordinates to Pt(1) and Pt(4) by a bridging mode and to the Pt(2) atom through the N(10) atom. A very similar bonding mode has been observed in $Os_6(CO)_{18}(4\text{-}MeC_6H_4NC)_2$.[13] The Pt(2), Pt(1), Pt(4), C(101), N(10), and C(102) atoms are approximately coplanar (mean deviation ca. 0.04 Å). The Pt(1)–C(101) and Pt(4)–C(101) distances show normal bond lengths [2.13 (5) and 1.99 (8) Å]. The Pt(2)–N(10) [2.02 (5) Å] and C(101)–N(10) [1.20 (10) Å] bond distances are comparable with those [2.16 (3) and 1.25 (4) Å] found in the osmium cluster.[13] The bent angles of Pt(1)–C(101)–N(10) [110 (4)°] and C(101)–N(10)–Pt(2) [114 (4)°] are smaller than those [132 (3)° and 128 (2)°] of the osmium complex, due to the longer Os–Os distances as compared with the Pt–Pt bond lengths.

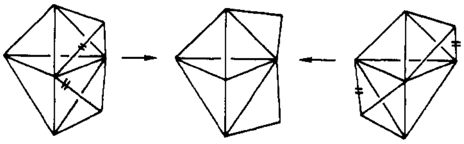
The closest interligand distance in the molecule [N(5)···C(11) = 3.12 (8) Å] is smaller than the sum of the van der Waals radii of these two atoms (ca. 3.7 Å). This illustrates the crowded situation in the cluster molecule.

Table III. Crystallographic Data and Data Collection Conditions in $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$

space group	$P2_1/a$
mol wt	2939.7
a, Å	28.565 (6)
b, Å	26.694 (25)
c, Å	15.278 (3)
β, deg	119.66 (2)
V, Å^3	10123.6 (10)
Z	4
d_{calcd}, g/cm^3	1.92
d_{obsd}, g/cm^3	1.903^a
cryst size, mm^3	0.28 × 0.29 × 0.053
radiation	graphite monochromated Mo Kα (λ = 0.7107 Å)
scan type	ω ($2\theta \leq 30°$), ω-2θ ($2\theta > 30°$)
collection range	$3° < 2\theta < 45°$
scan rate, deg/min	4
unique data collected	6755
data used for structural analysis $F_o > 4.0\sigma(F_o)$	5371
no. of variables	545
R	0.0806^b
R_w	0.0856^c

^{a} By flotation in aqueous KI. ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ [w = 0.5 ($|F_o| < 150$), w = 1.0 ($150 < |F_o| \leq 600$), and $w = 600/|F_o|^2$ ($|F_o| \geq 600$)].

Scheme I



A B

Cluster Geometry. The observed metal atom core can be obtained from the bicapped trigonal-bipyramidal structures A and B by splitting two metal–metal bonds as shown in Scheme I. These bicapped trigonal-bipyramidal geometries have not been considered in any of the several theoretical studies on cluster shapes of seven-atom clusters.[14,15] However, Wade's rules predict 96 electrons and six skeletal bonding electron pairs for bicapped trigonal-bipyramidal cores. Recently, a cluster with the aforementioned geometry, $Au_3CoRu_3(CO)_{12}(PPh_3)$, was prepared by Bruce and Nicholson, although its structure (C) is different from the other bicapped trigonal-bipyramidal geometries (A and B).[16]

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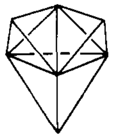
Table IV. Positional and Thermal Parameters for $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$[a]

atom	x	y	z	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
Pt(1)	1999 (1)	868 (1)	3401 (1)	46 (1)	45 (1)	64 (1)	−5 (1)	25 (1)	−4 (1)
Pt(2)	1193 (1)	806 (1)	3896 (2)	56 (1)	68 (1)	89 (2)	−10 (1)	41 (1)	−2 (1)
Pt(3)	2722 (1)	838 (1)	2722 (2)	61 (1)	54 (1)	73 (1)	−5 (1)	33 (1)	−8 (1)
Pt(4)	1905 (1)	160 (1)	2043 (2)	61 (1)	50 (1)	63 (1)	−3 (1)	21 (1)	−9 (1)
Pt(5)	1950 (1)	1564 (1)	4616 (2)	56 (1)	60 (1)	88 (2)	−8 (1)	39 (1)	−13 (1)
Pt(6)	2961 (1)	1286 (1)	4711 (2)	44 (1)	54 (1)	62 (1)	−3 (1)	20 (1)	−2 (1)
Pt(7)	2290 (1)	1793 (1)	3105 (2)	45 (1)	47 (1)	64 (1)	−3 (1)	17 (1)	1 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
N(1)	11 (2)	53 (2)	384 (3)	8.0 (1.2)	C(64)	478 (2)	250 (2)	557 (4)	7.6 (1.5)
N(2)	372 (2)	115 (2)	272 (3)	7.9 (1.2)	C(65)	492 (2)	262 (2)	659 (3)	5.0 (1.1)
N(3)	269 (2)	3 (1)	128 (3)	5.3 (0.9)	C(66)	455 (2)	266 (2)	692 (4)	7.1 (1.4)
N(4)	276 (2)	20 (2)	521 (3)	6.8 (1.0)	C(67)	402 (2)	257 (2)	621 (4)	7.0 (1.4)
N(5)	109 (2)	155 (2)	517 (3)	7.1 (1.1)	C(68)	357 (2)	261 (2)	648 (4)	7.3 (1.5)
N(6)	334 (1)	233 (1)	451 (3)	5.1 (0.9)	C(69)	412 (3)	236 (2)	380 (5)	9.7 (1.8)
N(7)	209 (2)	270 (2)	176 (3)	8.2 (1.2)	C(71)	215 (2)	235 (2)	229 (4)	6.2 (1.3)
N(8)	399 (2)	127 (2)	676 (3)	7.7 (1.2)	C(72)	210 (2)	314 (2)	115 (4)	6.3 (1.3)
N(9)	138 (2)	−70 (2)	51 (4)	8.3 (1.3)	C(73)	221 (2)	302 (2)	45 (4)	7.1 (1.4)
N(10)	114 (2)	24 (2)	298 (3)	8.8 (1.2)	C(74)	222 (3)	347 (3)	−22 (5)	9.9 (1.8)
N(11)	230 (2)	253 (2)	582 (4)	8.8 (1.3)	C(75)	200 (3)	385 (3)	1 (6)	13.2 (2.4)
N(12)	117 (2)	139 (1)	148 (3)	5.8 (1.0)	C(76)	181 (3)	398 (3)	56 (6)	11.8 (2.2)
C(11)	54 (3)	59 (3)	391 (5)	10.3 (1.9)	C(77)	185 (3)	353 (2)	125 (5)	9.2 (1.7)
C(12)	−35 (2)	43 (2)	388 (4)	5.8 (1.2)	C(78)	170 (3)	361 (3)	201 (6)	13.6 (2.5)
C(13)	−62 (2)	−1 (2)	357 (4)	6.8 (1.3)	C(79)	248 (4)	258 (3)	42 (7)	15.1 (2.8)
C(14)	−102 (3)	−5 (3)	377 (6)	13.2 (2.4)	C(81)	356 (2)	125 (2)	598 (5)	8.1 (1.6)
C(15)	−122 (3)	32 (3)	402 (5)	10.6 (1.9)	C(82)	442 (2)	122 (2)	784 (4)	6.9 (1.4)
C(16)	−98 (3)	84 (3)	436 (6)	13.2 (2.4)	C(83)	426 (2)	123 (2)	856 (5)	9.0 (1.6)
C(17)	−47 (2)	87 (2)	423 (4)	7.4 (1.4)	C(84)	468 (3)	120 (3)	954 (5)	10.0 (1.9)
C(18)	−20 (3)	138 (3)	453 (6)	12.1 (2.3)	C(85)	517 (3)	105 (3)	966 (5)	11.0 (2.1)
C(19)	−37 (3)	−38 (3)	324 (6)	13.4 (2.5)	C(86)	537 (3)	108 (2)	895 (5)	8.8 (1.7)
C(21)	332 (2)	108 (2)	275 (3)	5.1 (1.1)	C(87)	488 (2)	115 (2)	788 (4)	8.3 (1.6)
C(22)	414 (3)	132 (2)	251 (5)	8.8 (1.7)	C(88)	501 (3)	118 (3)	708 (5)	10.6 (2.0)
C(23)	462 (3)	107 (3)	334 (6)	11.7 (2.2)	C(89)	371 (3)	135 (3)	828 (5)	10.5 (1.9)
C(24)	512 (3)	115 (3)	338 (5)	10.0 (1.9)	C(91)	157 (2)	−34 (2)	112 (4)	7.3 (1.5)
C(25)	508 (2)	143 (2)	254 (4)	7.0 (1.4)	C(92)	122 (2)	−108 (2)	−25 (4)	6.5 (1.3)
C(26)	459 (2)	162 (2)	171 (4)	8.6 (1.6)	C(93)	96 (2)	−150 (2)	−7 (4)	8.3 (1.6)
C(27)	413 (2)	156 (2)	185 (4)	6.9 (1.4)	C(94)	86 (2)	−189 (2)	−90 (4)	9.2 (1.6)
C(28)	475 (3)	81 (3)	423 (6)	12.6 (2.4)	C(95)	95 (3)	−175 (3)	−164 (6)	12.6 (2.3)
C(29)	363 (4)	173 (3)	101 (7)	15.0 (2.8)	C(96)	122 (3)	−141 (2)	−174 (5)	9.6 (1.7)
C(31)	248 (2)	26 (2)	175 (3)	5.1 (1.1)	C(97)	139 (2)	−100 (2)	−94 (4)	6.8 (1.3)
C(32)	316 (2)	18 (2)	121 (4)	6.3 (1.3)	C(98)	163 (3)	−53 (3)	−104 (5)	10.5 (1.9)
C(33)	367 (2)	−6 (2)	197 (4)	6.3 (1.4)	C(99)	84 (3)	−150 (3)	71 (5)	10.9 (2.0)
C(34)	408 (2)	0 (2)	172 (4)	6.1 (1.3)	C(101)	146 (2)	26 (2)	269 (4)	7.5 (1.4)
C(35)	405 (2)	26 (2)	88 (4)	7.3 (1.4)	C(102)	77 (2)	−23 (2)	243 (4)	6.1 (1.2)
C(36)	355 (2)	45 (2)	26 (5)	8.4 (1.6)	C(103)	95 (2)	−69 (2)	294 (4)	7.1 (1.4)
C(37)	310 (2)	39 (2)	37 (4)	7.0 (1.4)	C(104)	52 (3)	−107 (3)	258 (5)	9.6 (1.8)
C(38)	258 (3)	57 (2)	−39 (5)	9.6 (1.8)	C(105)	6 (2)	−98 (2)	168 (4)	7.7 (1.5)
C(39)	371 (2)	−33 (2)	285 (4)	5.8 (1.2)	C(106)	−15 (3)	−51 (3)	121 (5)	10.6 (1.9)
C(41)	262 (2)	55 (2)	470 (4)	4.7 (1.2)	C(107)	26 (3)	−9 (3)	166 (5)	10.9 (2.0)
C(42)	323 (2)	10 (2)	612 (4)	6.0 (1.2)	C(108)	8 (2)	36 (2)	112 (5)	9.0 (1.7)
C(43)	316 (2)	10 (2)	693 (4)	6.8 (1.3)	C(109)	150 (2)	−83 (2)	379 (4)	7.2 (1.4)
C(44)	362 (3)	−2 (3)	788 (5)	10.8 (2.1)	C(111)	219 (2)	214 (2)	534 (4)	6.1 (1.2)
C(45)	413 (3)	−11 (2)	793 (5)	9.1 (1.7)	C(112)	237 (2)	304 (2)	631 (5)	8.7 (1.6)
C(46)	421 (2)	−13 (2)	707 (4)	7.5 (1.4)	C(113)	260 (2)	299 (2)	735 (5)	8.7 (1.6)
C(47)	368 (2)	−2 (2)	618 (4)	7.6 (1.5)	C(114)	260 (2)	359 (2)	773 (4)	8.1 (1.5)
C(48)	263 (3)	19 (2)	693 (5)	9.2 (1.7)	C(115)	241 (2)	386 (2)	693 (4)	8.3 (1.6)
C(49)	377 (2)	2 (2)	526 (4)	5.8 (1.2)	C(116)	215 (3)	397 (3)	590 (6)	14.0 (2.5)
C(51)	132 (2)	135 (2)	482 (4)	7.0 (1.4)	C(117)	213 (3)	339 (3)	554 (5)	10.5 (2.0)
C(52)	119 (2)	200 (2)	582 (4)	7.9 (1.5)	C(118)	188 (3)	335 (3)	445 (5)	10.2 (1.9)
C(53)	143 (3)	204 (3)	683 (5)	10.7 (1.9)	C(119)	284 (3)	257 (3)	794 (5)	10.0 (1.9)
C(54)	145 (2)	246 (2)	738 (4)	8.5 (1.6)	C(121)	162 (2)	138 (2)	229 (4)	5.6 (1.2)
C(55)	127 (3)	286 (3)	674 (5)	9.7 (1.9)	C(122)	100 (2)	181 (2)	77 (3)	4.4 (1.0)
C(56)	100 (3)	290 (3)	574 (5)	10.4 (1.9)	C(123)	117 (2)	174 (2)	11 (4)	7.0 (1.4)
C(57)	97 (3)	241 (2)	527 (5)	9.2 (1.7)	C(124)	102 (3)	211 (3)	−68 (5)	9.9 (1.9)
C(58)	72 (3)	243 (3)	416 (5)	10.7 (2.0)	C(125)	69 (2)	249 (2)	−63 (4)	7.0 (1.4)
C(59)	167 (3)	153 (3)	736 (5)	11.0 (2.1)	C(126)	56 (2)	258 (2)	8 (4)	8.0 (1.6)
C(61)	302 (2)	198 (2)	420 (4)	5.4 (1.2)	C(127)	69 (3)	217 (2)	76 (5)	9.1 (1.7)
C(62)	391 (2)	243 (2)	532 (4)	5.2 (1.2)	C(128)	60 (3)	220 (3)	220 (3)	12.6 (2.4)
C(63)	424 (2)	242 (2)	487 (4)	6.2 (1.3)	C(129)	149 (2)	131 (2)	−2 (4)	7.8 (1.5)

[a] Positional parameters [except the platinum atoms ($\times 10^4$)] are multiplied by 10^3. Anisotropic temperature factors are of the form is $\exp[-2\pi^2(U(11)h^2a^{*2} + U(22)k^2b^{*2} + U(33)l^2c^{*2} + 2U(12)hka^*b^* + 2U(13)hla^*c^* + 2U(23)klb^*c^*)]$.

According to Wade's rules, two more electron pairs should be added to the bicapped trigonal-bipyramidal core to yield the atom cluster geometry of the title compound because of the cleavage of two metal–metal bonds. However, electron counting shows that 1 is a 96-electron cluster, instead of the expected 100-electron species. It is known



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that many tri- and tetranuclear metal clusters containing platinum do not obey the 18-electron rule but follow a 16-electron bonding scheme for a platinum atom, e.g., $Pt_3(t\text{-}BuNC)_6$,[6] $Pt_3(CO)_3(PR_3)_3$,[17] and $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)$.[18]

The geometry of Pt(2) and Pt(4) can be considered to be similar to those of the platinum atoms in $Pt_3(t\text{-}BuNC)_6$ and $Pt_3(CO)_3(PR_3)_3$; they are involved in two metal–metal bonds and are bonded to a terminal and two bridging ligands. Thus, it is not unreasonable that 1 exists as an electron-deficient cluster. Furthermore, it has been pointed out that electron-deficient clusters are often stabilized by the steric effects of bulky ligands.[14]

Experimental Section

The following reaction was carried out under an atmosphere of nitrogen. 2,6-Xylyl isocyanide[19] and Pt(2,6-xylyl isocyanide)$_2$Cl$_2$[20] were prepared by procedures described in the literature.

Reaction of Dichlorobis(2,6-xylyl isocyanide)platinum(II) with Sodium Amalgam. A mixture of $Pt(2,6\text{-}Me_2C_6H_3NC)_2Cl_2$ (0.7 g, 1.33 mmol) and 0.2% sodium amalgam (150 g) was stirred in THF (25 mL) at room temperature. After 3 h, the THF solution was filtered and the solvent was evaporated in vacuo. The residue was chromatographed on alumina (10% H_2O) by using benzene and CH_2Cl_2–benzene (1:1) as eluants. The brown benzene solution was concentrated to ca. 5 mL, and *n*-hexane was added to the brown solution to give dark brown crystals (0.11 g, 19.7%) of **1**: IR (KBr) 2102 (b), 1667 (b) cm^{-1}; electronic spectrum (CH_2Cl_2) 507 (ϵ 10900), 418 (37800), 352 (612000), 318 nm (821000). Anal. Calcd for $C_{108}H_{108}N_{12}Pt_7$: C, 44.13; H, 3.70; N, 5.72; Pt, 46.45. Found: C, 44.50; H, 3.75; N, 5.51; Pt, 45.49. The solvent from the other band, a pale yellow solution, was evaporated to ca. 5 mL, and *n*-hexane was added to give colorless crystals of a mixture of **2** and **3**. Careful chromatography of a mixture gave **2** (3%) and **3** (6%).[9]

X-ray Data and Structure Determination.[21] Dark brown crystals of 1 were obtained from a mixture of benzene and *n*-hexane. A summary of crystal data is presented in Table III. X-ray photographic data from Weissenberg photographs showed the crystal to be monoclinic, with systematic extinctions (*h*0*l*, *h* = 2*n*; 0*k*0, *k* = 2*n*) consistent with the space group $P2_1/a$. The crystal with six faces of the form [(100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), (00$\bar{1}$)] was mounted such that the *b* axis was nearly parallel to the ϕ axis of a Rigaku four-circle diffractometer. Intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient is 11.0 mm^{-1}, and an absorption correction was made: the calculated transmission factors varied from 0.12 to 0.58. The positions of the seven Pt atoms were determined by direct methods using the program MULTAN.[22] The other atomic positions were subsequently found from a series of difference Fourier maps. The positions of the seven Pt atoms were refined anisotropically and those of the other atoms isotropically by using block-diagonal least-squares methods, minimizing $\sum\omega(|F_o| - |F_c|)^2$. Various weighting schemes were originally tried, associated with an examination of the data. Among these, the weighting scheme adopted here, the type suggested by Hughes, showed no unusual trends in an analysis of $\sum\omega(|F_o| - |F_c|)^2$ as a function of $(\sin\theta)/\gamma$ or $|F_o|$.[23] A final difference Fourier map showed smaller residual peaks than 2.0 e Å^{-3} around the Pt atoms and did not show any residual peaks greater than 0.9 e Å^{-3} associated with other light atoms. The presence of some residual peaks is probably due to a large molecular structure.

The atomic positional and thermal parameters are listed in Table IV. Tables of observed and calculated structure factors are available as supplementary material.

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Registry No. **1**, 86391-93-7; **2**, 86391-91-5; **3**, 86391-92-6; $Pt(2,6\text{-}Me_2C_6H_3NC)_2Cl_2$, 51014-40-5.

Supplementary Material Available: A listing of structure factor amplitudes for the platinum isocyanide cluster (30 pages). Ordering information is given on any current masthead page.

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