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Metal Vapor Routes to Metal-Isocyanide Complexes. Synthesis and Molecular Structure of Tris(μ-cyclohexyl isocyanide)-tris(cyclohexyl isocyanide)-*triangulo*-tripalladium

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The synthesis, structure, and reaction chemistry of metal clusters have received intensive study, the primary motivation being their importance as models for chemisorption and catalytic processes occurring at metal surfaces.[1] One particular group of such clusters comprises those of zerovalent Ni, Pd, or Pt, in which isocyanide molecules represent the only ligands.[2] However, while a number of binary isocyanide-nickel (Ni_4L_6, Ni_4L_7)[3] and isocyanide-platinum (Pt_3L_6,[4,5] Pt_7L_{12}[6]) species have been isolated and extensively characterized by spectroscopic and crystallographic methods, the known binary palladium(0)-isocyanide complexes remain ill-defined,[2,5,7] the existing data permitting only an empirical formula "Pd(CNR)$_2$" to be deduced. Various structures have been proposed:[2] including a monomer, a cyclic tetramer, and a cyclic trimer,[3] this last structure being arrived at by comparison with the known $Pt_3(CNR)_6$.[4] As far as we are aware, the only homoleptic palladium-isocyanide complexes known to contain more than one metal center are $[Pd_2(CNCH_3)_6][PF_6]_2$,[8] which consists of two $(CH_3NC)_3Pd^I$ units joined by a single metal-metal bond, and the linear $[Pd_3(CNCH_3)_8][PF_6]_2$.[8]

Recently, we have initiated a study of the reactions of metal vapors with organic isocyanides, and we now wish to report that palladium vapor reacts with cyclohexyl isocyanide (CN-c-Hx) to give, as the only product, the metal cluster complex Pd_3(CN-c-Hx)$_6$. It is interesting to note that a conference abstract[9] represents the only previous report of preparative metal vapor-isocyanide studies, the vapors of Cr, Fe, or Ni yielding the respective 18-electron M(CNR)$_n$ species. In addition, few macroscale metal vapor studies have been found to lead to well-defined metal clusters[10] despite the extensive evidence of controlled aggregation of metal atoms in low-temperature matrices.[11]

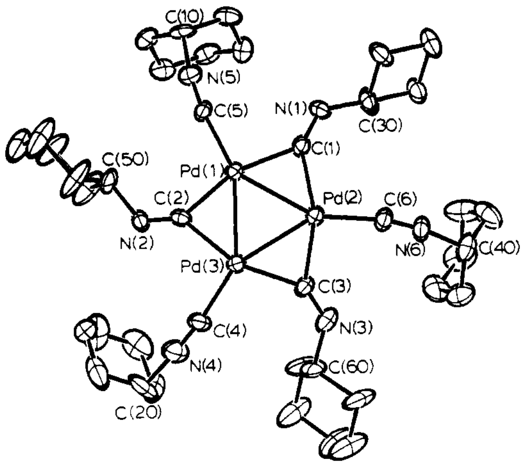

Figure 1. ORTEP plot of the Pd_3(CN-c-Hx) molecule. The atoms are shown as 50% probability ellipsoids. (For the numbering scheme of carbon atoms in the cyclohexyl rings, see the supplementary material.)

Table I. Crystal Data for Pd_3(CN-c-Hx)$_6$

space group: $P2_1/n$ (monoclinic)[14]
$a = 14.002\ (7)$ Å
$b = 10.966\ (4)$ Å
$c = 29.067\ (14)$ Å
$\beta = 92.30\ (4)°$
$V = 4460.16$ Å^3
$Z = 4$
ρ(calcd) = 1.409 g cm^{-3}
$R = 0.047$
$R_w = 0.051$ for 2624 nonzero reflcns with $I > 3\sigma(I)$

Experimental Section

In the present studies, palladium (~0.6 g) was evaporated over a period of 45 min and deposited into 200 mL of a 2.5% solution of CN-c-Hx in tetrahydrofuran cooled to 160 K within a metal vapor rotary solution reactor.[12] At the end of the reaction the resulting red-brown solution was removed from the reactor under an atmosphere of nitrogen and filtered to remove excess metal, prior to the removal of solvent and excess CN-c-Hx under vacuum. The product was recrystallized from toluene giving orange crystals of Pd_3(CN-c-Hx)$_6$ in 30-40% yield based on metal evaporated. IR spectrum: $\bar{\nu}$(CN) = 2111 (vs), 1733 cm^{-1} (s, br).[13] Anal. Calcd for $[C_{14}H_{22}N_2Pd]_n$: C, 51.78; H, 6.83; N, 8.63. Found: C, 51.89; H, 6.91; N, 8.63.

Molecular weight determinations failed to elucidate the nuclearity of the cluster, presumably due to dissociation of isocyanide ligand in the particular solvent medium. However, crystals suitable for X-ray diffraction were obtained by slow recrystallization from toluene at ~260 K. It is interesting to note that, while solutions of the complex are exceedingly air sensitive, the complex exhibits quite good oxidative stability in the solid state.

Structure Determination

The X-ray diffraction data were collected at room temperature on a crystal (approximately ellipsoidal, dimensions 0.22 × 0.22 × 0.26 mm) carefully mounted in a glass capillary. A total of 5443 reflections were collected in the range $3.5° < 2\theta < 45.0°$ by Mo Kα radiation in the $+h,-k,\pm l$ quadrant on a Nicolet/Syntex P2$_1$ diffractometer. The unit cell parameters and other crystallographic details are given in Table I.

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(13) These bands are in agreement with those reported by Fischer and Werner[7] for Pd(CN-c-Hx)$_2$.

(14) $P2_1/n$ is a nonstandard setting of space group $P2_1/c$ (C_{2h}^5, No. 14) with equivalent positions (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$, and $(^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$.

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Table II. Final Atomic Parameters for $Pd_3(CN\text{-}c\text{-}Hx)_6$[a]

	x	*y*	*z*
Pd(1)	53 559 (8)	19 841 (10)	80 250 (3)
Pd(2)	54 967 (8)	8 097 (10)	88 222 (4)
Pd(3)	44 034 (8)	−767 (10)	81 368 (3)
C(1)	62 127 (104)	23 464 (120)	86 090 (42)
C(2)	45 449 (88)	9 895 (112)	75 506 (45)
C(3)	47 299 (102)	−7 986 (122)	87 833 (41)
C(4)	35 730 (104)	−13 699 (141)	78 339 (48)
C(5)	58 432 (98)	33 523 (124)	76 495 (41)
C(6)	60 513 (106)	5 071 (126)	94 592 (45)
N(1)	68 663 (79)	30 229 (101)	87 289 (35)
N(2)	43 384 (74)	8 860 (101)	71 411 (34)
N(3)	46 718 (90)	−17 365 (109)	90 036 (37)
N(4)	32 013 (103)	−20 954 (134)	76 118 (44)
N(5)	62 798 (83)	40 963 (107)	74 620 (39)
N(6)	62 816 (88)	1 764 (106)	98 180 (35)
C(10)	70 242 (104)	48 636 (130)	72 664 (59)
C(11)	78 733 (113)	48 868 (154)	76 231 (60)
C(12)	83 065 (118)	35 893 (172)	76 731 (53)
C(13)	85 766 (118)	31 454 (156)	71 965 (61)
C(14)	77 134 (131)	31 031 (157)	68 330 (57)
C(15)	72 637 (125)	43 619 (167)	67 949 (52)
C(20)	28 046 (141)	−30 675 (240)	72 904 (60)
C(21)	24 549 (159)	−24 655 (223)	68 845 (78)
C(22)	31 817 (199)	−19 098 (199)	66 216 (68)
C(23)	39 704 (160)	−27 646 (333)	65 250 (71)
C(24)	43 938 (147)	−34 156 (229)	68 918 (102)
C(25)	36 484 (218)	−40 190 (163)	72 016 (62)
C(30)	74 865 (104)	29 861 (150)	91 458 (44)
C(31)	76 975 (127)	43 026 (152)	92 870 (57)
C(32)	90 962 (127)	22 965 (159)	94 649 (55)
C(33)	93 340 (114)	36 139 (176)	96 073 (51)
C(34)	83 908 (118)	23 079 (153)	90 305 (51)
C(35)	84 103 (127)	43 012 (158)	97 207 (53)
C(40)	65 241 (129)	−4 455 (154)	102 492 (51)
C(41)	63 159 (135)	−17 998 (167)	102 056 (66)
C(42)	69 946 (177)	−23 771 (162)	98 667 (70)
C(43)	82 249 (139)	−7 440 (195)	100 449 (96)
C(44)	80 450 (174)	−21 429 (210)	100 170 (85)
C(45)	75 294 (165)	−1 811 (177)	103 781 (76)
C(50)	46 194 (131)	17 749 (147)	67 776 (43)
C(51)	43 799 (179)	27 166 (189)	58 480 (64)
C(52)	52 542 (156)	19 963 (192)	59 985 (67)
C(53)	39 866 (196)	33 798 (214)	62 360 (64)
C(54)	37 259 (143)	24 915 (189)	66 338 (61)
C(55)	50 281 (154)	10 780 (192)	64 078 (65)
C(60)	41 768 (133)	−29 216 (131)	89 098 (53)
C(61)	39 651 (172)	−34 534 (160)	94 051 (61)
C(62)	43 098 (178)	−55 079 (175)	90 772 (78)
C(63)	49 207 (163)	−37 016 (154)	86 771 (68)
C(64)	44 730 (200)	−48 936 (199)	86 036 (74)
C(65)	35 907 (182)	−46 935 (208)	93 203 (81)

[a] All coordinate values have been multiplied by 10^5.

Solution and refinement of the structure were achieved as follows: Initial coordinates of the Pd atoms were obtained by direct methods,[15] prior to the location of the remaining non-hydrogen atoms from a series of difference Fourier maps. Full-matrix least-squares refinement,[16] with anisotropic temperature factors for all atoms, led to the final agreement factor $R = 0.047$ ($R_w = 0.051$) for 2624 nonzero reflections ($I > 3\sigma(I)$).

Results and Discussions

In Figure 1 is shown an ORTEP plot of the molecule $Pd_3(CN\text{-}c\text{-}Hx)_6$. The atomic positional parameters with their estimated standard deviations are given in Table II, with selected average bond distances and angles listed in Table III.

Table III. Average Distances (Å) and Angles (deg) for $Pd_3(CN\text{-}c\text{-}Hx)_6$[a]

	Bond Distances		
Pd–Pd	2.651 (2)	$[C\text{-}N]_t$	1.147 (18)
$Pd\text{-}C_t$	2.004 (14)	$[C\text{-}N]_b$	1.217 (17)
$Pd\text{-}C_b$	2.072 (13)		
	Bond Angles		
Pd–Pd–Pd	60.0 (0)	$[C\text{-}N\text{-}C]_t$	170.2 (14)
$Pd\text{-}C_b\text{-}Pd$	79.5 (5)	$[C\text{-}N\text{-}C]_b$	128.9 (12)
$Pd\text{-}C_t\text{-}N_t$	169.1 (13)		

[a] Subscripts t and b refer to terminal and bridging isocyanide ligands, respectively.

The molecule contains an equilateral triangle of Pd atoms, each metal being bound to one terminal and two bridging isocyanide ligands. This structure is very similar to that reported by Stone and co-workers[4] for the analogous $Pt_3(CN\text{-}t\text{-}Bu)_6$ and contains the same basic metal structural unit as in the known $Pd_3(SO_2)_2(CN\text{-}t\text{-}Bu)_5$.[17] The Pd–Pd distances [mean distance 2.651 (2) Å] are significantly shorter than those found in the $Pd_3(SO_2)_2(CN\text{-}t\text{-}Bu)_5$ complex[17] (2.743 Å), which contains bridging SO_2 groups and the isocyanide ligands in terminal positions. While this latter value approximates quite closely to the shortest metal–metal distance in bulk palladium (2.751 Å),[18] the Pd–Pd distances in $Pd_3(CN\text{-}c\text{-}Hx)_6$ appear to be intermediate between the bulk metal distance and that calculated from the sum of the single-bond metallic radii (2.57 Å).[18] For comparison, the Pd–Pd bond in $[Pd_2(CNCH_3)_6][PF_6]_2$ is 2.5310 (9) Å,[8] a distance that has been noted as being very short for a Pd(I) binuclear system.

The carbon atoms bound to the metal triangle are coplanar with the three Pd atoms. The terminal isocyanide ligands approximate to a linear C–N–C arrangement [CNC mean angle 170.2 (14)°], while the bridging isocyanide molecules contain essentially sp^2-type nitrogen atoms with a CNC mean angle of 128.9 (12)°. It is interesting to note that all of the cyclohexyl rings adopt the chair conformation.

The establishment of $[Pd(CNR)_2]_x$ as the trimer provides the missing link between the known tetranuclear clusters of Ni (Ni_4L_6, Ni_4L_7)[3] and the trinuclear Pt species (Pt_3L_6).[4] The demonstration that the metal atom route is able to yield the Pd_3L_6 in a simple, one-step procedure leads one to anticipate that other novel homonuclear or heteronuclear metal–isocyanide cluster complexes may be accessed in this way. However, an important question relates to whether $Pd_3(CN\text{-}c\text{-}Hx)_6$ is formed directly from the reaction of palladium vapor with CN-c-Hx or whether it is the product formed on warming the solution to room temperature. Studies are currently in progress to clarify this point.

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Registry No. $Pd_3(CN\text{-}c\text{-}Hx)_6$, 92127-06-5.

Supplementary Material Available: A figure depicting the complete atom-numbering scheme and listings of the thermal factors (Table A), interatomic distances (Table B), interatomic angles (Table C), and final observed and calculated structure factors for $Pd_3(CN\text{-}c\text{-}Hx)_6$ (25 pages). Ordering information is given on any current masthead page.

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