Rc–H distances, which vary relatively little within each structure, are reasonable for M–H distances determined by X-ray crystallography.[8] Since the shortest H···H distance is 1.4 Å (H-(1)–H(2) in Figure 1) and this is much longer than the value observed for η^2-H_2 complexes (ca. 0.9 Å),[16] it is clear that the present structural results signify that both **2** and **3** are "classical" hydrides.

Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Tables S1 and S2), positional parameters for all atoms except the hydrogen atoms of the phenyl groups (Tables S3 and S4), positional parameters for the hydrogen atoms of the phenyl groups (Tables S5 and S6), anisotropic thermal parameters (Tables S7 and S8), and complete bond distances (Tables S9 and S10) and bond angles (Tables S11 and S12) for **2** and **3** and a figure (Figure S1) showing the structure and full atomic numbering scheme for **3** (37 pages); tables of observed and calculated structure factors (85 pages). Ordering information is given on any current masthead page.

Figure 1. Structures of red and green [Rh2(μ-Cl)2(CNC8H9)4(μ-AuPPh3)]2(PF6)2.

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Pressure-Induced Isomerization of a Heterometallic Rhodium–Gold Cluster Compound: [Rh2(μ-Cl)2(CNC8H9)4(μ-AuPPh3)]2(PF6)2

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Introduction

Solid-state structural isomerization occurs when two or more configurations of a molecule or ion are of comparable stability. The existence of structural isomers reflects a delicate balance of competing intermolecular forces, and consequently the relative stability of different isomers is sensitive to minor chemical modifications (e.g. changing lattice counterions or substituent groups on ligands) and to changes in external physical parameters. High pressure is an effective tool for inducing transformations between structural isomers because high pressure is capable of altering intermolecular interactions and consequently the relative stabilities of isomers. Ferraro et al.[2,3] and Willett et al.[4] have examined the effect of pressure on five-coordinate Ni(II) and Co(II) complexes. More recently, Bray and Drickamer[5-7] have
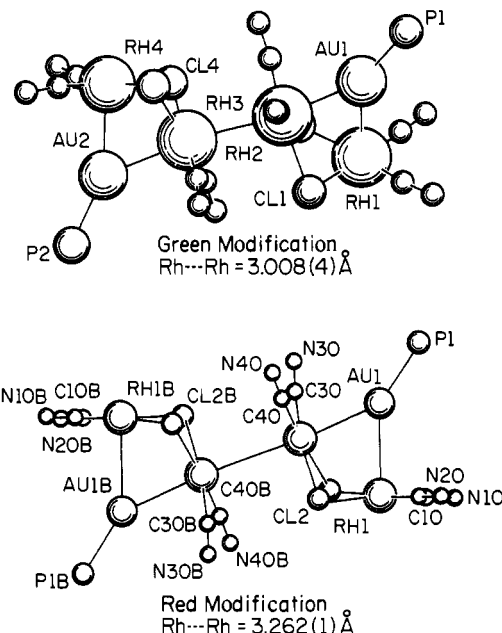
discussed pressure-induced isomerizations in several series of mononuclear Cu(II) complexes.

Structural isomerization in organometallic solids has been observed in systems ranging from mononuclear complexes to large clusters. In high-nuclearity clusters, isomers differ with respect to the skeletal arrangement of metal atoms. Mingos, for instance, has discussed isomers of the clusters $[Au_9(PR_3)_8]^{3+}$.[8,9] Two structural arrangements of the gold cluster framework were observed. When R = C_6H_5 or p-$C_6H_4CH_3$ and the anion is PF_6^-, the cluster is green and the arrangement of gold atoms may be viewed as a D_{2h} fragment of an icosahedron. A brown, D_{4d}-centered crown structure is observed when R = p-$C_6H_4OCH_3$ and the anion is BF_4^-. Coffer et al.[10] have recently discussed the first example of a pressure-induced structural transformation in a high-nuclearity metal cluster. Coffer et al.[10] demonstrated the ability of high pressure to convert the green D_{2h} form of [Au9-(PPh3)8](PF6)3 to the brown D_{4d} form.

In this work, we report the effect of pressure on [Rh2(μ-Cl)2(CNC8H9)4(μ-AuPPh3)]2(PF6)2. Mingos et al. have prepared two isomers of this cluster and a characterized them using single-crystal X-ray techniques.[11] Both isomers have very similar volumes per cluster cation, viz. 1410 Å^3 (red isomer) and 1413 Å^3 (green isomer). The clusters are derived from [Rh2(μ-Cl)2-(μ-AuPPh3)(CNC8H9)4]$^+$, fragments which are dimerized through a weak Rh–Rh bond (Figure 1). In the red isomer, the two cluster fragments adopt a trans, eclipsed conformation about the central Rh(2)–Rh(3) bond. A gauche, staggered conformation is observed in the green isomer. Pressure-dependent optical spectroscopy indicates that the two isomers become geometrically similar at high pressures.

Experimental Section

Synthesis of [Rh2(μ-Cl)2(CNC8H9)4(μ-AuPPh3)]2(PF6)2. Addition of excess TlPF6 to a stirred solution of Au(PPh3)Cl and Rh(CNC8H9)3Cl in THF yielded a dark green solution after 30 min. Removal of Tl(I) salts and subsequent addition of Et2O gave [Rh2(μ-Cl)2(CNC8H9)4(μ-

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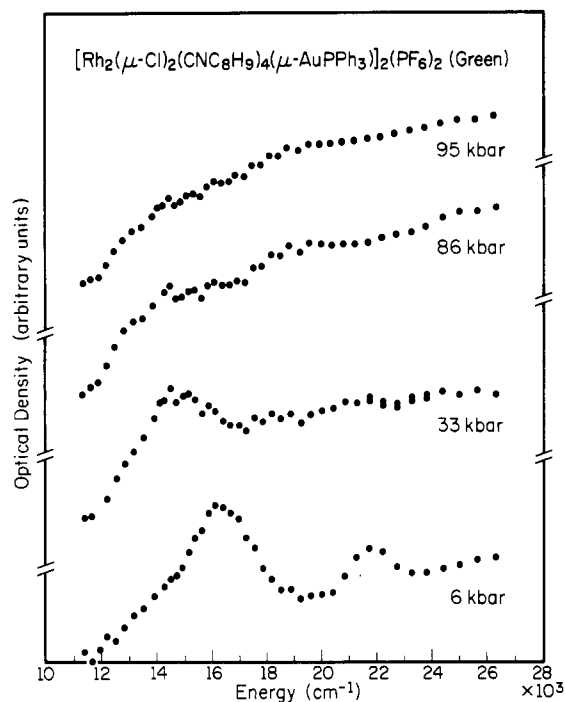
Figure 2. Electronic spectrum of green $[Rh_2(\mu\text{-Cl})_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)]_2(PF_6)_2$ as a function of pressure.

$AuPPH_3)]_2(PF_6)_2$ as a green powder in 35% yield. Conversion to the red isomer was achieved by washing the sample with THF. Both isomers gave similar elemental analyses and identical $^{31}P\{^1H\}$ and ^1H solution NMR spectra.

Crystal Data for the Green Isomer: M_r = 2811.30, $P\bar{1}$, a = 15.873 (3) Å, b = 18.250 (3) Å, c = 20.752 (2) Å, α = 74.21 (2)°, β = 89.57 (2)°, γ = 77.99 (1)°, V = 5650.1 Å^3, Z = 4, D_c = 1.65 g cm^{-3}, $F(000)$ = 2760.

Crystal Data for the Red Isomer: M_r = 2811.30, $P\bar{1}$, a = 11.852 (2) Å, b = 15.355 (3) Å, c = 15.542 (2) Å, α = 87.66 (1)°, β = 89.16 (1)°, γ = 86.22 (1)°, V = 2819.8 Å^3, Z = 2, D_c = 1.66 g cm^{-3}, $F(000)$ = 1380.

Samples of each isomer were studied at high pressure with the use of diamond anvil cells.[12] Mineral oil was used as a pressure-transmitting medium, and the pressure was measured with the ruby fluorescence method.[12] Optical spectra were obtained as previously described.[5-7] Pressure data were collected on two separate runs for each isomer, and all pressure effects were reproducible.

Results

The solid-state spectra of the green and red isomers of $[Rh_2(\mu\text{-Cl})_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)]_2(PF_6)_2$ as a function of pressure are shown in Figures 2 and 3. Two distinct maxima ($\nu_1 \sim$ 16 300 cm^{-1} and $\nu_2 \sim$ 22 000 cm^{-1}) are found in the spectrum (Figure 2) of the green isomer at ambient pressure in the solid. These spectral characteristics are very similar to those observed when either isomer is studied in solution ($\nu_1 \sim$ 16 700 cm^{-1} and $\nu_2 \sim$ 21 700 cm^{-1}). ν_1 shifts to lower energy and broadens with increasing pressure; ν_2 also broadens. At high pressure, the spectrum is featureless and shows a monotonic increase in intensity with frequency. The appearance of the spectrum changes continuously as the pressure is raised.

The spectrum of the red isomer (Figure 3) possesses a single maximum at $\sim$18 000 cm^{-1}. The band shifts to lower energy and broadens with increasing pressure. At high pressure, the band is no longer well-resolved and a broad, featureless spectrum is observed. Significant changes in the spectrum are observed above 76 kbar. The spectra of the red and green isomers at high pressure are very similar in appearance.

Discussion

The central dirhodium unit in these compounds can be viewed as two weakly interacting square-planar Rh(I) (d^8) centers, albeit perturbed by the axial $[AuPPh_3]^+$ cations. Gray and co-workers[13]
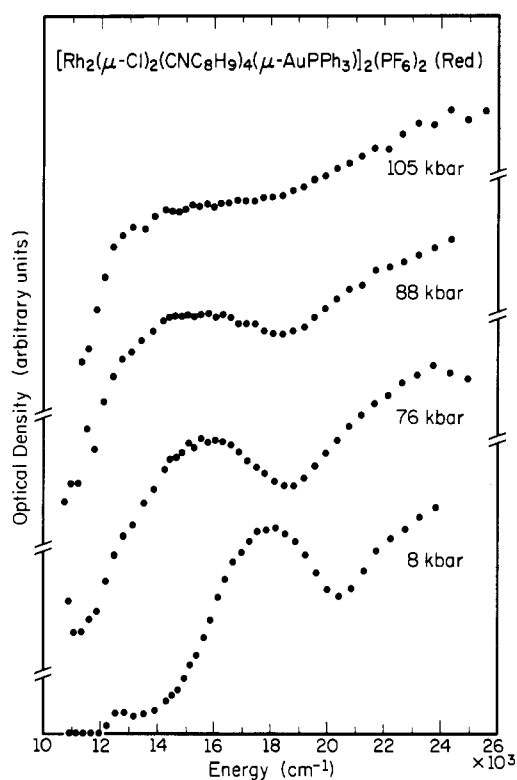
Figure 3. Electronic spectrum of red $[Rh_2(\mu\text{-Cl})_2(CNC_8H_9)_4(\mu\text{-}AuPPh_3)]_2(PF_6)_2$ as a function of pressure.

have demonstrated that simple d^8–d^8 dimers such as $[Rh(CNR)_4]_2^{2+}$ and related systems display Rh⋯Rh distances near 3.2 Å as well as characteristic, strong visible absorption bands near 18 000 cm^{-1} that are assigned as antibonding to bonding $d\sigma^* \rightarrow p\sigma$ transitions. If such a model can be applied to the present compounds, it would be consistent with two aspects of our results, namely (1) that the absorption band energy is *lower* for the isomer (green) with the *shorter* Rh⋯Rh distance and (2) that the bands for both isomers undergo initial *red* shifts with applied pressure.

The similarity of the spectra of the isomers at high pressure suggests that the two isomers have similar structures at high pressure. Pressure has induced a structural transformation in one or both of the isomers. Three possibilities merit consideration: pressure induces either a red → green isomerization, a green → red isomerization, or isomerizations of both isomers to an identical new structure. The behavior of the isomers upon release of pressure provides an indication of which possibility is most likely.

The change in the spectrum of the green isomer is completely reversed upon release, an indication that the green isomer returns to its original state. The effect of pressure on the red isomer is not completely reversible. The release spectrum of the red isomer resembles its spectrum at intermediate pressures. Visual inspection of the release form of the red isomer reveals a mixture of red material and green material, so that the release spectrum represents a superposition of red and green spectra. Partial reversibility of the red isomer suggests that a red → green transformation occurs at high pressure followed by incomplete back-conversion upon release. The similarity of the spectra of the red and green isomers at high pressure (Figures 2 and 3) is an indication that a large fraction of the red isomer is transformed. Complete conversion seems unlikely because the release spectra of the red and green isomers are different.

Complete reversibility of the green isomer and incomplete reversibility of the red isomer rule out the possibility of a green → red transformation at high pressure. Partial conversion of both

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isomers to an identical new configuration remains possible but seems less likely than the red → green transformation proposed above because of the need to postulate the existence of a third isomer for the cluster. This interpretation also fits with chemical intuition, since the green isomer, which has a staggered geometry, is expected to be the more stable under high-pressure conditions. However a structure intermediate between the eclipsed and staggered forms might be stable at high pressure, but we have no specific evidence for this.

These results differ in an interesting fashion from those reported earlier for the gold clusters $[Au_9(PR_3)_8]^{3+}$,[10] where the application of pressure induced rearrangement of the entire cluster skeleton. In this example, the cluster skeletal geometries in the two modifications differ only at an interior link, and applied pressure appears to be inducing a conformational transformation around this bond.

Tin(II) Poly(1-pyrazolyl)borates

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Ever since their first preparation,[1] poly(1-pyrazolyl)borates, $M[(pz)_{4-n}BR_n]$ (M = alkali metal, Hpz = pyrazole or C-substituted derivative thereof, R = noncoordinating substituent, n = 0–2), have found extensive use as chelating ligands in transition-metal chemistry.[2] However, studies of the poly(1-pyrazolyl)borate chemistry of main-group elements have been rather limited. Only most recently have some characterized poly(1-pyrazolyl)borates of main-group (other than alkali and alkaline earth) metals become available. The data include four (somewhat contradictory) reports on tin(IV)[3–6] and one on tin(II) derivatives;[7] silicon or germanium poly(1-pyrazolyl)borates have not yet been reported.

In an extension of recent studies on the interaction of boron compounds with poly(1-pyrazolyl)borates, the synthesis and characterization of other main-group element derivatives of the latter is currently being investigated. The present report describes a study of a series of Sn(II) poly(1-pyrazolyl)borates.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in CDCl₃ (unless otherwise noted) on a Varian VXR-400 (¹¹B, ¹¹⁹Sn, variable-temperature, high-resolution) or GEMINI-200 (¹H, ¹³C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal (CH₃)₄Si for ¹H and ¹³C NMR, external (C₂H₅)₂O·BF₃ for ¹¹B NMR, external (CH₃)₄Sn for ¹¹⁹Sn NMR); s = singlet,

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d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants *J* are given in hertz. ¹³C NMR spectra were recorded in the proton-decoupled mode.

All nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received.

Na[(C₆H₅)₂B(pz)₂] (Hpz = pyrazole) was prepared by the previously described reaction of Na[B(C₆H₅)₄] with Hpz.[8] After extensive purification, ultimately by subliming off traces of adhering Hpz, the pure compound has a mp 284–287 °C. NMR data: δ(¹H) 7.52 (1 H, d, *J* = 2.2), 7.41 (1 H, d, *J* = 1.7), 7.2 (3 H, m), 6.95 (2 H, m), 6.20 (1 H, unsym t = two overlapping d); δ(¹¹B) 1.3 (s, $h_{1/2}$ = 325 Hz).

[B(pz)₄]₂Sn (1). A mixture of 0.94 g (5 mmol) of SnCl₂, 3.15 g (10 mmol) of K[B(pz)₄],[1] and 50 mL of methylene chloride was stirred at room temperature for 5 h. The mixture was filtered, and solvent was evaporated from the clear filtrate under reduced pressure to leave 3.2 g (94%) of crude product. It was recrystallized from toluene to give a material of mp 208–210 °C. Anal. Calcd for $C_{24}H_{24}B_2N_{16}Sn$ (M_r = 676.5): C, 42.57; H, 3.58; B, 3.20; N, 33.11; Sn, 17.54. Found: C, 43.15; H, 3.50; B, 3.20; N, 33.37; Sn, 17.55.

NMR data: δ(¹H) 7.63 (1 H, unresolved d), 7.26 (1 H, d, *J* = 2.4), 6.32 (1 H, unsym t = two overlapping d, *J* = ca. 1.9); δ(¹¹B) 0.4 (s, $h_{1/2}$ = 16 Hz); δ(¹³C) 142.2, 135.9, 106.5; δ(¹¹⁹Sn) −744 (s, $h_{1/2}$ = 50 Hz); (solution in CD₂Cl₂) δ(¹H) 7.62 (1 H, d, *J* = 1.3), 7.27 (1 H, d, *J* = 2.1), 6.32 (1 H, unsym t = two overlapping d, *J* = ca. 2.1); (at −85 °C) δ(¹H) 7.93 (1 H, 7.59 (3 H), 7.40 (3 H), 6.81 (1 H), 6.38 (4 H).

[B(pz')₄]₂Sn (2, Hpz' = 3-methylpyrazole) was obtained from the reaction of 0.33 g (1.74 mmol) of SnCl₂ with 1.30 g (3.48 mmol) of K[B(pz')₄][9] (30 mL of methylene chloride, 4 h stirring). The crude material was obtained in quantitative yield; it was washed with cyclohexane to give a product of mp 176–180 °C. Anal. Calcd for $C_{32}H_{40}B_2N_{16}Sn$ (M_r = 788.6): C, 48.69; H, 5.11; B, 2.75; N, 28.40; Sn, 15.05. Found: C, 47.15; H, 4.70; B, 3.50; N, 26.99; Sn, 14.84.

NMR data: δ(¹H), 7.4* (s) + 7.2* (s) (1 H total, ratio 1:3), 6.05 (1 H, d, *J* = 1.7), 2.3* (s) +2.1* (s) (3 H total, ratio 1:3); δ(¹¹B) −0.8 (s, $h_{1/2}$ = 30 Hz); δ(¹³C) 151.8, 136.9, 106.5, 13.1; δ(¹¹⁹Sn) −808 (s, $h_{1/2}$ = 50 Hz); (at 50 °C) δ(¹H) 7.2* (1 H, s), 6.05 (1 H, d, *J* = 1.7), 2.1* (3 H, s).

[B(pz')₄]SnCl (8) was prepared from 0.50 g (2.64 mmol) of SnCl₂ and 0.99 g (2.64 mmol) of K[B(pz')₄][9] (30 mL of methylene chloride, 1 h stirring) in essentially quantitative yield. The crude material was washed with cyclohexane to give a product of mp 165–169 °C dec. Anal. Calcd for $C_{16}H_{20}BClN_8Sn$ (M_r = 489.1): C, 39.25; H, 4.12; B, 2.21; Cl, 7.26; N, 22.90; Sn, 24.26. Found: C, 39.27; H, 4.11; B, 2.34; Cl, 7.65; N, 22.40; Sn, 24.02.

NMR data: δ(¹H) 7.51* (1 H, s), 6.08* (1 H, s), 2.51 (3 H, s); δ(¹¹B) −1.3 (s, $h_{1/2}$ = 35 Hz); δ(¹³C) 151.7, 136.6, 106.6, 13.7; δ(¹¹⁹Sn) −533 (s, $h_{1/2}$ = 230 Hz); (at −70 °C, solution in CD₂Cl₂): δ(¹H) 7.80 (d, *J* = 2.1) +7.41* (s) (1 H total, ratio 1:3), 6.32 (d, *J* = 2.0) + 6.04 (d, *J* = 2.0) (1 H total, ratio 1:3), 2.45 (s) +2.34 (s) (3 H total, ratio 3:1).

[(HB(pz)₃]₂Sn (3) was prepared from 0.53 g (2.8 mmol) of SnCl₂ and 1.40 g (5.6 mmol) of K[HB(pz)₃][1] (30 mL of methylene chloride, 6 h stirring) to give 1.3 g (86%) of crude product. Traces of pyrazole were removed by sublimation under vacuum to leave a material of mp 162–165 °C. Anal. Calcd for $C_{18}H_{20}B_2N_{12}Sn$ (M_r = 544.4): C, 39.67; H, 3.70; B, 3.98; N, 30.86; Sn, 21.79. Found: C, 39.39; H, 3.51; B, 3.70; N, 30.50; Sn, 21.63.

NMR data: δ(¹H) 7.69 (1 H, d, *J* = 2.2, of d, *J* = 0.6), 7.35 (1 H, d, *J* = 1.5), 6.17 (1 H, unsym t = two overlapping d, *J* = ca. 2.1); δ(¹¹B) −2.8 (d, *J* = 95); δ(¹³C) 140.3, 135.7, 104.9; δ(¹¹⁹Sn) −877 (s, $h_{1/2}$ = 750 Hz; at −50 °C, $h_{1/2}$ = 270 Hz).

[HB(pz*)₃]₂Sn (4, Hpz* = 3,5-dimethylpyrazole).[7] NMR data: δ(¹H) 5.72 (1 H, s), 2.26 (3 H, s), 1.80 (3 H, s); δ(¹¹B) −8.3 (broad s, $h_{1/2}$ = 320 Hz); δ(¹³C) 148.9, 144.9, 106.0, 12.6, 12.3; δ(¹¹⁹Sn) −933 (s, $h_{1/2}$ = 350 Hz; at −50 °C, $h_{1/2}$ = 240 Hz). Lit.:[7] δ(¹H) 5.79 (3 H, s), 4.75* (1 H, s), 2.33 (9 H, s), 1.85 (9 H, s); δ(¹¹⁹Sn) (solution in CD₂Cl₂) −935 (s, $h_{1/2}$ = 300 Hz).

[HB(pz*)₃]SnCl[7] (9) decomposes near 250 °C. NMR data: δ(¹H) 5.82 (1 H, s), 2.50 (3 H, s), 2.37 (3 H, s); δ(¹¹B) −9.6 (d, *J* = 92); δ(¹³C) 149.8, 145.4, 106.3, 13.8, 12.5; δ(¹¹⁹Sn) −579 ($h_{1/2}$ = 200 Hz). Lit.:[7] δ(¹H) (solution in C₆D₆) 5.40 (1 H, s), 2.36 (3 H, s), 1.96 (3 H, s); δ(¹¹⁹Sn) (solution in CD₂Cl₂) −1460 (s, $h_{1/2}$ > 300 Hz).

[H₂B(pz)₂]₂Sn (5) was prepared from 0.75 g (3.95 mmol) of SnCl₂ and 1.47 g (7.9 mmol) of K[H₂B(pz)₂][1] (30 mL of methylene chloride, 2 h stirring) to give 1.23 g (75%) of material, sintering at 110 °C and decomposing at 116–124 °C. The material could not be purified by recrystallization but deteriorated in all relevant attempts; it decomposes

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