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Core conformational rearrangement accompanying two-center, bimetallic redox reactions. Chemical and structural properties of the pyrazolyl-bridged rhodium dimers [Rh(.eta.5-C5Me5)Cl(.mu.-pz)]2 and [Rh(.eta.5-C5H5)(.mu.-pz)]2

James A. Bailey, Stephen L. Grundy, and Stephen R. Stobart

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Supplementary Material Available: Tables of crystal data, atom coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates (7 pages); tables of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

Core Conformational Rearrangement Accompanying Two-Center, Bimetallic Redox Reactions. Chemical and Structural Properties of the Pyrazolyl-Bridged Rhodium Dimers $[Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-pz})]_2$ and $[Rh(\eta^5\text{-}C_5H_5)(\mu\text{-pz})]_2$

James A. Bailey, Stephen L. Grundy, and Stephen R. Stobart*

Department of Chemistry, University of Victoria
Victoria, British Columbia, Canada V8W 2Y2

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Summary: Reaction between $[Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-pz})]_2$ (**5**), which exhibits a "chair" conformation for the core pyrazolyl-bridged bimetallic unit in the crystal with Rh_2 separation 4.059 (2) Å, and $AgBF_4$ affords $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-pz})_2(\mu\text{-Cl})]BF_4$ (**6**), in which the cation core exists in a "boat" conformation with Rh centers 3.588 (2) Å apart; reduction (Zn/Cu) of **5** yields a purple product (**7**) tentatively identified as $[Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-pz})]_2$, the bright purple, reactive $\eta^5\text{-}C_5H_5$ analogue **9** of which has been synthesized from $[Rh(\eta^5\text{-}C_5H_5)Cl(\mu\text{-pz})]_2$ (**8**) and shown by using single-crystal X-ray diffraction to possess a deeply folded ("boat") geometry in which Rh–Rh = 2.657 (3) Å.

Concurrent activation of linked coordinatively unsaturated transition-metal centers, which may mediate critical steps in a range of natural and artificial catalytic cycles, is an emergent area of bimetallic chemistry for which so far only very sketchy mechanistic definition exists. We have found that in the family of diiridium(I) complexes $[IrL^1L^2(\mu\text{-pz})]_2$ (**1**, L^1L^2 = COD, cycloocta-1,5-diene, pzH = pyrazole; **2**, $L^1 = L^2$ = CO; **3**, L^1 = CO, $L^2 = PPh_3$) the pyrazolyl ligands are unusually flexible in bridging, accommodating major alterations in intermetallic separation along the Ir_2 axis.[1] Thus multisite redox reactions that are accompanied by metal–metal bond formation or fracture can proceed without disruption of the integrity of the cyclic bimetallic core.[2] Weak metal–metal interactions characteristic[3] of binuclear structures like those of **1**–**3** may act to constrain the geometry of the bridged framework (accounting, e.g., for the conformational rigidity of dimer **1**, where COD CH_2 resonances remain distinguishable in ^1H or ^{13}C NMR spectra even at elevated temperature); but whether ring inversion facilitates formation of axially substituted diiridium(II) products is not known, although it is a logical mechanistic idea. In fact to date the extensive redox chemistry[1-5] associated with compounds **1**–**3** has connected exclusively geometries that exist in "boat" conformations (including those[4,5] that afford d^6_2 products as cofacial bioctahedra). In examining further the d^7_2:d^6_2 redox manifold (i.e., that connecting the met-

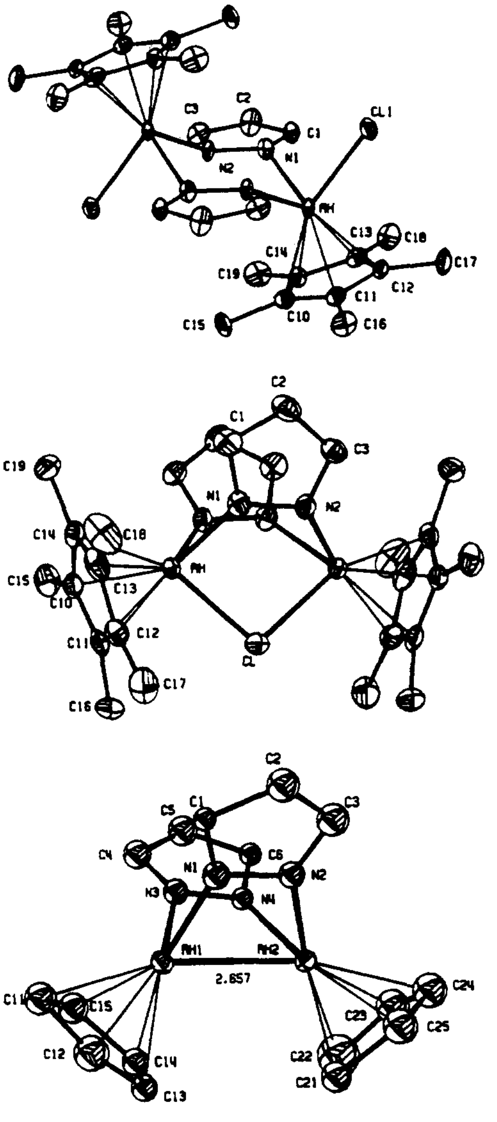

Figure 1. ORTEP drawings of (top) $[Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-pz})]_2$ (**5**) showing the "chair" conformation about the six-membered metallacycle, (middle) the cation in $\{[Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-pz})]_2(\mu\text{-Cl})\}BF_4$ (**6**) showing the "boat" conformation, and (bottom) $[Rh(\eta^5\text{-}C_5H_5)(\mu\text{-pz})]_2$ (**9**). Selected bond distances (Å) and angles (deg; ϕ is cp ring centroid): compound **5**, Rh···Rh′ 4.059 (2); Cl(1)–Rh 2.399 (2); N(1)–Rh 2.105 (7); N(2)′–Rh 2.110 (7); ϕ–Rh 1.782 (10); N(1)–Rh–Cl(1) 89.6 (2); N(2)′–Rh–N(1) 90.8 (2); N(2)′–Rh–Cl 88.5 (2); ϕ–Rh–Rh′ 131.6 (3); compound **6**, Rh···Rh′ 3.588 (2); Cl–Rh 2.378 (2); N(1)–Rh 2.081 (7); N(2)′–Rh 2.101 (9); ϕ–Rh 1.777 (2); N(1)–Rh–Cl 88.3 (2); Rh–Cl–Rh′ 97.9 (1); N(2)′–Rh–N(1) 79.9 (2); N(2)′–Rh–Cl 88.0(2); ϕ–Rh–Rh′ 163.8 (2); compound **9**, Rh(2)–Rh(1) 2.657 (3); N(1)–Rh(1) 2.04 (3); N(3)–Rh(1) 2.06 (2); N(2)–Rh(2) 2.00 (2); N(4)–Rh(2) 2.02 (2); ϕ(1)–Rh(1) 1.84 (3); ϕ(2)–Rh(2) 1.83 (3); N(1)–Rh(1)–Rh(2) 70.7 (7); N(3)–Rh(1)–Rh(2) 70.7 (7); N(3)–Rh(1)–N(1) 83.4 (9); N(2)–Rh(2)–Rh(1) 72.4 (7); N(4)–Rh(2)–Rh(1) 69.3 (6); N(4)–Rh(2)–N(2) 86.1 (10); ϕ(1)–Rh(1)–Rh(2) 131.7 (9); ϕ(2)–Rh(2)–Rh(1) 135.2 (9). Estimated standard deviations are given in parentheses.

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al-metal bonded M^{II}_2 state with metal-separated M^{III}_2, M = Rh or Ir), we have identified a transformation that results in a "boat":"chair" rearrangement.

Mononuclear (pentamethylcyclopentadienyl)(pyrazole) complexes of Rh and Ir have recently been prepared by us as well as by others.[6] Addition of NEt_3 to a solution in CH_2Cl_2 of orange $Rh(\eta^5\text{-}C_5Me_5)Cl_2(pzH)$ (**4**), followed by stirring (2 h), elution from a short alumina column using 20:1 CH_2Cl_2/MeOH, redissolution, and then precipitation with Et_2O afforded[7] $[Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-pz})]_2$ (**5**, 81% yield), the molecular geometry of which (as established[8] by using X-ray crystallography) is illustrated as Figure 1, top. After treatment of compound **5** with $AgBF_4$ in acetone solution, a white precipitate formed, which was removed by filtration; subsequent introduction of Et_2O by vapor diffusion led to crystallization (95%) of the known[6] dirhodium species $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-pz})_2(\mu\text{-Cl})]BF_4$ (**6**), the cation geometry for which[9] possesses 2-fold symmetry and is shown in Figure 1, middle. During stirring (48 h) of an orange solution of compound **6** in MeOH with excess Zn dust and Cu sand (ca. 1:1), the mixture gradually turned black and then to a deep purple color: we attribute the latter to the dirhodium(II) complex $[Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-pz})]_2$ (**7**), although this product has not yet been isolated as a pure solid.

Starting from the precursor[10] $[Rh(\eta^5\text{-}C_5H_5)Cl_2]_2$, similar strategy afforded (55%) the analogue[11] $[Rh(\eta^5\text{-}C_5H_5)Cl(\mu\text{-pz})]_2$ (**8**) of **5**, a methanolic solution of which when stirred with excess Zn dust underwent an abrupt color change from orange to purple after 30 min. Filtration, evacuation, then extraction into Et_2O led to recovery of the bright purple analogue $[Rh(\eta^5\text{-}C_5H_5)(\mu\text{-pz})]_2$ (**9**) of **7**, which (unlike the latter) was obtained (ca. 20% yield) as crystals suitable for X-ray diffraction,[12] by sublimation in vacuo (95 °C): the molecular geometry is reproduced as Figure 1, bottom. Reaction of compound **9** with $NOBF_4$ results in reoxidation to a red, cationic dirhodium nitrosyl[13] $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-pz})_2(\mu\text{-NO})]BF_4$ (**10**, 50%), while treatment with I_2 in Et_2O yields the diiodo analogue $[Rh(\eta^5\text{-}C_5H_5)I(\mu\text{-pz})]_2$ (**11**, 71% yield) of **8**. Diiridium(III) analogues of compounds **5** and **6** have been isolated; reduction to a diiridium(II) species (cf. **7** or **9**) is being pursued.

Compound **5** adopts a rigorously centrosymmetric "chair" conformation (Figure 1) for the bridging unit (to our knowledge this is paralleled[14] in related chemistry only in two structures, those of $[Ti(\eta^5\text{-}C_5H_5)_2(\mu\text{-pz})]_2$ and $[Rh(\eta^5\text{-}C_5H_5)pz(\mu\text{-pz})]_2)$, with the two Rh(III) centers 4.059 (2) Å apart; it is formally the dichlorine adduct of the dirhodium(II) complex **7** (cf. the relationship between **9** and **11**), which we anticipate will possess a metal–metal bonded geometry folded into a "boat" shape like that confirmed for **9** (Rh–Rh = 2.657 Å, Figure 1). This supposition is supported by the close similarity between the electronic absorption spectra of **7** and **9**, both of which contain low-energy maxima (respectively at 560, 502 nm) attributable to a σ:σ^* transition from a Rh_2 bonding HOMO. The "chair":"boat" rearrangement is represented explicitly by chloride abstraction from **5** to give **6** (Figure 1), while the reverse conformational change is implicit in the **9**:**11** conversion (i.e., assuming **11** is structurally analogous to **5**). In crystals of complex **5** the pz heterocycles are within 1° of coplanarity, i.e., as they would be oriented in transition during ring inversion of the more familiar "boat" structures (vide supra). Such relationships imply that core conformational change is an energetically feasible mechanistic pathway in redox phenomena associated with **1**–**3** and could also be responsible for racemization of the inherently chiral molecular configuration[2] of **3**, thereby limiting stereochemical usefulness of the latter.

Acknowledgment. We thank the NSERC, Canada, for financial support including provision of a graduate fellowship (J.A.B.).

Supplementary Material Available: Listings of fractional atomic coordinates and isotropic temperature parameters, anisotropic temperature parameters, interatomic distances, and bond angles for **5**, **6**, and **9** (9 pages); listings of observed and calculated structure factors for **5**, **6**, and **9** (17 pages). Ordering information is given on any current masthead page.

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(7) Compound **5**. Anal. Calcd for $C_{26}H_{36}Cl_2N_4Rh_2$: C, 45.81; H, 5.29; N, 7.72. Found: C, 45.56; H, 5.28; N, 8.01. ^1H NMR (250 MHz, $CDCl_3$) δ 1.78 (s), 6.14 (t), 7.36 (d).

(8) Crystal data for compound **5**: $M = 798$; triclinic; space group $P\bar{1}$; $a = 8.785$ (2), $b = 10.469$ (4), $c = 8.675$ (2) Å; $\alpha = 79.34$ (2), $\beta = 80.43$ (2), $\gamma = 114.90$ (2)°; $V = 684$ (2) Å^3; $Z = 1$; $d_{calc} = 1.64$ g cm^{-3}; Mo Kα radiation, $\lambda = 0.71069$ Å; Nonius CAD4 diffractometer; 1348 reflections with $F_o^2 > 6\sigma(F_o^2)$ were used in the least-squares refinement to yield $R = 0.0602$, $R_w = 0.0644$.

(9) Crystal data for compound **6**: $M = 676.6$; monoclinic; space group $P2/n$; $a = 15.043$ (2), $b = 8.360$ (1), $c = 12.316$ (2) Å; $\beta = 110.58$ (2)°; $V = 1450.0$ (5) Å^3; $Z = 2$; $d_{calc} = 1.55$ g cm^{-3}; Mo Kα radiation, $\lambda = 0.71069$ Å; Nonius CAD4 diffractometer; 1676 reflections with $F_o^2 > 4\sigma(F_o^2)$ were used in the least-squares refinement to yield $R = 0.0507$, $R_w = 0.0519$.

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(11) Compound **8**. Anal. Calcd for $C_{16}H_{16}Cl_2N_4Rh_2$: C, 35.52; H, 2.98; N, 10.36; Cl, 13.11. Found: C, 35.58; H, 3.25; N, 9.92; Cl, 13.84. ^1H NMR (250 MHz, $CDCl_3$) δ 6.24 (s), 6.31 (t), 8.07 (d). Compound **9**. Anal. Calcd for $C_{16}H_{16}N_4Rh_2$: C, 40.88; H, 3.43; N, 11.91. Found: C, 40.96; H, 3.81; N, 11.15. ^1H NMR (250 MHz, $CDCl_3$) δ 5.29 (s), 5.90 (t), 7.32 (d). Compound **10**. Anal. Calcd for $C_{16}H_{16}BF_4N_5ORh_2$: C, 32.74; H, 2.75, N, 11.93. Found: C, 32.36; H, 2.91; N, 10.91. ^1H NMR (250 MHz, $CDCl_3$) δ 5.61 (s), 6.35 (t), 7.96 (d). Compound **11**. Anal. Calcd for $C_{16}H_{16}I_2N_4Rh_2$: C, 26.55; H, 2.23; N, 7.74. Found: C, 27.37; H, 2.98; N, 7.48. ^1H NMR (250 MHz, $CDCl_3$) δ 6.15 (s), 6.25 (t), 7.96 (d).

(12) Crystal data for compound **9**: $M = 470.1$; orthorhombic; space group $P2_12_12_1$; $a = 11.758$ (2), $b = 12.710$ (3), $c = 10.736$ (2) Å; $V = 1604.4$ (6) Å^3; $Z = 4$; $d_{calc} = 2.02$ g cm^{-3}; Mo Kα radiation, $\lambda = 0.71069$ Å; Nonius CAD4 diffractometer; 903 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the least-squares refinement to yield $R = 0.0799$, $R_w = 0.0791$.

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Soluble Mono(pentamethylcyclopentadienyl)zirconium Hydrides: X-ray Structure of $(C_5Me_5)_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$

Johannes R. van den Hende, Bart Hessen, Auke Meetsma, and Jan H. Teuben*

Department of Chemistry, Rijksuniversiteit Groningen
Nijenborgh 16, 9747 AG Groningen, The Netherlands

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Summary: The 14-electron alkyl complex $Cp^*Zr[(CH_2)_3NMe_2]Cl_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$), containing a chelating (dimethylamino)propyl ligand, reacts with H_2 to form a soluble crystallizable mono-Cp* zirconium hydride with a complicated stoichiometry, tentatively formulated as "$Cp^*_3Zr_3H_4Cl_5$". Reaction of this compound with PMe_3 induces disproportionation, in which $Cp^*ZrCl_3(PMe_3)$ and $Cp^*_2Zr_2(\mu\text{-}H)_3Cl_3(PMe_3)$, the first early-transition-metal $(\mu\text{-}H)_3$-bridged dimer, are formed. An X-ray structure determination of this compound (space group $P2_1/c$, $a =$

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