Table V. ^{1}H NMR Shift and T_1 Values[a] and Estimated Cu–H Distances for the Protons of His-46 in Cu_2Co_2SOD at 300 MHz and 303 K in the Presence of a Saturating Amount of N_3

signal	His-46 proton	shift value, ppm	T_1, ms	r_{Cu-H}, Å
K	Hδ1	15.9	19.1	5.0
L	Hδ2	12.5	10.9	4.4
O	Hε1	10.5	2.8	3.4

[a] Taken from ref 13.

not the farthest from the metal, but it is just an ortho-like proton of a histidine (His-46). This is the surprising result from the theoretical point of view: it means that the T_1–distance correlation may break down even from a qualitative point of view. A possible explanation for this inconsistency is that ligand-centered effects are, at this stage of our knowledge, absolutely unpredictable and that the Hε2 of His-46 has the smallest ligand-centered contribution with respect to the other ortho-like protons. A careful inspection of the structure shows that such a proton is very close to the z axis of an xy plane formed by the coordinating nitrogens of the other histidines. If the unpaired electron is mainly delocalized into this xy plane, the metal-centered point dipole model may fail, and delocalization of the unpaired electron within the cage formed by the donor atoms might instead be considered. If this qualitative picture holds true, then signal L is the one experiencing the smallest contribution from the delocalization of the unpaired electron in the xy plane. The problem of the deviations from the point dipole model has been discussed by Golding and Golding and McGarvey with respect to pseudocontact shifts.[26,27] In any case, in the present system the T_1^{-1} ratio between ortho-like and meta-like protons (the three histidine NH, besides signal G) is always much smaller than the value of 15–20 expected on the basis of the r^6 dependence. Although a lengthy discussion of the general problem of unpaired electron spin delocalization on histidine rings is not appropriate here, we would like to draw attention to the experimental fact that while copper(II) in SOD seems to induce efficient delocalization into its histidine ligands, this does not hold for nickel(II) or cobalt(II) in the zinc site. For the former there is about 1 order of magnitude difference in both T_1^{-1} and line widths between ortho- and meta-like protons; for the latter, the recent experiments on the his-deuteriated sample[22] have established that the ortho-like protons on the cobalt side in SOD are so broad to have always escaped detection. Clearly, this is an important issue to be addressed by everyone wishing to relate distances to T_1 values in this kind of system. In particular, unpaired spin delocalization mechanisms onto histidine rings should be better understood. Work is currently being planned to this end.

Anion Binding. The new assignment leads to the important conclusion that when cyanide and azide interact with copper, the histidine whose interaction with the paramagnetic center is virtually abolished is His-46 instead of His-44. Therefore, anions bind at a site between Arg-141 and the metal, where the semicoordinated water is located. By considering the experimental T_1 of the protons of His-46 in the azide adduct and making the reasonable assumption that ligand centered contributions have dropped to zero, it is possible to estimate new Cu–H distances through a metal-centered dipolar model, and the results are shown in Table V. It is possible that, besides small movements of His-46, the major change involves the copper ion itself, which could move up into the plane formed by the anion and the three nitrogens of the other histidines and away from His-46.

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Interactions between Cyanoborohydrides and $Cl_2Pt(dppm)$. X-ray Structural Characterization of the Complexes $[Pt(dppm)(CNBH_2CN)]_2{\cdot}CHCl_3$, $[Pt(dppm)(CN)]_2{\cdot}{}^1/_2C_5H_5N$, and $[Pt(dppm)(CNBH_3)]_2{\cdot}H_2O$. Isomerization of *trans*-$[Pt(dppm)(NCBH_2CN)]_2$ to *trans*-$[Pt(dppm)(CNBH_2CN)]_2$

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A series of complexes $[Pt(dppm)L]_2$ (L = $NCBH_3$ (**1**), $NCBH_2CN$ (**2**), $CNBH_2CN$ (**3**), CN (**4**), $CNBH_3$ (**5**)) have been prepared from $NaBH_3CN$ or $NaBH_2(CN)_2$ and $Cl_2Pt^{II}(dppm)$ or $[Pt^I(dppm)Cl]_2$. The particular complex or linkage isomer obtained is dependent on the choice of solvent. X-ray structural characterizations of **3**–**5** have been performed. The linkage isomerization of $NCBH_3$ upon coordination to the dinuclear platinum complex is described. With $BH_2(CN)_2$, isomerization of only one BCN linkage is found in $[Pt^I(dppm)(CNBH_2CN)]_2$. Compounds **3**–**5** crystallize in the space groups $P\bar{1}$, $P2_1/c$, and C_2/c, respectively, with the following cell constants: a = 12.665 (4) Å, b = 12.706 (3) Å, c = 18.297 (5) Å, α = 75.80 (2)°, β = 82.20 (2)°, γ = 84.85 (2)°, V = 2833 (3) Å^3 for **3**; a = 13.773 (7) Å, b = 16.404 (8) Å, c = 21.496 (7) Å, β = 105.81 (3)°, V = 4673 (4) Å^3 for **4**; a = 15.719 (2) Å, b = 16.842 (3) Å, c = 20.217 (4) Å, β = 104.781 (1)°, V = 5176 (1) Å^3 for **5**. The refinement converged to R = 0.0414 and R_w = 0.0452 for **3**, R = 0.0360 and R_w = 0.0365 for **4**, and R = 0.0329 and R_w = 0.0524 for **5**. The Pt–Pt bond distances of 2.665 (1) Å in **3**, 2.704 (1) Å in **4**, and 2.667 (1) Å in **5** indicate metal–metal bonding interactions. The Pt centers in these d^9 complexes possess square-planar geometries. The Pt–C bond distances are 1.963 (10), 1.993 (11), and 2.037 (11) Å in **3**, 2.054 (9) Å in **4**, and 2.015 (10) Å in **5**. Complex **5** has a center of symmetry. Compounds **1** and **2** slowly isomerize in solution to **5** and **3** at room temperature and rapidly isomerize at elevated temperature via inorganic linkage mechanisms.

Introduction

Transition-metal complexes of the cyanotrihydroborate anion containing M–$NCBH_3$, M–HBH_2CN, or M–H–BH_2–CN–M linkages with a wide variety of phosphine and non-phosphine ligands have been known for several years.[1-10] Of particular

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Table I. Crystallographic Data for **3–5**

	complex **3**	complex **4**	complex **5**
formula	$C_{54}H_{48}B_2N_4P_4$-$Pt_2 \cdot CHCl_3$	$C_{52}H_{44}N_2P_4$-$Pt_2 \cdot {}^1/_2$py	$C_{52}H_{50}B_2N_2P_4$-$Pt_2 \cdot H_2O$
a, Å	12.665 (4)	13.773 (7)	15.719 (2)
b, Å	12.706 (3)	16.404 (8)	16.842 (3)
c, Å	18.297 (5)	21.496 (7)	20.217 (4)
α, deg	75.80 (2)	90.000	90.000
β, deg	82.20 (2)	105.81 (3)	104.78 (1)
γ, deg	84.85 (2)	90.000	90.000
V, Å^3	2833 (3)	4673 (4)	5176 (1)
Z	2	4	4
fw	1407.18	1243.56	1255.68
space group	$P\bar{1}$	$P2_1/c$	C_2/c
temp, °C	22	22	22
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)		
d_{calc}, g/cm^3	1.64	1.76	1.61
μ(Mo Kα), cm^{-1}	54.97	62.12	58.35
transm factors: max, min	0.449, 0.297	0.591, 0.406	0.777, 0.668
R^a	0.0411	0.0360	0.0329
$R_w{}^b$	0.0452	0.0365	0.0524
g	0.00025	0.00019	0.00124

[a] $R = \sum||F_o| - |F_c||\sum|F_o|$. [b] $R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$. [c] Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

interest is the mode of attachment of the BH_3CN^- group to the transition-metal ions. Most BH_3CN^- complexes are assumed (from infrared data) to have N-coordinated cyanotrihydroborate units; the structures of only four such complexes have been determined by X-ray methods. Among these, two are binuclear systems and show[5,8] bridging of the type M–HBH_2CN–M, while in the other two[7,9] a M–$NCBH_3$ linkage is observed. Besides these interaction modes, BH_3CN^- has the ability to reduce transition-metal ions to metal hydrides in the presence of complex ligands.[9,10] Recently, Manzer et al. reported the synthesis[11] and kinetic studies[12] of monomeric Pt^{II} complexes with cyanotrialkyl- or cyanotriarylboron in the presence of monodentate trialkyl- or triarylphosphine ligands. These studies have shown that, upon heating, the complexes isomerize from the N-coordinated Pt–$NCBR_3$ (kinetically stable) to the C-coordinated Pt–$CNBR_3$ (thermodynamically stable) products. The isomerization occurs via the thermal dissociation of trialkyl- or triarylboron (BR_3) to give unstable isocyano (Pt–NC) complexes which then flip (possibly through a π-bonded CN) to give the stable cyanide Pt–CN complexes.

Very recently, the X-ray structure of an interesting copper complex containing dicyanodihydroborate with monodentate phosphine ligands has been reported.[13,14] In this complex, $[BH_2(CN)_2]^-$ bridges two copper atoms through the two CN groups coordinated via N to the metal.

The interaction between Cl_2Pt(dppm) and $NaBH_3CN$ was investigated here for several reasons. First, no cyanotrihydroborate complexes of $[Pt^I(dppm)]_2{}^{2+}$ have been reported. Cyanotrihydroborate has a wide variety of bonding modes toward transition-metal ions. It was not certain what this would be for the metal-metal-bonded dimer. Since BH_3CN^- is a milder reducing agent than BH_4^-, a wide range transition-metal complexes with unusual oxidation states can be produced in the presence of phosphine and non-phosphine ligands.

In this paper, we describe the synthesis and characterization of $[Pt(dppm)(BH_3CN)]_2$ (**1**) and $[Pt(dppm)(BH_2(CN)_2]_2$ (**2**), in which BH_3CN^- and $BH_2(CN)^-{}_2$ coordinate to the Pt(I) centers through N atoms, and the synthesis and structural characterization of $[Pt(dppm)(CNBH_2CN)]_2$ (**3**), $[Pt(dppm)(CN)]_2$ (**4**), and $[Pt(dppm)(CNBH_3)]_2$ (**5**), in which $CNBH_2NC$, CN, and $CNBH_3$ are coordinated to Pt(I) via the C atom. The isomerization of **1** and **2** to **5** and **3**, respectively, is observed.

Experimental Section

The reagents and solvents used in this work were purchased from commercial sources and used without further purification. $NaBH_3CN$ and dppm, [bis(diphenylphosphino)methane], were obtained from Aldrich. Because of their hygroscopic nature, they were stored over $CaCl_2$. All solvents were freshly distilled prior to use. All experiments were carried out in oven-dried Schlenk glassware by using standard inert-atmosphere techniques.[15] The compounds Cl_2Pt(dppm) and $[Pt(dppm)Cl]_2$ were prepared according to a literature procedure.[16] Infrared spectra (Nujol mulls) were recorded on a Perkin-Elmer 783 spectrophotometer (polystyrene reference film) using CsI or KBr (200–4000 cm^{-1}) plates. ^1H and ^{31}P NMR spectra were recorded on a Varian XL-200 Fourier transform spectrometer.

Synthesis of $[Pt(dppm)(BH_3CN)]_2$ (1). To a stirred mixture of $[Pt(dppm)Cl]_2$ (15 mg, ~0.012 mmol) in THF (5 mL) was added $NaBH_3CN$ (1.5 mg, 0.024 mmol) in one portion under inert atmosphere. After 2 h of stirring at room temperature, solvent was evaporated to dryness in vacuo to yield a yellow solid. This solid was dissolved in CH_2Cl_2 to remove NaCl. The solvent was removed to yield a yellow solid (67.0 mg, ca. 70%). Anal. Calcd for $C_{52}H_{50}B_2N_2P_4Pt_2$: C, 50.41; H, 4.03; N, 2.26. Found: C, 50.65; H, 4.12; N, 2.30. IR: ν_{CN}, 2205 (s) cm^{-1}; B–H terminal, 2340 (s, br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 4.6 (t, J_{P-H} = 10.5 Hz, CH_2), 7.2 and 7.3 (m, aromatic protons). ^{31}P NMR in $CDCl_3$: δ 27.5 (s).

Synthesis of $[Pt(dppm)(BH_2(CN)_2)]_2$ (2). To a stirred suspension of $[Pt(dppm)Cl]_2$ (50 mg, ~0.04 mmol) in THF (5 mL) was added $NaBH_2(CN)_2$[17] (22 mg, 0.08 mmol) in one portion at room temperature. After addition of $NaBH_2(CN)_2$, the suspended $[Pt(dppm)Cl]_2$ was immediately dissolved, forming a yellow solution with some colorless solid, NaCl. After $2^1/_2$ hr of stirring at room temperature, the colorless solid was removed by filtration and the solvent was evaporated to dryness to yield a yellow solid (50 mg, ca. 90%). Further purification was carried out by dissolving in CH_2Cl_2 and filtering to remove any insoluble impurities. Upon evaporation of CH_2Cl_2, a fine crystalline yellow solid was obtained. IR: ν_{CN}, 2270 (s) and 2210 (s) cm^{-1} (terminal and bridging CN, respectively); B–H terminal, 2370 (s, br) cm^{-1}.

Synthesis of $[Pt(dppm)(CNBH_2CN)]_2$ (3). $NaBH_3CN$ (24.18 mg, 0.39 mmol) was added to a stirred suspension of Cl_2Pt(dppm) (50 mg, 0.077 mmol) in a mixture of MeOH/THF (1:3). After addition of $NaBH_3CN$, the colorless suspension gave within 5 min a yellow solution with the liberation of H_2 gas. The resultant yellow solution was further stirred for 3 h at room temperature. The white solids produced in the reaction were filtered out, and the solvent was evaporated to dryness to yield a yellow solid (78.57 mg ~75%). The yellow solid was further dissolved in CH_2Cl_2 to remove $NaBH_3CN$. The solvent was removed under high vacuum to give a yellow solid that decomposed above 300 °C. Anal. Calcd for $C_{55}H_{49}B_2Cl_3N_4P_4Pt_2$ (crystallized product—see below): C, 46.90; H, 3.48; N, 3.97. Found: C, 46.85; H, 3.50; N, 3.90. IR: ν_{CN}, 2240 (s) cm^{-1} (terminal CN) and 2185 cm^{-1} (bridging CN); B–H terminal, 2370 (s, br) cm^{-1}. ^1H NMR in $CDCl_3$: δ 4.8 (t, J_{P-H} = 10.4 Hz, CH_2 of dppm), 7.3 and 7.5 (m, aromatic protons). ^{31}P NMR in CH_2Cl_2: δ 24.30 (s).

Synthesis of $[Pt(dppm)(CN)]_2$ (4). Cl_2Pt(dppm) (100 mg, 0.15 mmol) was suspended in MeOH (5 mL). While the mixture was stirred at room temperature, $NaBH_3CN$ (71 mg, 1.13 mmol) in MeOH (3 mL) was added dropwise via a syringe over 5 min, during which time the colorless suspension changed to a yellow suspension with the liberation of gas. The resultant yellow mixture was stirred overnight to give a bulk of yellow solid. The yellow solid was separated by filtration and washed with MeOH (2 mL) and Et_2O (5 mL) to yield a yellow solid (100 mg, ~ 95%). Decomposition occurred at 195–200 °C to form a red material. Anal. Calcd for $C_{52}H_{44}N_2P_4Pt_2$: C, 51.56; H, 3.63; N, 2.31. Found: C, 51.50; H, 3.68; N, 2.25. IR: ν_{CN}, 2125 (s) cm^{-1}. ^1H NMR in $CDCl_3$, δ 4.2 (t, J_{P-H} = 10 Hz, CH_2 of dppm), 7.1 and 7.3 (m, aromatic protons). ^{31}P NMR in $CDCl_3$: δ −1.76.

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Table II. Bond Lengths (Å) and Angles (deg) for $[Pt(dppm)(CNBH_2CN)]_2 \cdot CHCl_3$ (**3**)[a]

Pt(1)–Pt(2)	2.665 (1)	Pt(1)–P(1)	2.279 (4)	C(24)–C(25)	1.370 (25)	C(25)–C(26)	1.348 (17)
Pt(1)–P(3)	2.280 (4)	Pt(1)–C(1a)	1.963 (10)	C(31)–C(32)	1.342 (25)	C(31)–C(36)	1.377 (21)
Pt(2)–P(2)	2.293 (4)	Pt(2)–P(4)	2.292 (4)	C(32)–C(33)	1.346 (35)	C(33)–C(34)	1.364 (33)
P(2)–C(2a)	1.993 (11)	P(1)–C(5)	1.823 (11)	C(34)–C(35)	1.364 (25)	C(35)–C(36)	1.390 (19)
P(1)–C(16)	1.837 (13)	P(1)–C(36)	1.782 (12)	C(41)–C(42)	1.397 (24)	C(41)–C(46)	1.372 (18)
P(2)–C(5)	1.833 (11)	P(2)–C(26)	1.790 (12)	C(42)–C(43)	1.358 (32)	C(43)–C(44)	1.347 (30)
P(2)–C(46)	1.816 (12)	P(3)–C(6)	1.828 (11)	C(44)–C(45)	1.351 (26)	C(45)–C(46)	1.395 (21)
P(3)–C(56)	1.836 (11)	P(3)–C(76)	1.781 (13)	C(51)–C(52)	1.371 (18)	C(51)–C(56)	1.348 (16)
P(4)–C(6)	1.848 (10)	P(4)–C(66)	1.804 (11)	C(52)–C(53)	1.374 (21)	C(53)–C(54)	1.329 (21)
P(4)–C(86)	1.808 (13)	B(1)–N(1a)	1.549 (20)	C(54)–C(55)	1.403 (16)	C(55)–C(56)	1.375 (17)
B(1)–C(1b)	1.514 (24)	B(2)–N(2a)	1.556 (23)	C(61)–C(62)	1.383 (22)	C(61)–C(66)	1.376 (18)
B(2)–C(2b)	1.444 (34)	C(1a)–N(1a)	1.180 (14)	C(62)–C(63)	1.363 (30)	C(63)–C(64)	1.315 (27)
N(1b)–C(1b)	1.101 (21)	C(2a)–N(2a)	1.154 (14)	C(64)–C(65)	1.374 (23)	C(65)–C(66)	1.388 (18)
N(2b)–C(2b)	1.111 (31)	C(7)–Cl(1)	1.710 (23)	C(71)–C(72)	1.378 (20)	C(71)–C(76)	1.388 (21)
C(7)–Cl(2)	1.769 (23)	C(7)–Cl(3)	1.702 (20)	C(72)–C(73)	1.354 (24)	C(73)–C(74)	1.369 (25)
C(11)–C(12)	1.373 (23)	C(11)–C(16)	1.376 (17)	C(74)–C(75)	1.371 (20)	C(75)–C(76)	1.367 (18)
C(12)–C(13)	1.321 (32)	C(13)–C(14)	1.373 (33)	C(81)–C(82)	1.385 (26)	C(81)–C(86)	1.381 (19)
C(14)–C(15)	1.377 (25)	C(15)–C(16)	1.369 (21)	C(82)–C(83)	1.262 (27)	C(83)–C(84)	1.341 (27)
C(21)–C(22)	1.368 (23)	C(21)–C(26)	1.417 (16)	C(84)–C(85)	1.400 (22)	C(85)–C(86)	1.375 (18)
C(22)–C(23)	1.328 (29)	C(23)–C(24)	1.339 (30)				

Pt(2)–Pt(1)–P(1)	87.4 (1)	Pt(2)–Pt(1)–P(3)	86.2 (1)	C(21)–C(22)–C(23)	122.9 (16)	C(22)–C(23)–C(24)	117.4 (21)
P(1)–Pt(1)–P(3)	173.4 (1)	Pt(2)–Pt(1)–C(1a)	179.4 (4)	C(23)–C(24)–C(25)	122.8 (17)	C(24)–C(25)–C(26)	120.5 (14)
P(1)–Pt(1)–P(1a)	92.1 (4)	P(3)–Pt(1)–C(1a)	94.2 (4)	P(2)–C(26)–C(21)	118.9 (9)	P(2)–C(26)–C(25)	123.7 (9)
Pt(1)–Pt(2)–P(2)	90.4 (1)	Pt(1)–Pt(2)–P(4)	89.9 (1)	C(21)–C(26)–C(25)	116.9 (12)	C(32)–C(31)–C(36)	120.1 (17)
P(2)–Pt(2)–P(4)	177.7 (1)	Pt(1)–Pt(2)–C(2a)	175.6 (4)	C(31)–C(32)–C(33)	122.8 (21)	C(32)–C(33)–C(34)	117.6 (19)
P(2)–Pt(2)–C(2a)	90.2 (4)	P(4)–Pt(2)–C(2a)	89.6 (4)	C(33)–C(34)–C(35)	122.0 (19)	C(34)–C(35)–C(36)	119.0 (16)
Pt(1)–P(1)–C(5)	104.5 (5)	Pt(1)–P(1)–C(16)	116.7 (4)	P(1)–C(36)–C(31)	121.8 (10)	P(1)–C(36)–C(35)	119.8 (11)
C(5)–P(1)–C(16)	103.7 (6)	Pt(1)–P(1)–C(36)	117.8 (5)	C(31)–C(36)–C(35)	118.4 (13)	C(42)–C(41)–C(46)	120.5 (15)
C(5)–P(1)–C(36)	107.8 (5)	C(16)–P(1)–C(36)	105.1 (6)	C(41)–C(42)–C(43)	117.2 (16)	C(42)–C(43)–C(44)	123.0 (18)
Pt(2)–P(2)–C(5)	114.6 (4)	Pt(2)–P(2)–C(26)	111.7 (5)	C(43)–C(44)–C(45)	120.2 (20)	C(44)–C(45)–C(46)	119.4 (15)
C(5)–P(2)–C(26)	106.9 (5)	Pt(2)–P(2)–C(46)	115.8 (4)	P(2)–C(46)–C(41)	120.9 (11)	P(2)–C(46)–C(45)	119.6 (9)
C(5)–P(2)–C(46)	103.2 (6)	C(26)–P(2)–C(46)	103.5 (5)	C(41)–C(46)–C(45)	119.5 (13)	C(52)–C(51)–C(56)	122.2 (12)
Pt(1)–P(3)–C(6)	108.2 (4)	Pt(1)–P(3)–C(56)	116.1 (4)	C(51)–C(52)–C(53)	118.6 (13)	C(52)–C(53)–C(54)	120.9 (13)
C(6)–P(3)–C(56)	106.3 (5)	Pt(1)–P(3)–C(76)	115.9 (5)	C(53)–C(54)–C(55)	120.1 (14)	C(54)–C(55)–C(56)	119.6 (12)
C(6)–P(3)–C(76)	106.7 (6)	C(56)–P(3)–C(76)	102.9 (5)	P(3)–C(56)–C(51)	119.3 (9)	P(3)–C(56)–C(55)	121.7 (8)
Pt(2)–P(4)–C(6)	115.6 (4)	Pt(2)–P(4)–C(66)	112.6 (4)	C(51)–C(56)–C(55)	118.6 (10)	C(62)–C(61)–C(66)	119.3 (14)
C(6)–P(4)–C(66)	104.9 (5)	Pt(2)–P(4)–C(86)	113.3 (4)	C(61)–C(62)–C(63)	122.4 (15)	C(62)–C(63)–C(64)	117.9 (17)
C(6)–P(4)–C(86)	104.9 (6)	C(66)–P(4)–C(86)	104.5 (5)	C(63)–C(64)–C(65)	122.5 (17)	C(64)–C(65)–C(66)	120.4 (14)
N(1a)–B(1)–C(1b)	112.0 (13)	N(2a)–B(2)–C(2b)	116.1 (20)	P(4)–C(66)–C(61)	122.5 (10)	P(4)–C(66)–C(65)	119.9 (9)
Pt(1)–C(1a)–N(1a)	178.8 (13)	Pt(2)–C(2a)–N(2a)	178.9 (12)	C(61)–C(66)–C(65)	117.4 (11)	C(72)–C(71)–C(76)	122.5 (14)
B(1)–N(1a)–C(1a)	174.8 (13)	B(2)–N(2a)–C(2a)	173.7 (16)	C(71)–C(72)–C(73)	118.5 (16)	C(72)–C(73)–C(74)	120.6 (15)
B(1)–C(1b)–N(1b)	173.2 (18)	B(2)–C(2b)–N(2b)	173.6 (25)	C(73)–C(74)–C(75)	120.1 (14)	C(74)–C(75)–C(76)	121.4 (14)
P(1)–C(5)–P(2)	106.0 (6)	P(3)–C(6)–P(4)	106.1 (6)	P(3)–C(76)–C(71)	121.8 (10)	P(3)–C(76)–C(75)	121.4 (11)
Cl(1)–C(7)–Cl(2)	110.8 (11)	Cl(1)–C(7)–Cl(3)	109.2 (11)	C(71)–C(76)–C(75)	116.8 (12)	C(82)–C(81)–C(86)	120.2 (14)
Cl(2)–C(7)–Cl(3)	104.6 (12)	C(12)–C(11)–C(16)	119.0 (14)	C(81)–C(82)–C(83)	123.6 (18)	C(82)–C(83)–C(84)	119.8 (19)
C(11)–C(12)–C(13)	123.2 (17)	C(12)–C(13)–C(14)	117.3 (20)	C(83)–C(84)–C(85)	119.5 (16)	C(84)–C(85)–C(86)	121.7 (14)
C(13)–C(14)–C(15)	122.3 (19)	C(14)–C(15)–C(16)	118.5 (16)	P(4)–C(86)–C(81)	124.4 (10)	P(4)–C(86)–C(85)	120.6 (10)
P(1)–C(16)–C(11)	117.8 (10)	P(1)–C(16)–C(15)	122.4 (10)	C(81)–C(86)–C(85)	115.0 (13)		
C(11)–C(16)–C(15)	119.6 (12)	C(22)–C(21)–C(26)	119.2 (13)				

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Synthesis of $[Pt(dppm)(CNBH_3)]_2$ (5). To a stirred suspension of $[Pt(dppm)(CN)]_2$ (**4**) (30 mg, 0.03 mmol) in THF (3 mL) was added THF·BH_3 (excess) dropwise over 3 min. After addition of THF·BH_3, the yellow solid disappeared and then reappeared. The resultant mixture was stirred for 2 h at room temperature. A light yellow solid was separated by filtration, (27.91 mg, ~90%). The crude product was purified by recrystallization from CH_2Cl_2/pentane overnight. Decomposition occurred at 230–235 °C, yielding a red material. Anal. Calcd for $C_{52}H_{52}B_2N_2OP_4Pt_2$: C, 49.69; H, 4.14; N, 2.23. Found: C, 49.60; H, 4.10; N, 2.30. IR: ν_{CN}, 2195 (vs) cm^{-1}. ^{31}P NMR in $CDCl_3$: δ 12.82.

X-ray Crystallography. The structure determination procedure (Nicolet R3m/E diffractiometer, SHELXTL 5.1 software) is described in detail elsewhere.[18] Compounds **3**–**5** were recrystallized from $CHCl_3/Et_2O$, CH_2Cl_2/pyridine/Et_2O, and CH_2Cl_2 (wet)/Et_2O mixed solvents, respectively. Compounds **3**–**5** crystallize with $CHCl_3$, pyridine, and H_2O in the lattices, respectively. Single well-formed crystals of $[Pt(dppm)(CNBH_2CN)]_2 \cdot CHCl_3$ (**3**), $[Pt(dppm)(CN)]_2 \cdot {}^1/_2C_5H_5N$ (**4**), and $[Pt(dppm)(CNBH_3)] \cdot H_2O$ (**5**) had approximate dimensions of 0.2 × 0.2 × 0.03, 0.5 × 0.5 × 0.5, and 0.5 × 0.2 × 0.2 mm, respectively. Crystals were mounted on glass fibers by using epoxy cement. No decay in the standard reflections was observed. Crystallographic details appear in Table I. The data were corrected for decay and for Lorentz and polarization effects. An empirical absorption correction was applied. The heavy-atom positions were determined from a sharpened Patterson map and used as the initial phasing model for difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed to the carbon atoms at idealized positions and a distance of 0.96 Å. Bond lengths and angles are given in Tables II–IV and atomic coordinates and thermal parameters are given in Tables V–VII for compounds **3**–**5**, respectively.

Results

All compounds presented in this paper are air stable and soluble in CH_2Cl_2, $CHCl_3$, CH_3CN, and THF. Reactions between $Cl_2Pt(dppm)$ and $NaBH_3CN$ are summarized in Scheme I. No hydrides have been obtained. Spectroscopic data for the complexes are given in the Experimental Section. Isomerization of the N-coordinate (kinetic product) $[Pt(dppm)(NCBH_2R)]_2$ (R = H (**1**), CN (**2**)) to the C-coordinate (thermodynamic product) $[Pt(dppm)(CNBH_2R)]_2$ (R = H (**5**), CN (**3**)) is observed. X-ray structural characterizations of the compounds $[Pt(dppm)(CNBH_2CN)]_2$ (**3**), $[Pt(dppm)(CN)]_2$ (**4**), and $[Pt(dppm)(CNBH_2)]_2$ (**5**) have been carried out.

Discussion

The reductive coupling of $Cl_2Pt^{II}(dppm)$ by cyanoborohydrides is accompanied by isomerization of the B–CN bond. The isolated

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(18) Porter, L. C.; Fackler, J. P., Jr. *Acta Crystallogr.* **1987**, *C43*, 993–996.

Table III. Bond Lengths (Å) and Angles (deg) for $Pt_2(dppm)_2(CN)_2$ (**4**)[a]

C(1a)–C(2a)	1.275 (42)	C(1a)–C(3aa)	1.491 (38)	C(36)–C(31)	1.375 (16)	C(35)–C(34)	1.353 (17)
C(2a)–C(3a)	1.310 (37)	C(3a)–C(1aa)	1.491 (38)	C(34)–C(33)	1.361 (18)	C(33)–C(32)	1.349 (14)
Pt(1)–Pt(2)	2.704 (1)	Pt(1)–P(1)	2.276 (3)	C(32)–C(31)	1.372 (14)	C(46)–C(45)	1.348 (19)
Pt(1)–P(2)	2.261 (3)	Pt(1)–C(3)	2.039 (11)	C(46)–C(41)	1.407 (17)	C(45)–C(44)	1.365 (26)
Pt(2)–P(3)	2.277 (3)	Pt(2)–P(4)	2.293 (3)	C(44)–C(43)	1.380 (21)	C(43)–C(42)	1.367 (16)
Pt(2)–C(4)	2.054 (9)	P(1)–C(1)	1.811 (10)	C(42)–C(41)	1.347 (18)	C(56)–C(55)	1.363 (19)
P(1)–C(11)	1.812 (11)	P(1)–C(21)	1.825 (12)	C(56)–C(51)	1.354 (16)	C(55)–C(54)	1.350 (19)
P(2)–C(2)	1.836 (11)	P(2)–C(31)	1.825 (9)	C(54)–C(53)	1.361 (17)	C(53)–C(52)	1.376 (17)
P(2)–C(41)	1.814 (10)	P(3)–C(1)	1.819 (10)	C(52)–C(51)	1.384 (17)	C(66)–C(65)	1.389 (18)
P(3)–C(51)	1.848 (11)	P(3)–C(61)	1.854 (10)	C(66)–C(61)	1.346 (17)	C(65)–C(64)	1.373 (22)
P(4)–C(2)	1.823 (9)	P(4)–C(71)	1.841 (11)	C(64)–C(63)	1.358 (22)	C(63)–C(62)	1.370 (17)
P(4)–C(81)	1.839 (10)	C(3)–N(3)	1.131 (14)	C(62)–C(61)	1.355 (16)	C(76)–C(75)	1.379 (18)
C(4)–N(4)	1.118 (12)	C(16)–C(15)	1.355 (19)	C(76)–C(71)	1.375 (17)	C(75)–C(74)	1.352 (18)
C(16)–C(11)	1.404 (20)	C(15)–C(14)	1.365 (24)	C(74)–C(73)	1.374 (20)	C(73)–C(72)	1.412 (17)
C(14)–C(13)	1.332 (22)	C(13)–C(12)	1.379 (16)	C(72)–C(71)	1.385 (15)	C(86)–C(85)	1.381 (19)
C(12)–C(11)	1.373 (17)	C(26)–C(25)	1.382 (18)	C(86)–C(81)	1.384 (15)	C(85)–C(84)	1.330 (20)
C(26)–C(21)	1.337 (15)	C(25)–C(24)	1.330 (22)	C(84)–C(83)	1.385 (20)	C(83)–C(82)	1.392 (17)
C(24)–C(23)	1.338 (17)	C(23)–C(22)	1.393 (18)	C(82)–C(81)	1.386 (15)		
C(22)–C(21)	1.377 (19)	C(36)–C(35)	1.396 (16)				

C(2a)–C(1a)–C(3aa)	99.3 (20)	C(1a)–C(2a)–C(3a)	133.6 (27)	C(24)–C(23)–C(22)	118.5 (13)	C(23)–C(22)–C(21)	121.6 (11)
C(2a)–C(3a)–C(1aa)	127.0 (27)	Pt(2)–Pt(1)–P(1)	88.2 (1)	P(1)–C(21)–C(26)	120.2 (10)	P(1)–C(21)–C(22)	122.0 (8)
Pt(2)–Pt(1)–P(2)	83.6 (1)	P(1)–Pt(1)–P(2)	170.9 (1)	C(26)–C(21)–C(22)	117.6 (11)	C(35)–C(36)–C(31)	120.8 (11)
Pt(2)–Pt(1)–C(3)	175.0 (4)	P(1)–Pt(1)–C(3)	95.8 (4)	C(36)–C(35)–C(34)	119.9 (11)	C(35)–C(34)–C(33)	118.4 (10)
P(2)–Pt(1)–C(3)	92.7 (4)	Pt(1)–Pt(2)–P(3)	90.2 (1)	C(34)–C(33)–C(32)	122.8 (11)	C(33)–C(32)–C(31)	120.1 (11)
Pt(1)–Pt(2)–P(4)	88.8 (1)	P(3)–Pt(2)–P(4)	175.8 (1)	P(2)–C(31)–C(36)	119.9 (8)	P(2)–C(31)–C(32)	122.0 (8)
Pt(1)–Pt(2)–C(4)	178.8 (3)	P(3)–Pt(2)–C(4)	89.6 (3)	C(36)–C(31)–C(32)	118.1 (9)	C(45)–C(46)–C(41)	119.2 (14)
P(4)–Pt(2)–C(4)	91.5 (3)	Pt(1)–P(1)–C(1)	105.9 (4)	C(46)–C(45)–C(44)	124.1 (15)	C(45)–C(44)–C(43)	116.5 (13)
Pt(1)–P(1)–C(11)	118.2 (4)	P(1)–P(1)–C(11)	107.9 (5)	C(44)–C(43)–C(42)	120.1 (14)	C(43)–C(42)–C(41)	123.3 (12)
Pt(1)–P(1)–C(21)	117.0 (4)	C(1)–P(1)–C(21)	103.3 (5)	P(2)–C(41)–C(46)	120.1 (9)	P(2)–C(41)–C(42)	123.0 (9)
C(11)–P(1)–C(21)	103.4 (5)	Pt(1)–P(2)–C(2)	105.7 (4)	C(46)–C(41)–C(42)	116.9 (10)	C(55)–C(56)–C(51)	122.5 (13)
Pt(1)–P(2)–C(31)	119.7 (4)	C(2)–P(2)–C(31)	102.6 (5)	C(56)–C(55)–C(54)	119.2 (11)	C(55)–C(54)–C(53)	120.6 (12)
Pt(1)–P(2)–C(41)	118.4 (4)	C(2)–P(2)–C(41)	105.6 (5)	C(54)–C(53)–C(52)	119.6 (12)	C(53)–C(52)–C(51)	120.5 (11)
C(31)–P(2)–C(41)	103.0 (5)	Pt(2)–P(3)–C(1)	114.9 (3)	P(3)–C(51)–C(56)	119.3 (9)	P(3)–C(51)–C(52)	123.1 (8)
Pt(2)–P(3)–C(51)	116.3 (4)	C(1)–P(3)–C(51)	104.9 (5)	C(56)–C(51)–C(52)	117.5 (11)	C(65)–C(66)–C(61)	121.9 (13)
Pt(2)–P(3)–C(61)	113.7 (4)	C(1)–P(3)–C(61)	102.6 (5)	C(66)–C(65)–C(64)	118.2 (13)	C(65)–C(64)–C(63)	119.8 (13)
C(51)–P(3)–C(61)	102.8 (4)	Pt(2)–P(4)–C(2)	114.5 (4)	C(64)–C(63)–C(62)	120.5 (13)	C(63)–C(62)–C(61)	120.6 (12)
Pt(2)–P(4)–C(71)	116.2 (3)	C(2)–P(4)–C(71)	101.9 (5)	P(3)–C(61)–C(66)	120.0 (9)	P(3)–C(61)–C(62)	121.1 (8)
Pt(2)–P(4)–C(81)	112.7 (4)	C(2)–P(4)–C(81)	105.8 (4)	C(66)–C(61)–C(62)	119.0 (10)	C(75)–C(76)–C(71)	121.0 (11)
C(71)–P(4)–C(81)	104.5 (5)	P(1)–C(1)–P(3)	109.8 (6)	C(76)–C(75)–C(74)	120.6 (13)	C(75)–C(74)–C(73)	120.2 (13)
P(2)–C(2)–P(4)	105.8 (5)	Pt(1)–C(3)–N(3)	175.9 (11)	C(74)–C(73)–C(72)	119.7 (11)	C(73)–C(72)–C(71)	119.6 (11)
Pt(2)–C(4)–N(4)	175.7 (10)	C(15)–C(16)–C(11)	120.6 (15)	P(4)–C(71)–C(76)	121.3 (8)	P(4)–C(71)–C(72)	119.5 (8)
C(16)–C(15)–C(14)	121.7 (16)	C(15)–C(14)–C(13)	118.7 (13)	C(76)–C(71)–C(72)	118.9 (10)	C(85)–C(86)–C(81)	120.5 (11)
C(14)–C(13)–C(12)	121.0 (13)	C(13)–C(12)–C(11)	121.8 (12)	C(86)–C(85)–C(84)	120.2 (12)	C(85)–C(84)–C(83)	121.9 (12)
P(1)–C(11)–C(16)	121.2 (9)	P(1)–C(11)–C(12)	122.7 (9)	C(84)–C(83)–C(82)	118.1 (12)	C(83)–C(82)–C(81)	120.7 (10)
C(16)–C(11)–C(12)	116.1 (10)	C(25)–C(26)–C(21)	120.1 (13)	P(4)–C(81)–C(86)	118.2 (8)	P(4)–C(81)–C(82)	123.3 (8)
C(26)–C(25)–C(24)	121.9 (12)	C(25)–C(24)–C(23)	119.9 (13)	C(86)–C(81)–C(82)	118.5 (10)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Table IV. Bond Lengths (Å) and Angles (deg) for $Pt_2(dppm)_2(CNBH_3)_2$ (**5**)[a]

Pt(1)–P(2)	2.288 (2)	Pt(1)–C	2.015 (10)
Pt(1)–Pt(1a)	2.667 (1)	Pt(1)–P(1a)	2.302 (2)
P(1)–C(16)	1.813 (7)	P(1)–C(26)	1.817 (7)
P(1)–C(1)	1.845 (10)	P(1)–Pt(1a)	2.301 (2)
P(2)–C(36)	1.831 (7)	P(2)–C(46)	1.813 (6)
P(2)–C(1)	1.805 (9)	C–N	1.144 (14)
N–B	1.543 (19)		

P(2)–Pt(1)–C	93.0 (2)	P(2)–Pt(1)–Pt(1a)	85.6 (1)
C–Pt(1)–Pt(1a)	176.5 (2)	P(2)–Pt(1)–P(1a)	174.3 (1)
C–Pt(1)–P(1a)	92.2 (2)	Pt(1a)–Pt(1)–P(1a)	89.1 (1)
C(16)–P(1)–C(26)	103.7 (3)	C(16)–P(1)–C(1)	104.4 (4)
C(26)–P(1)–C(1)	104.4 (4)	C(16)–P(1)–Pt(1a)	114.6 (2)
C(26)–P(1)–Pt(1a)	115.0 (2)	C(1)–P(1)–Pt(1a)	113.5 (3)
Pt(1)–P(2)–C(36)	120.5 (2)	Pt(1)–P(2)–C(46)	116.5 (2)
C(36)–P(2)–C(46)	102.6 (3)	Pt(1)–P(2)–C(1)	106.0 (3)
C(36)–P(2)–C(1)	105.6 (4)	C(46)–P2–C1	104.2 (4)
P(1)–C(16)–C(11)	122.4 (2)	P(1)–C(16)–C(15)	117.5 (2)
P(1)–C(26)–C(21)	121.1 (2)	P(1)–C(26)–C(25)	118.9 (2)
P(2)–C(36)–C(31)	120.2 (2)	P(2)–C(36)–C(35)	119.6 (2)
P(2)–C(46)–C(41)	118.1 (2)	P(2)–C(46)–C(45)	121.8 (2)
P(1)–C(1)–P(2)	108.5 (4)	Pt(1)–C–N	177.1 (7)
C–N–B	177.0 (9)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

and crystallized products contain Pt–CN bonding. Although we did not anticipate this isomerization, mononuclear Pt^{II} complexes of $NCBR_3$ (R = alkyl or aryl) are known to isomerize.[11] Since hydrides are well established for Pt^{I} dimers, we had expected Pt–H or $PtH-BH_2CN$ bond formation. The formation of $[Pt(dppm)(CNBH_2CN)]_2$ from $NaBH_3CN$ does demonstrate that B–H bond rupture occurs in this system.

Synthesis. The products obtained from the reactions of $Cl_2Pt(dppm)$ with $NaBH_3CN$ are found to be dependent on the choice of solvent. Reactions in THF/MeOH (3:1) at room temperature with $NaBH_3CN$ yield $[Pt(dppm)(CNBH_2CN)]_2$ (**3**) as a major product, with a trace of $[Pt(dppm)CN]_2$ (**4**). Reactions in MeOH at room temperature produce only $[Pt(dppm)CN]_2$. The compound $[Pt(dppm)(CNBH_2CN)]_2$ was purified by recrystallization from $CHCl_3/Et_2O$ for elemental analysis and X-ray studies. The compound $[Pt(dppm)(NCBH_3)]_2$ was purified by rapid precipitation from CH_2Cl_2/Et_2O. Recrystallization of $[Pt(dppm)(NCBH_3)]_2$ for X-ray crystal studies was unsuccessful, as during recrystallization linkage isomerization occurred, with the N-coordinated $NCBH_3$ isomer, **1**, becoming the C-coordinated isomer, **5**.

IR Spectra. The $C\equiv N$ stretching frequency in the platinum cyanotrihydroborate dimer $[Pt(dppm)(BH_3CN)]_2$ (**1**) appears at 2205 (s) cm^{-1}. This is 26 cm^{-1} higher than the $C\equiv N$ stretch in uncoordinated BH_3CN^-. The terminal B—H stretch is at 2340

Table V. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Pt(dppm)(CNBH_2CN)]_2 \cdot CHCl_3$ (3)[a]

atom	*x*	*y*	*z*	U_{iso}[b]
Pt(1)	2106 (1)	3241 (1)	1478 (1)	46 (1)*
Pt(2)	1758 (1)	1356 (1)	2479 (1)	50 (1)*
P(1)	2775 (3)	3795 (3)	2408 (2)	55 (1)*
P(2)	3273 (3)	1480 (3)	3004 (2)	56 (1)*
P(3)	1460 (3)	2488 (2)	631 (2)	48 (1)*
P(4)	204 (3)	1258 (3)	1993 (2)	50 (1)*
B(1)	2620 (16)	6634 (15)	−207 (12)	116 (11)*
B(2)	1334 (21)	−2162 (18)	4019 (14)	175 (16)*
C(1a)	2354 (10)	4638 (9)	750 (7)	56 (5)*
N(1b)	4567 (12)	7031 (12)	−831 (9)	167 (9)*
C(2a)	1550 (10)	−111 (10)	3165 (7)	64 (6)*
N(2b)	2965 (18)	−3045 (17)	4663 (10)	190 (12)*
N(1a)	2511 (9)	5484 (8)	321 (6)	83 (5)*
N(2a)	1446 (10)	−963 (8)	3563 (6)	88 (5)*
C(1b)	3753 (12)	6811 (10)	−581 (8)	91 (7)*
C(2b)	2264 (18)	−2698 (15)	4359 (10)	129 (11)*
C(5)	3869 (9)	2800 (9)	2674 (7)	61 (5)*
C(6)	110 (9)	2078 (9)	1016 (6)	52 (5)*
C(7)	6328 (16)	5112 (16)	4040 (11)	130 (11)*
Cl(1)	5478 (6)	5058 (6)	3401 (4)	198 (4)*
Cl(2)	5882 (8)	6145 (6)	4525 (4)	249 (6)*
Cl(3)	7535 (7)	5498 (8)	3565 (4)	233 (6)*
C(11)	4296 (11)	5190 (11)	1590 (8)	80 (7)*
C(12)	4740 (14)	6180 (15)	1328 (10)	110 (9)*
C(13)	4394 (21)	7044 (18)	1591 (15)	157 (15)*
C(14)	3489 (19)	6956 (14)	2103 (13)	129 (13)*
C(15)	2993 (14)	5992 (12)	2380 (9)	100 (8)*
C(16)	3414 (10)	5099 (10)	2126 (7)	63 (4)
C(21)	4202 (11)	−614 (11)	3255 (8)	78 (7)*
C(22)	4943 (16)	−1400 (14)	3091 (11)	107 (10)*
C(23)	5708 (17)	−1207 (20)	2510 (14)	126 (13)*
C(24)	5794 (14)	−177 (17)	2113 (11)	111 (10)*
C(25)	5077 (11)	652 (13)	2241 (8)	83 (7)*
C(26)	4290 (9)	472 (9)	2824 (7)	57 (3)
C(31)	2272 (14)	4044 (11)	3878 (8)	100 (8)*
C(32)	1592 (19)	4089 (15)	4501 (11)	127 (11)*
C(33)	541 (20)	3953 (15)	4548 (11)	129 (12)*
C(34)	161 (15)	3802 (13)	3920 (12)	112 (10)*
C(35)	817 (11)	3742 (10)	3274 (9)	76 (7)*
C(36)	1904 (10)	3856 (9)	3249 (7)	60 (4)
C(41)	2127 (12)	1217 (10)	4440 (8)	82 (7)*
C(42)	2014 (15)	1105 (14)	5225 (10)	101 (9)*
C(43)	2920 (20)	1065 (15)	5554 (10)	115 (10)*
C(44)	3903 (17)	1078 (14)	5165 (12)	111 (10)*
C(45)	4022 (12)	1211 (12)	4404 (9)	93 (8)*
C(46)	3121 (10)	1266 (9)	4031 (7)	58 (3)
C(51)	2238 (10)	3547 (12)	−820 (8)	84 (7)*
C(52)	2239 (12)	4292 (12)	−1503 (8)	99 (8)*
C(53)	1302 (12)	4873 (11)	−1681 (8)	78 (7)*
C(54)	414 (14)	4725 (10)	−1199 (7)	77 (7)*
C(55)	423 (11)	3969 (9)	−497 (7)	64 (6)*
C(56)	1354 (9)	3376 (9)	−316 (6)	51 (3)
C(61)	−1883 (11)	2129 (10)	2247 (8)	77 (6)*
C(62)	−2753 (13)	2422 (12)	2715 (11)	98 (8)*
C(63)	−2749 (14)	2250 (14)	3480 (12)	104 (10)*
C(64)	−1874 (16)	1805 (15)	3770 (10)	119 (10)*
C(65)	−966 (12)	1548 (11)	3330 (7)	80 (7)*
C(66)	−959 (9)	1698 (9)	2552 (6)	49 (3)
C(71)	1853 (11)	731 (10)	−38 (7)	73 (6)*
C(72)	2392 (14)	−205 (12)	−176 (9)	92 (8)*
C(73)	3317 (14)	−538 (12)	126 (9)	98 (8)*
C(74)	3704 (11)	39 (12)	563 (8)	90 (8)*
C(75)	3144 (10)	952 (10)	711 (8)	70 (6)*
C(76)	2199 (10)	1313 (10)	426 (7)	61 (4)
C(81)	−1020 (11)	−571 (13)	2207 (9)	96 (8)*
C(82)	−1135 (15)	−1632 (15)	2172 (12)	134 (12)*
C(83)	−388 (16)	−2229 (14)	1929 (11)	115 (11)*
C(84)	581 (16)	−1841 (12)	1685 (10)	101 (9)*
C(85)	747 (12)	−769 (11)	1691 (7)	80 (7)*
C(86)	−50 (10)	−107 (9)	1963 (6)	51 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic *U* is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table VI. Atomic Coordinates (×10^4) and isotropic Thermal Parameters (Å^2 × 10^3) for $Pt_2(dppm)_2(CN)_2$ (4)[a]

atom	*x*	*y*	*z*	U_{iso}[b]
C(1a)	6087 (17)	9857 (17)	432 (13)	171 (6)
C(2a)	5255 (23)	9611 (15)	518 (11)	171 (6)
C(3a)	4308 (19)	9697 (16)	191 (14)	171 (6)
Pt(1)	4061 (1)	721 (1)	3306 (1)	30 (1)*
Pt(2)	2097 (1)	605 (1)	2633 (1)	30 (1)*
P(1)	4469 (2)	167 (2)	2440 (1)	35 (1)*
P(2)	3428 (2)	1339 (2)	4052 (1)	32 (1)*
P(3)	2511 (2)	875 (2)	1699 (1)	34 (1)*
P(4)	1725 (2)	238 (2)	3572 (1)	32 (1)*
C(1)	3849 (7)	793 (6)	1753 (5)	32 (4)*
C(2)	2652 (7)	566 (6)	4308 (5)	38 (4)*
C(3)	5504 (9)	781 (6)	3885 (6)	40 (5)*
C(4)	603 (7)	544 (6)	2123 (4)	33 (4)*
N(3)	6288 (7)	784 (7)	4230 (5)	64 (5)*
N(4)	−196 (7)	539 (6)	1817 (4)	54 (4)*
C(16)	4576 (10)	−1334 (8)	1834 (7)	83 (7)*
C(15)	4321 (12)	−2124 (8)	1692 (8)	106 (9)*
C(14)	3580 (11)	−2496 (9)	1899 (7)	80 (7)*
C(13)	3143 (10)	−2084 (8)	2284 (6)	64 (6)*
C(12)	3410 (8)	−1289 (7)	2457 (5)	44 (5)*
C(11)	4122 (8)	−885 (6)	2235 (5)	41 (4)*
C(26)	6487 (9)	−210 (8)	2883 (5)	57 (5)*
C(25)	7491 (9)	−174 (10)	2886 (7)	87 (7)*
C(24)	7807 (10)	298 (9)	2477 (6)	79 (7)*
C(23)	7140 (8)	728 (8)	2029 (7)	71 (6)*
C(22)	6129 (9)	708 (8)	2029 (7)	66 (6)*
C(21)	5794 (8)	206 (7)	2441 (5)	41 (5)*
C(36)	4571 (9)	2472 (7)	4904 (6)	58 (5)*
C(35)	5243 (10)	2733 (8)	5480 (6)	70 (6)*
C(34)	5595 (9)	2197 (7)	5967 (6)	58 (5)*
C(33)	5297 (9)	1405 (8)	5872 (5)	54 (5)*
C(32)	4665 (8)	1135 (7)	5315 (5)	44 (5)*
C(31)	4280 (8)	1669 (6)	4818 (5)	36 (4)*
C(46)	2477 (10)	2555 (7)	3187 (6)	59 (6)*
C(45)	1860 (13)	3202 (8)	3011 (8)	94 (8)*
C(44)	1338 (12)	3555 (8)	3397 (8)	96 (8)*
C(43)	1474 (9)	3219 (8)	4003 (6)	71 (6)*
C(42)	2110 (8)	2571 (7)	4191 (6)	52 (5)*
C(41)	2610 (8)	2214 (6)	3805 (5)	38 (4)*
C(56)	1141 (9)	2080 (8)	1131 (7)	74 (6)*
C(55)	802 (9)	2786 (8)	812 (7)	80 (7)*
C(54)	1478 (9)	3336 (7)	719 (6)	61 (6)*
C(53)	2485 (9)	3173 (7)	914 (6)	62 (6)*
C(52)	2816 (9)	2451 (7)	1224 (6)	55 (5)*
C(51)	2133 (8)	1885 (7)	1331 (5)	38 (4)*
C(66)	1888 (11)	366 (8)	417 (6)	80 (7)*
C(65)	1469 (14)	−152 (9)	−98 (7)	100 (9)*
C(64)	1112 (11)	−895 (9)	35 (7)	82 (7)*
C(63)	1152 (10)	−1095 (8)	654 (7)	71 (7)*
C(62)	1548 (8)	−562 (7)	1148 (5)	51 (5)*
C(61)	1931 (8)	164 (6)	1031 (5)	37 (4)*
C(76)	74 (8)	288 (8)	4105 (5)	48 (5)*
C(75)	−752 (9)	643 (8)	4240 (5)	63 (5)*
C(74)	−1092 (9)	1378 (8)	3989 (6)	63 (6)*
C(73)	−645 (9)	1763 (7)	3571 (6)	55 (5)*
C(72)	183 (8)	1394 (6)	3413 (5)	42 (4)*
C(71)	546 (7)	653 (7)	3691 (5)	36 (4)*
C(86)	1038 (9)	−1300 (7)	3120 (5)	57 (5)*
C(85)	943 (12)	−2136 (9)	3148 (7)	79 (7)*
C(84)	1412 (11)	−2540 (8)	3682 (8)	72 (8)*
C(83)	1964 (9)	−2143 (8)	4233 (8)	68 (7)*
C(82)	2071 (8)	−1301 (7)	4206 (5)	43 (5)*
C(81)	1608 (7)	−871 (6)	3649 (5)	37 (4)*

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic *U* is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

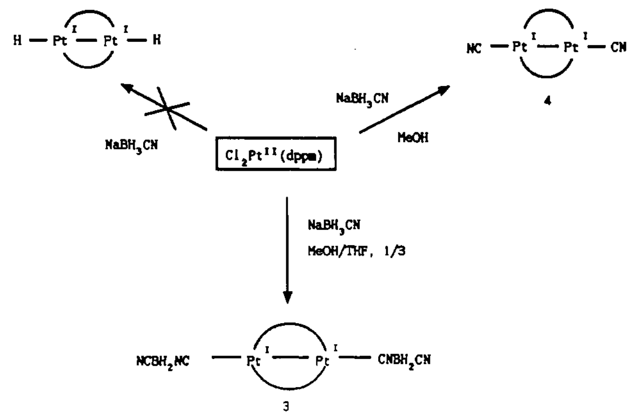
(br) cm^{-1}. When BH_3CN^- coordinates via nitrogen (monodentate), or both nitrogen and hydrogen (bridging mode), the C≡N and B—H stretching modes usually occur at higher frequencies than in the free[4,7,8] BH_3CN^-. Infrared spectra of such complexes generally show[4,7] an increase in ν_{CN} of up to 30 cm^{-1} above 2179 cm^{-1}. This has been attributed to rehybridization about the N atom and an increase in the C≡N stretching force constant. X-ray studies[7] have identified both linear and nonlinear M—N≡C bonding. Essentially, an sp orbital (shorter C≡N bond) on the

Table VII. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Pt$_2$(dppm)$_2$(CNBH$_3$)$_2$ (**5**)[a]

atom	*x*	*y*	*z*	U_{iso}[b]
Pt(1)	5616 (1)	834 (1)	2153 (1)	25 (1)*
P(1)	3403 (2)	318 (1)	1898 (1)	28 (1)*
P(2)	4534 (2)	1302 (1)	1256 (1)	27 (1)*
C(11)	1942 (4)	1300 (4)	1344 (3)	49 (4)*
C(12)	1066 (4)	1527 (4)	1252 (3)	80 (6)*
C(13)	529 (4)	1117 (4)	1589 (3)	86 (7)*
C(14)	867 (4)	481 (4)	2017 (3)	90 (7)*
C(15)	1743 (4)	254 (4)	2109 (3)	64 (5)*
C(16)	2281 (4)	664 (4)	1772 (3)	36 (3)*
C(21)	2728 (4)	−1149 (4)	1347 (3)	51 (4)*
C(22)	2685 (4)	−1976 (4)	1341 (3)	66 (5)*
C(23)	3213 (4)	−2411 (4)	1878 (3)	67 (5)*
C(24)	3785 (4)	−2019 (4)	2421 (3)	73 (6)*
C(25)	3829 (4)	−1192 (4)	2427 (3)	51 (4)*
C(26)	3300 (4)	−757 (4)	1890 (3)	34 (3)*
C(31)	3906 (5)	2504 (4)	1967 (2)	50 (4)*
C(32)	3418 (5)	3185 (4)	2014 (2)	64 (5)*
C(33)	3002 (5)	3601 (4)	1424 (2)	77 (6)*
C(34)	3074 (5)	3337 (4)	786 (2)	82 (6)*
C(35)	3562 (5)	2657 (4)	739 (2)	54 (4)*
C(36)	3978 (5)	2241 (4)	1330 (2)	35 (3)*
C(41)	5434 (4)	1995 (3)	399 (3)	45 (4)*
C(42)	5685 (4)	2092 (3)	−211 (3)	46 (4)*
C(43)	5322 (4)	1607 (3)	−771 (3)	48 (4)*
C(44)	4708 (4)	1026 (3)	−722 (3)	51 (4)*
C(45)	4458 (4)	929 (3)	−113 (3)	43 (4)*
C(46)	4820 (4)	1414 (3)	447 (3)	32 (3)*
C(1)	3682 (6)	556 (5)	1088 (4)	32 (3)*
C	6507 (6)	780 (5)	1593 (4)	32 (3)*
N	6985 (5)	735 (5)	1253 (4)	37 (3)*
B	7614 (10)	718 (8)	778 (7)	61 (6)*
O	5334 (7)	4321 (5)	343 (5)	100 (4)*

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic *U* is defined as one-third of the trace of the U_{ij} tensor.

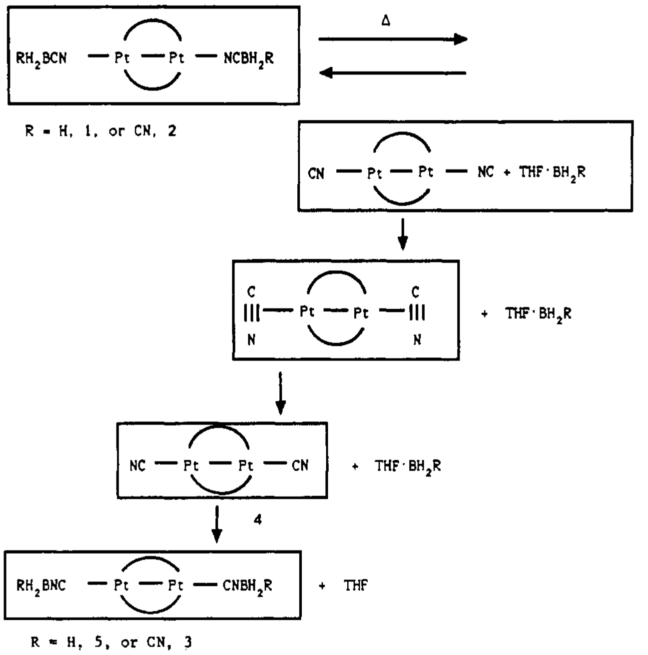
Scheme I. Reactions between Cl$_2$Pt(dppm) and NaBH$_3$CN



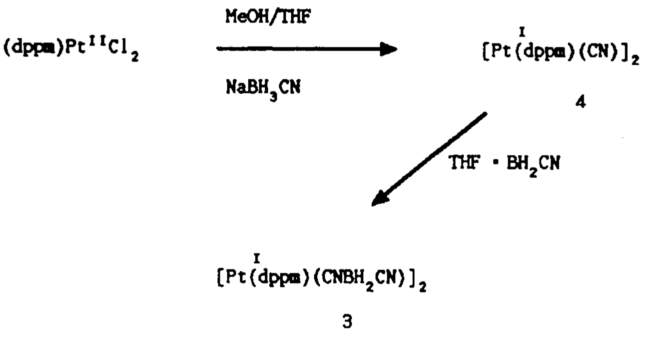
N is involved in the linear case, while some sp^2 character (longer C≡N bond) is involved in the nonlinear structure. Two different BH$_3$CN groups were observed in the structures[4,7] of [(Ph$_3$P)$_2$Cu(NCBH$_3$)]$_2$ and (Me$_5$dien)Cu(NCBH$_3$)$_2$. The ν_{CN} with the larger shift (31 cm^{-1}) from free BH$_3$CN$^-$ is assigned to the more weakly bound BH$_3$CN$^-$ (shorter C≡N bond), which contains a linear Cu—N—C unit. The ν_{CN} with the smallest shift (13 cm^{-1}) was assigned to the more strongly bound BH$_3$CN$^-$ group (shorter Cu—N bond and longer C≡N). In [Pt(dppm)(BH$_3$CN)]$_2$ (**1**), the ν_{CN} suggests a linear coordination of BH$_3$CN, as observed in the Cu complex. Unfortunately, this platinum complex did not give crystals suitable for X-ray crystallography.

The IR spectrum of the complex [Pt(dppm)(BH$_2$(CN)$_2$]$_2$ (**2**) contains two strong absorptions in the C≡N stretching region. The band at 2270 cm^{-1} is assigned to the terminal C≡N stretch, and the other at 2210 cm^{-1} is assigned to the coordinated C≡N, bonded through the N atom of BH$_2$(CN)$_2$ to the Pt center. This result is in good agreement with the result observed in the copper dicyanoborate complexes[13] but contrasts with the bonding observed for **3**.

Scheme II



Scheme III



$$\mathrm{MeOH + NaBH_3CN + THF = NaOMe + THF{\cdot}BH_2CN + H_2}$$

The IR spectrum of the complex [Pt(dppm)(CNBH$_2$CN)]$_2$ (**3**) shows strong peaks at 2240 and 2185 cm^{-1}, assigned to the terminal and bridging C≡N groups, respectively. These two stretching frequencies are lower than found in complex **2** (C≡N group coordinated to Pt through N atom). This result clearly indicates that the BH$_2$(CN)$_2^-$ groups in **3** have a different coordination mode to the Pt centers than present in **2**. In compound **3**, the BH$_2$(CN)$_2^-$ groups coordinate to the Pt centers via C atoms (vide infra). The reduced stretching frequencies in **3** are due to weaker C≡N and stronger Pt—C bonds. The strengthening of the Pt—C bond in **3** arises from the considerable dπ back-donation to the CN π^* orbital. The stronger Pt—C bond and kinematic effects lead to a lowering of the stretching frequencies of the ν_{CN} in compound **3**. This result is consistent with the X-ray crystallographic results for **3**, in which the Pt—C bond length is 1.963 (10) Å, somewhat shorter[19] than normal. The B—H (terminal) stretch appears between 2340 and 2360 cm^{-1}.

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(19) (a) Badley, E. M.; Chatt, J.; Richards, R. L.; Sim, G. A. *J. Chem. Soc. D* **1969**, 1322. (b) Butler, W. M.; Enemark, J. H.; Parks, J.; Balch, A. L. *Inorg. Chem.* **1973**, *12*, 451. (c) Cardin, D. J.; Centinkaya, B.; Lappart, M. F.; Manojlovic-Muir, Lj.; Muir, K. W. *J. Chem. Soc. D* **1971**, 400.

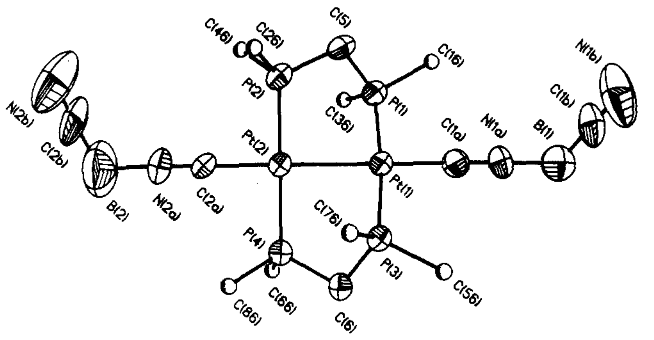

Figure 1. Structure of $[Pt(dppm)(CNBH_2CN)]_2$ (**3**). Phenyl rings are omitted for clarity.

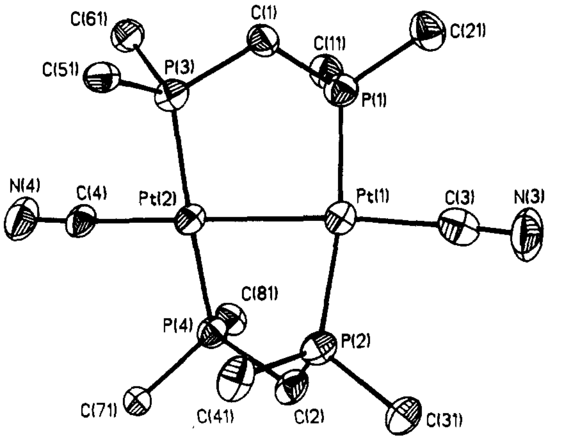

Figure 2. Structure of $[Pt(dppm)(CN)]_2$ (**4**). Phenyl rings are omitted for clarity.

The IR spectrum of $[Pt(dppm)(CN)]_2$ (**4**) contains a single ν_{CN} peak at 2125 cm^{-1}, in good agreement with the C≡N stretching frequency in[20] $(Ph_3P)_2Pt(CN)_2$. The ν_{CN} stretching frequency in $[Pt(dppm)(CNBH_3)]_2$ (**5**) occurs at 2195 cm^{-1}. This is 10–15 cm^{-1} lower than the bridging C≡N stretch in $[Pt(dppm)(NCBH_2CN)]_2$ (**2**) and $[Pt(dppm)(NCBH_3)]_2$ (**1**).

^1H and ^{31}P NMR Spectra. ^1H NMR spectra for compounds **1**, **3**, and **4** show a triplet at around 4.0–4.5 ppm for the methylene protons of the dppm ligand with a coupling constant ($J_{P-H} \approx 10$ Hz) that is normal for dimeric complexes containing dppm as a bridging ligand.[11] The ^{31}P NMR spectra show a sharp singlet for compounds **1**, **3**, **4**, and **5** with chemical shifts 27.5, 24.30, −1.76, and 12.82 ppm, respectively, indicating equivalent phosphorus atoms in these complexes in solution.

Isomerization Reactions of *trans*-$[Pt(dppm)(NCBH_3)]_2$ and *trans*-$[Pt(dppm)(NCBH_2CN)]_2$. Complex **1** isomerizes during the recrystallization from $CHCl_3/Et_2O$ at room temperature in 7 days. Complex **2** also isomerizes thermally in THF. Manzer et al. studied[12] the isomerization in mononuclear platinum complexes of R_3BCN (R = alkyl or aryl) and suggested that it probably occurred by the thermal dissociation of BR_3 to give an unstable "isocyano" product which then flips to give the thermodynamically stable cyanide complex. Isomerization reactions for **1** and **2** are summarized in Scheme II.

The formation of an intermediate containing the Pt–CN linkage is an essential requirement for the observed isomerizations. This intermediate has been synthesized separately as complex **4**. It was also obtained as a minor product in the $NCBH_3$ reactions and identified in the IR spectrum of the crude product of **3**. The bonding of the solvated BH_2R (already present in the system as $THF{\cdot}BH_2R$) to the intermediate (cyanide complex) leads to the final product **3** or **5**. Confirmation was obtained by the addition of the Lewis acid $THF{\cdot}BH_3$ in THF at room temperature to $[Pt(dppm)(CN)]_2$ (**4**), which produces **3**.

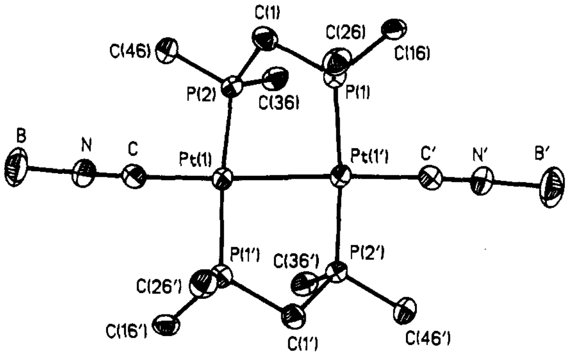

Figure 3. Structure of $[Pt(dppm)(CNBH_3)]_2$ (**5**). Phenyl rings are omitted for clarity.

Formation of $[Pt(dppm)(CNBH_2CN)]_2$ from $Cl_2Pt(dppm)$ and $NaBH_3CN$. As indicated above, $[Pt(dppm)(CNBH_2CN)]_2$ is the major product obtained when $Pt(dppm)Cl_2$ is reacted with $NaBH_3CN$ in MeOH/THF. A plausible mechanism for this reaction is presented in Scheme III. Since $NaBH_3CN$ is a mild reducing agent as well as a CN^- donor, formation of $[Pt(dppm)(CN)]_2$ is expected from the reduction. The observation that formation of $[Pt(dppm)(CN)]_2$ requires the presence of MeOH is supported by the formation of **4** from a similar reaction in MeOH. The presence of THF is important to stabilize BH_2CN as $THF{\cdot}BH_2CN$ and to give the final product $[Pt(dppm)(CNBH_2CN)]_2$. The formation of $THF{\cdot}BH_2CN$ may also require MeOH, although B–H bond rupture occurs in the reduction of Pt^{II}.

Structures of 3–5. The molecular structures of **3**–**5** are shown in Figures 1–3. Bond distances and angles are presented in Tables I–III. The molecules of **3**–**5** each contain two Pt–X (X = $CNBH_2CN$, CN, $CNBH_3$) fragments linked to each other through a metal–metal bond and bridged by two dppm ligands. Compound **5** contains an inversion center.

The Pt(1)–Pt(2) bond distances of **3**–**5** are 2.665 (1), 2.704 (1), and 2.667 (1) Å, respectively, and are somewhat longer than the Pt(1)–Pt(2) distance [2.651 (1) Å] in the $[Pt(dppm)Cl]_2$ analogue.[21] The Pt–C bond lengths 1.99 (1) and 1.96 (1) Å in **3**, 2.054 (9) and 2.039 (11) Å in **4**, and 2.015 (10) Å in **5** are within the range 1.95–2.06 Å found for other Pt–C distances.[19] The average C–N distance in **3** (bridging), 1.17 (1) Å, is longer than the distance for the terminal C≡N, 1.11 (1) Å, indicating a decrease in the C≡N bond order as noted above in the discussions of the IR spectra. The average B–C distance, 1.48 (3) Å, in **3** is somewhat shorter than that in $(Me_5dien)Cu(NCBH_3)_2$[7] and $[(Ph_3P)_3Co(H)(BH_3CN)]$,[9] in which BH_3CN^- coordinates to the metal through the N atom, and $[(tren)Ni(BH_3CN)]_2(BPh_4)_2$.[8] In this last compound, BH_3CN^- is a bridging ligand coordinated to the metal centers via N and H atoms.

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Registry No. **1**, 123676-62-0; **2**, 123676-63-1; **3**, 123676-65-3; **4**, 123676-67-5; **5**, 123676-68-6; $[Pt(dppm)Cl]_2$, 61250-65-5; $Cl_2Pt(dppm)$, 52595-94-5; $THF{\cdot}BH_3$, 14044-65-6; CN, 57-12-5; Pt, 7440-06-4.

Supplementary Material Available: For compounds **3**–**5**, tables containing anisotropic thermal parameters, hydrogen atom coordinates, and data collection parameters (11 pages); tables of calculated and observed structure factors (100 pages). Ordering information is given on any current masthead page.

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