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Synthesis and X-ray Structural Characterization of Heterobimetallic Rhodium-Platinum and Rhodium-Palladium Benzothiazole-2-thiolate Compounds. The First Binuclear Complexes Having Two Short-Bite Anionic Bridging Ligands in a Trans Disposition

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Reactions of the binuclear complex $[\text{Rh}(\mu\text{-bzta})(\text{CO})(\text{PPh}_3)_2]$ (**1**) (bzta = benzothiazole-2-thiolate) with the complexes $\text{MCl}_2(\text{cod})$ ($\text{M} = \text{Pd}, \text{Pt}$; cod = 1,5-cyclooctadiene) afford the new diamagnetic heterobinuclear compounds $(\text{Ph}_3\text{P})\text{M}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})$ [$\text{M} = \text{Pt}$ (**2**), Pd (**3**)] as well as $\text{MCl}_2(\text{PPh}_3)_2$ and $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$ through a complicated process. The new mononuclear complexes *trans*-Pt(bzta)₂(PPh₃)₂ and *trans*-PtH(bzta)(PPh₃)₂ react with $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$ to give $(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})$ (**2**) in moderate or low yield. Characteristic features of the structures of compounds **2** and **3** are revealed by their IR and ¹H and ³¹P NMR spectra. **2** crystallizes with a molecule of CH₂Cl₂ in the triclinic space group P1̄ with $a = 11.425$ (1) Å, $b = 11.819$ (1) Å, $c = 14.393$ (1) Å, $\alpha = 107.88$ (1)°, $\beta = 99.85$ (1)°, $\gamma = 93.43$ (1)°, $V = 1809.3$ (3) Å³, and $Z = 2$. On the basis of 4546 independent observations and 332 parameters, the structure was refined to $R = 0.0224$ and $R_w = 0.0247$. The metal centers, which are joined by a short metal-metal bond [2.6266 (4) Å], are bridged in a mutually trans and head-to-head fashion by the two benzothiazole-2-thiolate groups, which are bound to platinum through the exocyclic sulfur and to rhodium through the nitrogen. One triphenylphosphine on platinum, and chloro and carbonyl ligands on rhodium, complete the square planar and square pyramidal coordinations around the platinum and rhodium atoms, respectively.

Introduction

The development of binuclear systems has arisen from the idea that two metal atoms in close proximity could react in a cooperative manner with substrate molecules.¹ A major role in the building of binuclear complexes has been played by tertiary diphosphines, bis(diphenylphosphino)methane (dppm) being particularly efficient for this purpose.² Substitution of one of the donor atoms in the dppm skeleton for a softer (As) or harder (N) center has been introduced to create heterobinuclear complexes of the platinum group metals. Such ligand systems studied by Balch are (diphenylarsino)(diphenylphosphino)methane (dapm)³ and 2-(diphenylphosphino)pyridine (Ph₂PPy),⁴ which have led to a controlled synthesis of platinum-rhodium complexes having two bridging ligands.

We have followed another approach for the synthesis of binuclear complexes of rhodium and iridium based upon the use of anionic, small-bite bridging ligands having a structural donor unit (N-C-X) basically similar to that of dppm. Ligands of these type bridge the two metal centers through the N and X atoms and bring the metal atoms in a close proximity. Representative examples are $[\text{Rh}(\mu\text{-az})(\text{nbd})]_2$ (az = 7-azaindolate, X = N; nbd = 2,5-norbornadiene),⁵ $[\text{Rh}(\mu\text{-OPy})(\text{CO})_2]_2$ (OPy = 2-pyridonate, X = O),⁶ and $[\text{Rh}(\mu\text{-SPy})(\text{CO})_2]_2$ (SPy = 2-pyridinethiolate, X = S).⁷

Those ligands having two dissimilar (S and N) donor centers should be especially appropriate to bridge two metal atoms in

different oxidation states and to build heterobinuclear complexes. This behavior can be observed in the structure of the first linear tetrametallic iridium complex $\text{Ir}_4(\mu\text{-bzta})_4\text{I}_2(\text{CO})_8$ (bzta = C₇H₄NS₂ = benzothiazole-2-thiolate).⁸ The outermost iridium atoms in a formal oxidation state +2 are bonded to the hard N atoms while the internal metals, in a formal oxidation state +1, are bonded to the soft sulfur atoms. In addition, the binuclear complexes $[\text{Rh}(\mu\text{-bzta})\text{L}]_2$ behave as metalloligands toward metal fragments (ML_x), giving trinuclear complexes $[\text{L}_4\text{Rh}_2(\mu_3\text{-bzta})_2\text{ML}_x]$ in a controlled way; i.e., the incoming metal fragment binds to the binuclear complexes through the already coordinated sulfur atoms.⁹ In this way, the result of the reactions of the binuclear complexes $[\text{Rh}(\mu\text{-bzta})(\text{CO})(\text{PPh}_3)_2]$ with compounds of the soft metals palladium and platinum were unpredictable. We report herein these reactions leading to new heterobinuclear Pt-Rh and Pd-Rh complexes, which are the first examples where the two short-bite N-C-X bridging ligands mentioned above adopt a mutually trans disposition.

Experimental Section

The compounds $\text{PtCl}_2(\text{cod})$,¹⁰ $\text{PdCl}_2(\text{cod})$,¹¹ $\text{PdCl}_2(\text{PPh}_3)_2$,¹² $\text{Pt}(\text{PPh}_3)_4$,¹³ and $[\text{Rh}(\mu\text{-bzta})(\text{CO})(\text{PPh}_3)_2]$ (**1**)⁷ were prepared by published procedures. All the reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen prior to use.

IR spectra were recorded on a Perkin-Elmer 783 spectrometer using Nujol mulls between polyethylene sheets or in solution in NaCl windows. ¹H and ³¹P NMR spectra were recorded on a Varian XL-200 spectrometer in CDCl₃. Chemical shifts are reported in ppm relative to external standards (TMS for ¹H and 85% H₃PO₄ for ³¹P). Elemental analyses were carried out with a Perkin-Elmer 240-B microanalyzer.

Preparation of $(\text{PPh}_3)\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})\cdot\text{CH}_2\text{Cl}_2$ (2**).** A mixture of $[\text{Rh}(\mu\text{-bzta})(\text{CO})(\text{PPh}_3)_2]$ (0.220 g, 0.196 mmol) and $\text{PtCl}_2(\text{cod})$ (0.147 g, 0.392 mmol) in toluene (15 mL) was refluxed for 2 h to give a dark brown solution. The solvent was pumped off, and the residue was extracted with dichloromethane (10 mL) and filtered. The white residue was identified as *trans*-PtCl₂(PPh₃)₂ by comparison with a pure sample. The extract was evaporated to ca. 1 mL and chromatographed on a silica-gel column (20 × 1.5 cm). Elution with dichloromethane-hexane (1:1) afforded a yellow band of the complex $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$. Elution with dichloromethane gave a yellow-green solution from which, once

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Table I. Crystallographic Data for $(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})$

chem formula, fw	$\text{C}_{33}\text{H}_{23}\text{Cl}_2\text{N}_2\text{OPPtRhS}_4 \cdot \text{CH}_2\text{Cl}_2$; 1041.15
space group	$P\bar{1}$ (No. 2)
a - c , Å	11.425 (1), 11.819 (1), 14.393 (1)
α - γ , deg	107.88 (1), 99.85 (1), 93.43 (1)
V , Å ³ ; Z	1809.3 (3); 2
T , °C	20
$\lambda(\text{Mo K}\alpha)$, Å	0.71069
ρ_{calcd} , g cm ⁻³	1.911
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	48.72
transm coeff	0.660–0.342
R ; R_w	0.0224; 0.0247

evaporated to ca. 2 mL, green crystals of the complex **2** were obtained by slow addition of diethyl ether (10 mL) and cooling to -15°C . The crystals were isolated by filtration, washed with diethyl ether, and vacuum-dried. Yield: 0.067 g (18% based on Pt). Anal. Calcd for $\text{C}_{34}\text{H}_{25}\text{Cl}_3\text{N}_2\text{OPPtRhS}_4$: C, 39.22; H, 2.42; N, 2.69. Found: C, 39.02; H, 2.73; N, 2.66. Infrared spectra (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO})$ 2025. ^1H NMR (20 °C, CDCl_3): δ 9.31 (d, 2 H, H^4), 7.83 (m, 6 H, o - PPh_3), 7.55 (m, 13 H, H^5 , H^6 , p - PPh_3 and m - PPh_3), 7.37 (d, 2 H, H^7), 5.30 (s, CH_2Cl_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (20 °C, CDCl_3): δ 3.85 (d, $^2J_{\text{P-Rh}} = 17$ Hz, $^1J_{\text{P-Pt}} = 3640$ Hz).

Preparation of $(\text{PPh}_3)_2\text{Pd}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})\cdot 0.5\text{Et}_2\text{O}$ (3). A mixture of $[\text{Rh}(\mu\text{-bzta})(\text{CO})(\text{PPh}_3)_2]$ (0.100 g, 0.090 mmol) and $\text{PdCl}_2(\text{cod})$ (0.051 g, 0.18 mmol) in toluene (15 mL) was refluxed for 2 h to give a dark brown solution. Separation of the mixture through column chromatography was as described above. The yellow-green solution was concentrated to 2 mL, and then diethyl ether (10 mL) was slowly added. Green crystals of the complex **3** were obtained by cooling to -15°C . They were isolated by filtration and vacuum-dried. Yield: 0.026 g, (16% based on Pd). Anal. Calcd for $\text{C}_{35}\text{H}_{28}\text{ClN}_2\text{O}_{1.5}\text{PPdRhS}_4$: C, 46.47; H, 3.11; N, 3.09. Found: C, 46.66; H, 3.64; N, 2.88. Infrared spectra (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO})$ 2020. ^1H NMR (20 °C, CDCl_3): δ 8.23 (d, 2 H, H^4), 7.80 (m, 6 H, o - PPh_3), 7.54 (m, 13 H, H^5 , H^6 , p - PPh_3 and m - PPh_3), 7.31 (d, 2 H, H^7), 3.50 (q, 2 H, Et_2O), 1.20 (t, 3 H, Et_2O). $^{31}\text{P}\{^1\text{H}\}$ NMR (20 °C, CDCl_3): δ 13.3 (d, $^2J_{\text{Rh-P}} = 25$ Hz).

Preparation of *trans*- $\text{Pt}(\mu\text{-bzta})_2(\text{PPh}_3)_2$ (4). A solution of lithium benzothiazole-2-thiolate was prepared by addition of *n*-butyllithium (0.248 mL, 1.61 mol·L⁻¹ in hexane, 0.40 mmol) to a solution of 2-mercaptobenzothiazole (0.067 g, 0.40 mmol) in tetrahydrofuran (10 mL). The solid compound $\text{PtCl}_2(\text{PPh}_3)_2$ (0.158 g, 0.20 mmol) was then added to the solution to give immediately a yellow suspension, which was stirred for 30 min. The complex was separated by filtration, washed with diethyl ether, and dried under vacuum. Yield: 0.089 g, 90%. Anal. Calcd for $\text{C}_{50}\text{H}_{38}\text{N}_2\text{P}_2\text{PtS}_4$: C, 57.08; H, 3.64; N, 2.66. Found: C, 57.03; H, 3.90; N, 2.67. $^{31}\text{P}\{^1\text{H}\}$ NMR (20 °C, CDCl_3): δ 24.0 (s, $J_{\text{P-Pt}} = 2747$ Hz).

Preparation of $\text{PtH}(\text{bzta})(\text{PPh}_3)_2$ (5). Solid 2-mercaptobenzothiazole (0.033 g, 0.20 mmol) was added to a solution of $\text{Pt}(\text{PPh}_3)_4$ (0.248 g, 0.20 mmol) in acetone (15 mL). The original yellow solution became colorless, and immediately a white solid began to crystallize. This suspension was stirred for 30 min and then was concentrated to 5 mL. Diethyl ether was added to complete the crystallization. The solid was filtered off, washed with diethyl ether, and vacuum-dried. Yield: 0.126 g, 88%. Anal. Calcd for $\text{C}_{43}\text{H}_{35}\text{NP}_2\text{PtS}_2$: C, 58.46; H, 4.37; N, 1.48. Found: C, 58.58; H, 4.72; N, 1.47. Infrared spectrum (Nujol mull; cm^{-1}): $\nu(\text{Pt-H})$ 2158. $^{31}\text{P}\{^1\text{H}\}$ NMR (20 °C, CDCl_3): δ 29.7 (s, $J_{\text{P-Pt}} = 3026$ Hz).

Crystallographic Structure Determination of $(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})\cdot\text{CH}_2\text{Cl}_2$. Crystals of the title complex suitable for X-ray diffraction studies were prepared by slow evaporation of a concentrated solution of the compound in dichloromethane. A green prismatic block of approximate dimensions 0.049 × 0.125 × 0.177 mm was mounted in a glass fiber. A set of randomly searched reflections indexed to a triclinic symmetry. A fast data collection in the range $20 \leq 2\theta \leq 35^\circ$ showed strong reflections from which a group of 68 were carefully centered and used to obtain by least-squares methods the unit cell dimensions listed in Table I. A Siemens AED four-circle diffractometer was used for data acquisition ($\omega/2\theta$ scan mode), with graphite-monochromated Mo K α radiation and 2θ range 3.0 – 50° ($-12 \leq h \leq 12$; $-13 \leq k \leq 13$; $-15 \leq l \leq 15$). A total of 9478 reflections were measured; from 4722 unique reflections ($R_{\text{merg}} = 0.0208$, 4546 having $F \geq 4\sigma(F)$) were considered observed and used in the refinement. Three standard reflections were measured approximately every 1 h as a check on crystal and instrument stability; no deviation was observed. A numerical absorption correction was applied on the basis of the indexed morphological faces of the crystal.

The molecular structure was solved by Patterson and conventional Fourier techniques. Isotropic displacement parameters first, and subsequent anisotropic thermal parameters, were refined for all non-hydrogen atoms (except C atoms of the phenyl groups of the PPh_3 ligand). Hy-

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic or Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^4$) for the Non-Hydrogen Atoms of Complex **2**

atom	x/a	y/b	z/c	$U_{\text{eq}}^a/U_{\text{iso}}$
Rh ^b	14202 (3)	64569 (3)	41298 (2)	319 (1)
Pt ^b	16361 (1)	66815 (1)	24052 (1)	330 (1)
Cl	2842 (1)	8036 (1)	5176 (1)	619 (5)
S(1)	3268 (1)	5616 (1)	2370 (1)	449 (5)
S(2)	4245 (1)	3938 (1)	3392 (1)	463 (4)
S(3)	-67 (1)	7634 (1)	2379 (1)	492 (5)
S(4)	-1393 (1)	8974 (1)	3889 (1)	502 (5)
P	2104 (1)	7299 (1)	1170 (1)	346 (4)
O(10)	-477 (3)	4510 (3)	2909 (3)	664 (17)
N(1)	2698 (3)	5309 (3)	4037 (2)	360 (15)
N(2)	148 (3)	7605 (3)	4275 (2)	342 (13)
C(10)	248 (4)	5231 (4)	3363 (3)	429 (18)
C(1)	3309 (4)	5028 (4)	3324 (3)	375 (16)
C(2)	3802 (4)	3879 (4)	4476 (3)	396 (16)
C(3)	4178 (4)	3190 (4)	5077 (3)	489 (19)
C(4)	3693 (4)	3332 (4)	5907 (4)	547 (21)
C(5)	2866 (4)	4112 (5)	6149 (4)	549 (22)
C(6)	2478 (4)	4795 (4)	5555 (3)	493 (20)
C(7)	2966 (4)	4674 (4)	4713 (3)	390 (16)
C(11)	-333 (4)	8001 (4)	3566 (3)	386 (17)
C(12)	-1185 (4)	8807 (4)	5061 (3)	434 (16)
C(13)	-1781 (5)	9279 (4)	5829 (4)	569 (22)
C(14)	-1488 (5)	8975 (5)	6679 (4)	593 (21)
C(15)	-630 (5)	8204 (5)	6766 (3)	572 (21)
C(16)	-24 (4)	7737 (4)	6005 (3)	484 (18)
C(17)	-324 (4)	8036 (4)	5142 (3)	365 (17)
Cl(1)	6694 (2)	-913 (2)	1267 (2)	1170 (11)
Cl(2)	7489 (2)	1591 (2)	1702 (1)	1117 (10)
C(21)	821 (4)	7601 (4)	375 (3)	366 (10) ^c
C(22)	322 (4)	8667 (4)	695 (3)	445 (11)
C(23)	-724 (4)	8840 (5)	131 (3)	541 (12)
C(24)	-1285 (5)	7972 (5)	-727 (4)	580 (13)
C(25)	-792 (5)	6926 (4)	-1047 (4)	553 (13)
C(26)	257 (4)	6733 (4)	-497 (3)	446 (11)
C(31)	2855 (4)	6292 (4)	295 (3)	385 (10)
C(32)	3775 (4)	6715 (4)	-62 (3)	517 (12)
C(33)	4283 (5)	5918 (5)	-778 (4)	683 (15)
C(34)	3877 (5)	4748 (5)	-1126 (4)	685 (15)
C(35)	2960 (5)	4293 (5)	-787 (4)	637 (14)
C(36)	2440 (4)	5078 (4)	-61 (3)	509 (12)
C(41)	3098 (4)	8700 (4)	1722 (3)	387 (10)
C(42)	3777 (4)	8954 (4)	2680 (3)	470 (11)
C(43)	4566 (5)	10002 (4)	3118 (4)	571 (13)
C(44)	4673 (5)	10786 (5)	2600 (4)	582 (13)
C(45)	4011 (4)	10548 (4)	1646 (3)	554 (13)
C(46)	3235 (4)	9501 (4)	1210 (3)	475 (11)
C(1S)	7556 (6)	356 (6)	2119 (5)	822 (18)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^b Atomic coordinates for these atoms are expressed as multiplied by 10^5 . ^c From this atom downward, isotropic thermal parameters are expressed.

drogen atoms were found in successive Fourier maps and were refined riding on their carbon atoms with a common thermal parameter. Full-matrix least-squares refinements were carried out by using the SHELX program.¹⁴ The final weighting scheme used was $w = k/[\sigma^2(F) + gF^2]$ with $k = 2.9594$ and $g = 0.000078$. Maximum shift/esd was 0.007. The highest residual peak in the last refinement was $0.76 \text{ e}/\text{\AA}^3$ situated close to the C(34) atom. Atomic and thermal parameters are summarized in Table II.

Results and Discussion

Heating of a equimolar mixture of $\text{PtCl}_2(\text{cod})$ ($\text{cod} = 1,5$ -cyclooctadiene) and $[\text{Rh}(\mu\text{-bzta})(\text{CO})(\text{PPh}_3)_2]$ (**1**) in toluene under reflux gives a red-brown solution containing a mixture of products and unreacted complex **1**, as detected by its infrared spectrum ($\nu(\text{CO})$ 1990 cm^{-1}). To complete the reaction, a further addition of 1 mol of $\text{PtCl}_2(\text{cod})$ /mol of **1** is required.

Examination of the reaction mixture by ^{31}P NMR spectroscopy (Figure 1) reveals the presence of mainly three compounds having

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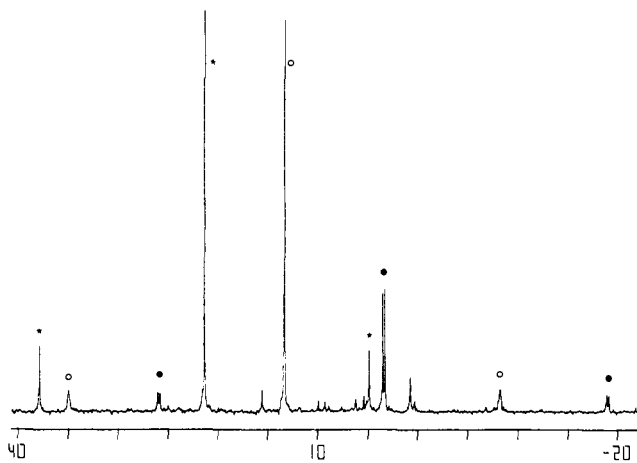


Figure 1. ^{31}P NMR spectrum of the reaction mixture of **1** with $\text{PtCl}_2(\text{cod})$: *, *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$; O, *cis*- $\text{PtCl}_2(\text{PPh}_3)_2$; ●, $(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})$ (**2**).

triphenylphosphine bonded to platinum in roughly 1:1 molar proportions. Surprisingly, there is not a resonance assignable to a phosphine ligand bonded directly to rhodium. Two of these compounds are identified as *cis*- and *trans*- $\text{PtCl}_2(\text{PPh}_3)_2$ ($\delta = 13.5$ ppm, $^1J_{\text{P-Pt}} = 3494$ Hz and $\delta = 21.6$ ppm, $^1J_{\text{P-Pt}} = 2670$ Hz, respectively) by comparison with authentic samples. The third resonance (at $\delta = 3.85$ ppm) is due to the new heterobinuclear diamagnetic green complex $(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})$ (**2**). Separation of the components of the mixture can be accomplished by crystallization and column chromatography. A fourth product, $[\text{RhCl}(\text{cod})]_2$, is also isolated.

Structural characterization of complex **2** in solution and in the solid state relies upon spectroscopic data and single-crystal X-ray analysis. The ^{31}P NMR spectrum of complex **2** exhibits a doublet ($^2J_{\text{P-Rh}} = 17$ Hz) flanked by two platinum satellites ($^1J_{\text{P-Pt}} = 3640$ Hz). The relatively small value of $^2J_{\text{P-Rh}}$ is consistent with the presence of the P-Pt-Rh unit. The two-bond Rh-P coupling constant is in good agreement with those found for the compounds $\text{PtRh}_2(\mu\text{-CO})_2(\text{CO})(\text{PPh}_3)(\text{Cp}^*)_2$ (17 Hz)¹⁵ and $[\text{PtRh}_2(\mu\text{-H})(\mu\text{-CO})_2(\text{PPh}_3)(\text{Cp}^*)_2]\text{BF}_4$ (6 Hz),¹⁶ which have a triphenylphosphine ligand trans to a dative Pt-Rh bond. The value of $^1J_{\text{P-Pt}}$ is also comparable with trinuclear complexes (4004 and 3260 Hz, respectively). Since the benzothiazole-2-thiolate ligands are equivalent in the ^1H NMR spectrum, both bridging ligands are in a head-to-head disposition and mutually trans. The IR spectrum of complex **2** shows one $\nu(\text{CO})$ band at 2025 cm^{-1} (in CH_2Cl_2). The shift toward higher frequency is indicative of the oxidation of the rhodium atom relative to the starting compound. In the solid state this $\nu(\text{CO})$ band is split in two at 2010 and 1988 cm^{-1} due probably to lattice effects. The compound **2** crystallizes with solvent of crystallization, CH_2Cl_2 , which is supported by elemental analysis and integration of the characteristic resonance in its ^1H NMR spectrum. Nevertheless, in view of its novelty full confirmation and details of the structure of the compound **2** required a single-crystal X-ray diffraction study.

Crystal and Molecular Structure of $(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})\cdot\text{CH}_2\text{Cl}_2$ (2**).** The heterobinuclear complex crystallizes with a dichloromethane molecule as crystallization solvent. The molecular structure with the numbering scheme is shown in Figure 2. Final positional parameters and selected bond distances and angles are reported in Tables II and III, respectively. Within the complex the two metal centers are bonded by a metal-metal bond and bridged by two benzothiazole-2-thiolate ligands in a trans,trans and head-to-head arrangement. The exocyclic sulfurs are coordinated to the platinum atom while the heterocyclic nitrogen atoms are bonded to rhodium. The Pt atom completes a distorted

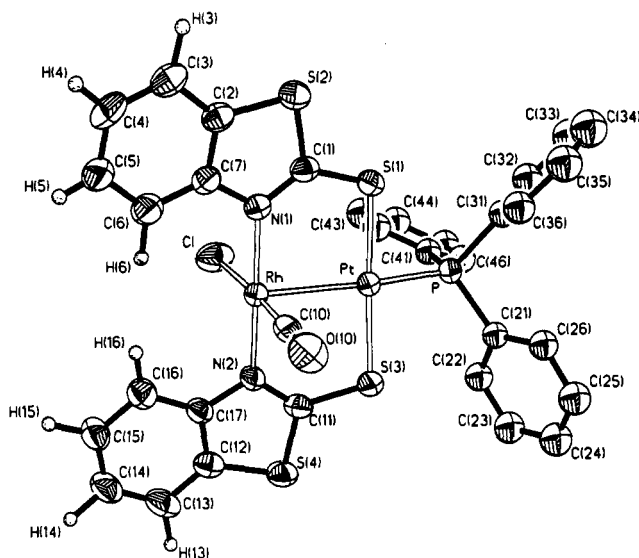


Figure 2. ORTEP view of the molecular structure of $(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})$ (**2**).

Table III. Selected Bond Distances (Å) and Angles (deg) for $(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})$

Rh-Cl	2.338 (1)	Pt-Rh	2.6266 (4)
Rh-N(1)	2.045 (4)	Pt-S(1)	2.3103 (1)
Rh-N(2)	2.040 (4)	Pt-S(3)	2.306 (1)
Rh-C(10)	1.841 (4)	Pt-P	2.249 (1)
N(1)-C(1)	1.309 (6)	N(2)-C(11)	1.303 (6)
C(1)-S(1)	1.714 (5)	C(11)-S(3)	1.714 (5)
C(1)-S(2)	1.737 (5)	C(11)-S(4)	1.743 (5)
C(2)-S(2)	1.741 (5)	C(12)-S(4)	1.736 (5)
C(10)-O(10)	1.108 (5)		
Cl-Rh-N(1)	90.3 (1)	Rh-Pt-S(1)	90.73 (4)
Cl-Rh-N(2)	89.0 (1)	Rh-Pt-S(3)	89.65 (4)
Cl-Rh-C(10)	176.6 (2)	Rh-Pt-P	165.71 (4)
N(1)-Rh-N(2)	177.9 (1)	S(1)-Pt-S(3)	176.39 (5)
N(1)-Rh-C(10)	91.5 (2)	S(1)-Pt-P	89.78 (5)
N(2)-Rh-C(10)	89.1 (2)	S(3)-Pt-P	90.73 (5)
Pt-Rh-Cl	99.08 (4)	Pt-Rh-N(2)	91.3 (1)
Pt-Rh-N(1)	90.7 (1)	Pt-Rh-C(10)	83.7 (1)
Rh-N(1)-C(1)	124.7 (3)	Rh-N(2)-C(11)	123.5 (3)
N(1)-C(1)-S(1)	127.0 (4)	N(2)-C(11)-S(3)	127.3 (4)
N(1)-C(1)-S(2)	114.1 (3)	N(2)-C(11)-S(4)	114.1 (3)
S(1)-C(1)-S(2)	118.9 (3)	S(3)-C(11)-S(4)	118.5 (3)
Pt-S(1)-C(1)	105.5 (2)	Pt-S(3)-C(11)	105.7 (2)
Rh-C(10)-O(10)	178.4 (5)		

square-planar coordination with the phosphorus atom of a triphenylphosphine group; the distortion of this planar arrangement ranges, in terms of deviations from the mean plane through coordinated atoms, between 0.077 and 0.342 (1) Å. The environment around the rhodium can be described either as square pyramidal—with the Rh atom in the base—or, better, as octahedral—with a vacant coordination site trans to the Rh-Pt bond. This latter description is endorsed by the small deviation observed for the Rh atom, 0.042 (1) Å, from the mean plane through N(1), C(10), N(2), and Cl or, in other words, by the values of the bond angles between cis ligands (range 89.1 – 91.5 (2)°), which are close to the ideal value of 90° . The interatomic distances between H(6) and H(16) of the bzta ligands and the rhodium (2.810 (6) and 2.950 (5) Å) are short enough to suppose interatomic contacts, which are localized in the spatial area of the vacant position. This fact is detected in the ^1H NMR spectrum as a shift of the resonance due to these protons to lower field. We have previously described this shift as characteristic of the coordination of the bzta ligand as binucleating⁷ and as bridging^{9,17} to three metal atoms.

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The metal-metal separation, 2.6266 (4) Å, is one of the shortest observed for Rh-Pt bonds¹⁸ and is also smaller than the bite of the bzta ligands, N(1)···S(1) = 2.711 (4) and N(2)···S(2) = 2.709 (4) Å. This metal-metal distance is clearly shorter than other intermetallic distances reported in related complexes where metals are bridged by two bzta ligands, e.g. 2.676 (2) Å in the binuclear $[\text{Ir}(\mu\text{-C}_7\text{H}_4\text{NS}_2)_2\text{I}(\text{CO})_2]_2$ ⁸ or 2.731 (2) Å in the tetranuclear $[\text{Ir}_4(\mu\text{-C}_7\text{H}_4\text{NS}_2)_4\text{I}_2(\text{CO})_8]$ ⁸, although in these cases the benzothiazole-2-thiolate ligands are in a relative cis disposition.

Both bridging ligands exhibit a coarse planarity with atom deviations from the least-square planes through all atoms of the ligand lower than 0.035 (5) Å. The dihedral angle between both ideal ligand planes is 12.5 (1)°. These planes are tilted from the platinum coordination plane by 13.3 (1) and 12.9 (1)°. The bonding of the rhodium and platinum atoms to the bridging ligands appears to be unexceptional with all metal-ligand bonds agreeing well with those in related species.¹⁹ The C(1)-S(1) and C(11)-S(3) bond distances, 1.714 (5) Å, are in the lower part of the range found in related complexes²⁰ with the analogous pyridine-2-thiolate ligand, 1.72–1.86 Å, and indicate that the exocyclic C-S bond of the bridging ligands has a significant thione character. All the endocyclic C-S distances (mean 1.739 Å) are significantly shorter than typical C-S single-bond distances, showing clearly the aromaticity of the bridging ligands, but are slightly longer than the exocyclic C-S distances, suggesting somewhat greater multiple-bond character for the latter ones.

The almost linear disposition of the Rh-Pt-P atoms (165.71 (4)°) is noteworthy. This allows the observation of the $^2J_{\text{RhPt}}$ coupling (17 Hz). The observed Pt-P bond distance, 2.249 (1) Å, is unexpectedly shorter than the Pt-PPh₃ bond distances reported in tetracoordinated Pt(II) complexes (mean value 2.298 (3) Å).²¹ Furthermore, a lengthening of the metal-donor atom distance trans to the metal-metal bond would be expected, as it has been described in several reports due to the high structural trans effect of intermetallic bonds.²² That is the case in $[\text{Pt}_2(\mu\text{-dpm})_2\text{H}(\text{dpm})]^+$, where the length of the Pt-P unit trans to the Pt-Pt bond is 2.347 (4) Å while the range of the other four Pt-P bonds is 2.248 (3)–2.289 (4) Å.²³ In our case, no evidence of the proposed structural trans effect is observed as the above mentioned Pt-P distance is even smaller than the mean Pt-PPh₃ bond distance. This Pt-P distance is also shorter than all previous values reported for heterometallic Rh-Pt complexes where a PPh₃ group is coordinated in a relative trans disposition to the Rh-Pt single bond.²⁴

The Rh-Cl bond distance, 2.338 (1) Å, is also markedly smaller than the mean for terminal chloride ligands linked to penta- and hexacoordinated Rh atoms (2.400 and 2.374 Å, respectively).²¹ This distance is also shorter than the described values in structurally related heteronuclear complexes $\text{RhPd}(\mu\text{-Ph}_2\text{Ppy})_2(\text{CO})\text{Cl}_3$ (2.399 (3) Å)^{4f} or in $\text{Rh}(\text{CO})\text{Cl}(\mu\text{-Ph}_2\text{AsCH}_2\text{PPh}_2)_2\text{PtCl}_2$ (2.363 (2) Å),²⁵ where the chloro ligand is also trans to a carbonyl group. Except for the presence of the vacant coordination site, no apparent reason justifies these anomalous distances.

On the other hand, the carbonyl group is linearly coordinated (Rh-C(10)-O(10) = 178.4 (5)°, showing a Rh-C length of 1.841

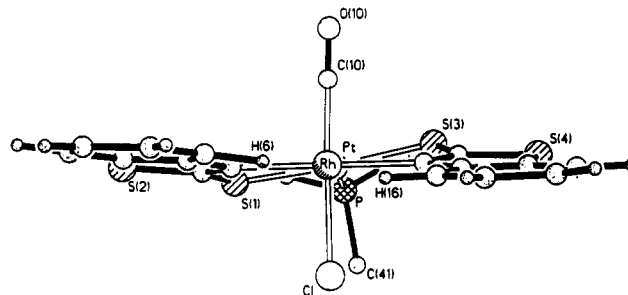
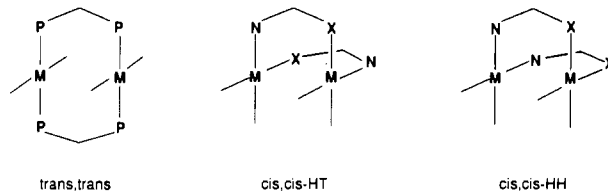


Figure 3. Molecular view of **2** along the metal-metal bond from the vacant coordination site.

(4) Å within the normal range described for this ligand.

The bzta ligand is a member of a class of anionic bifunctional groups that have two donor atoms linked by a carbon, N-C-X⁻. They have the correct geometry and have been shown to act as binucleating ligands binding two metals by the N and X atoms and displaying short bites. 2-Pyridonate,^{6,26} 2-pyridylphenylamide (PhNPy),²⁷ pyridine-2-thiolate,^{7,20,28} 2-mercaptobenzothiazolate,^{20,29} and 2-pyridylmethyl (PyCH₂)³⁰ are known examples. The structures obtained with two of these bridging ligands are invariably in a cis arrangement both in head-to-head (HH) and head-to-tail (HT) isomers, showing cradle structures in contrast with the trans arrangement generally displayed by dpmm and related ligands in binuclear complexes.



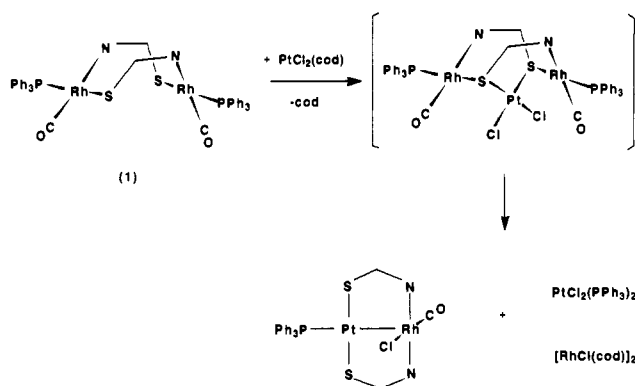
Molecular models show clearly a high flexibility of the bridge framework for the cis arrangement, which allows a wide range of intermetallic distances. This preferred arrangement is maintained on formation of metal-metal bonds as observed in $\text{Ir}_2(\mu\text{-PyS})_2(\text{CO})_4\text{I}(\text{CH}_2\text{I})$ ³¹ and $[\text{Ir}(\mu\text{-bzta})_2(\text{CO})_2]_2$.⁸ The trans arrangement does not show the mentioned flexibility. Moreover, the metal-metal separation in the trans arrangement is similar to the bite of the ligand which corresponds to a short metal-metal bond distance. In this way, the trans arrangement should be found when there is a metal-metal bond.

Compound **2** is the first example of a compound containing just two anionic short-bite ligands in which those ligands adopt a trans disposition. Its diamagnetism and 30 valence electron count requires a metal-metal bond. This gives 16 electrons per metal atom. Such an electron count is usual for diplatinum(I) compounds, but it is rare for dirhodium(II) complexes. Clearly there is an apparent vacant coordination position on the rhodium atom trans to the metal-metal bond. Nevertheless, attempts to introduce ligands, either small molecules such as carbon monoxide, acetonitrile, and pyridine or triphenylphosphine, in this position were not successful. Trying to understand the reasons for the presence of this vacancy together with the lack of reactivity, we have built a model placing a sterically undemanding ligand such as carbon monoxide in this position. This carbonyl group was added to the crystal structure colinear with the Pt-Rh bond (Pt-Rh-C = 180°) and having the same bonding parameters as the real carbonyl

(18) See for instance: (a) ref 15 (range of Pt-Rh = 2.705–2.805 Å); (b) ref 16 (range of Pt-Rh = 2.618–2.691 Å); (c) Martinengo, S.; Ciani, G.; Sironi, A. *J. Am. Chem. Soc.* **1982**, *104*, 328 (range of Pt-Rh = 2.680–2.752 Å); (d) Fumagalli, A.; Martinengo, S.; Ciani, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1381 (range of Pt-Rh = 2.743–2.812 Å).
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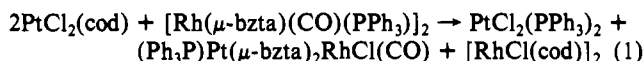
Scheme I



group. This construction shows very short interatomic contacts between the hydrogens H(6) and H(16) and the C and O of the artificially added carbonyl (H(6)-C = 1.33 Å, H(16)-C = 1.54 Å, H(6)-O = 1.17 Å, H(16)-O = 1.36 Å). From these data it is evident that there is not room even for a small ligand, as can be seen in Figure 3, so that the coordination site vacancy is primarily due to steric effects. In fact, this situation is comparable to that in dirhodium(II) and diruthenium(II) complexes with a "lantern" structure³² and in *cis*,HH-(2-methylpyridonato)diplatinum(III) compounds,³³ where steric reasons have been argued to justify the presence of just one single axial ligand.

A second remarkable feature of the structure is the HH disposition of the bridging ligands in the solid state and in solution. Moreover, fluxionality and chemical exchange processes commonly observed in systems with two bridging N-C-S ligands^{2,7,8,34} are not detected for compound **2**. Generally, the complexes with two binucleating N-C-S ligands show the HT arrangement. Even heterobinuclear complexes with the Ph_2PPy ligand have a HT arrangement, for example in $\text{RhPd}(\mu\text{-Ph}_2\text{PPy})\text{Cl}_3(\text{CO})$. In accord with its spectroscopic properties and the charge of the Pt-Rh³⁺ unit, it can be reasonably assumed that platinum and rhodium are in the formal oxidation states +1 and +2, respectively,³⁵ in compound **2**, although the negative charge of the bridging ligands should be delocalized in the N-C-S units. In this way, the reason for the HH arrangement with Rh bonded to the nitrogen atoms is determined by the hard-soft acid-base principle in addition to steric effects.

The process by which the compound **2** is formed is rather complex. The following tentative reaction



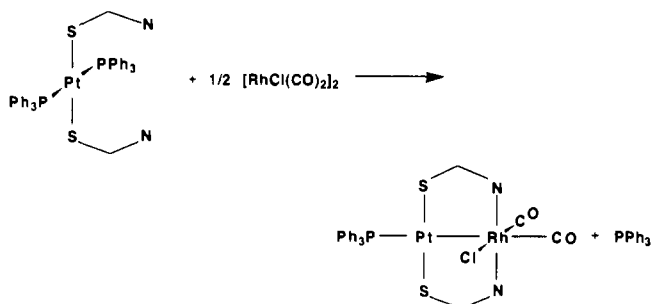
can be written to give account of the isolated compounds although there are other unidentified products. The redistribution of ligands is noteworthy. Remarkably, the ligands chloro and 1,5-cyclo-octadiene, initially coordinated to the platinum, end up in the coordination sphere of the rhodium in the isolated products. Furthermore, the triphenylphosphine migrates in the opposite way. We suggest in view of the observed reorganizations that an associative mechanism leading to an internal redox process should be operative. Although no intermediates are isolated, the reaction should start via coordination of $\text{PtCl}_2(\text{cod})$ to the exocyclic sulfur atoms in complex **1**, which has lone pairs, to give a heterotrimeric complex (see Scheme I). This intermediate could be similar to the complexes $[(\text{cod})_2\text{Rh}_2(\mu_3\text{-bzta})_2\text{AgO}_2\text{ClO}_2]$, $[(\text{cod})_2\text{Rh}_2(\mu_3\text{-bzta})\text{CuCl}]$, and $[(\text{CO})_2(\text{PPh}_3)_2\text{Rh}_2(\mu_3\text{-bzta})_2\text{ML}_2]^+ [\text{ML}_2$

= $\text{Ir}(\text{cod})$, $\text{Pd}(\text{allyl})]$ ¹⁷ where the unit ML_2 would be " PtCl_2 ". In fact, reaction of **1** with PtCl_2 gives a mixture of products in which complex **2** is included.

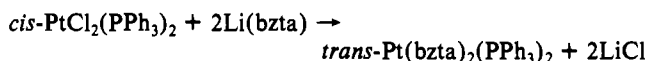
The close proximity of the metallic centers should allow the oxidative addition of a Pt-Cl bond to one of the Rh(I) centers unchaining the redistribution of ligands mentioned before. A precedent of this type of reaction has been observed in the synthesis³⁶ of $[\text{Rh}_2\text{Pd}(\mu\text{-Cl})\text{Cl}_2(\mu\text{-dpma})_2]\text{BPh}_4$ (dpma = bis(diphenylphosphinomethyl)phenylarsine) from $\text{PdCl}_2(\text{PhCN})_2$ and $[\text{Rh}(\text{CO})\text{Cl}(\mu\text{-dpma})]_2$.

The green diamagnetic homologous compound $(\text{Ph}_3\text{P})\text{Pd}(\mu\text{-bzta})_2\text{RhCl}(\text{CO})$ (**3**) is obtained similarly by reaction of $\text{PdCl}_2(\text{cod})$ and $[\text{Rh}(\mu\text{-bzta})(\text{CO})(\text{PPh}_3)]_2$ in moderate yield. Its spectroscopic properties resemble closely those of compound **2**, and hence they should have the same structure. Thus, the doublet observed in the ³¹P NMR spectrum is associated with the linear unit P-Pd-Rh having a small coupling constant (²J_{P-Rh} = 25 Hz); both benzothiazole-2-thiolate ligands are equivalent, giving the expected four resonances in the aromatic region of the ¹H NMR spectrum, and the ν(CO) band (at 2020 cm⁻¹ in CH₂Cl₂) is indicative of the oxidation of the rhodium center. In the solid state this band is split in two at 2008 and 1980 cm⁻¹ and the compound crystallizes with a half-molecule of diethyl ether.

In order to prepare compound **2** or related complexes through a high-yield synthesis, the new compounds $\text{Pt}(\text{bzta})_2(\text{PPh}_3)_2$ and $\text{PtH}(\text{bzta})(\text{PPh}_3)_2$ were prepared. These mononuclear complexes already contain the fragment " $(\text{Ph}_3\text{P})\text{Pt}(\text{bzta})_2$ " or " $(\text{Ph}_3\text{P})\text{Pt}(\text{bzta})$ ", which should avoid redistribution reactions. In addition, they have uncoordinated N donor atoms and hence they should act as metalloligands toward rhodium species which could give rise to a "RhCl(CO)" fragment. For example the following controlled synthesis can be envisaged:



The compound *trans*-Pt(bzta)₂(PPh₃)₂ is readily obtained in good yield by reacting Li(bzta) with *cis*-PtCl₂(PPh₃)₂ in tetrahydrofuran.



Isomerization occurs in the reaction under very mild conditions to give the *trans* isomer as the single product. This isomer displays a singlet resonance flanked by its platinum satellites; the value of ¹J_{P-Pt} (2745 Hz) is characteristic of *trans*-PtX₂(PR₃)₂ compounds.

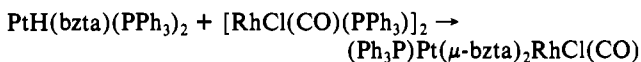
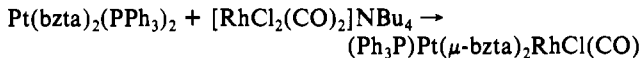
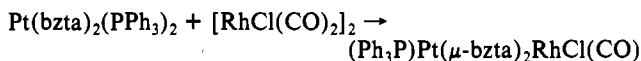
Oxidative addition of 2-mercaptobenzothiazole to $\text{Pt}(\text{PPh}_3)_4$ gives the mononuclear complex *trans*-PtH(bzta)(PPh₃)₂ in high yield. The *trans* disposition of the triphenylphosphine ligands in this complex is supported by the equivalence of the phosphorus nuclei, which display a singlet in the ³¹P NMR spectrum. The value of ¹J_{P-Pt} (3026 Hz) is large in comparison with the range found in *trans*-PtX₂(PR₃)₂ complexes but still smaller than the typical values for *cis*-PtX₂(PR₃)₂ complexes. Selective decoupling experiments split this signal into a doublet (¹J_{P-H} = 12 Hz) on irradiation on the ¹H aromatic region due to coupling with the hydride ligand.

Attempts to obtain complex **2** by reacting mononuclear complexes of platinum with appropriate complexes of rhodium in

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toluene at reflux give the desired product. In particular, oxidation of the neutral and anionic carbonyl complexes of rhodium in the following reactions by complexes **4** and **5** occurs:



Nevertheless mixtures of compounds result, from which the isolated yield of compound **2** is similar or even smaller than in the full described preparation.

In conclusion, we describe here the synthesis and characterization of the first two heterobinuclear complexes with just two short-bite bridging anionic ligands in which they adopt a relative trans disposition. Acting in this way, they bridge a short metal-metal bond as can be anticipated by steric arguments.

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Supplementary Material Available: Tables of thermal parameters (Table S1), positional parameters for hydrogen atoms (Table S2), and full details of crystal data and data collection (Table S3) and listings of bond lengths and bond angles, least-squares planes, and interatomic contacts (17 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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1,5-Cyclooctanediylbis(pyrazol-1-yl)borate: A Ligand with Enhanced Agostic Interaction

Swiatoslaw Trofimenko, Joseph C. Calabrese, and Jeffery S. Thompson*

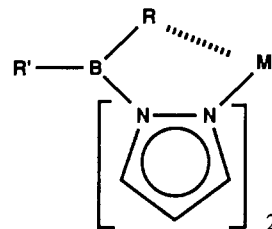
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1,5-Cyclooctanediylbis(pyrazol-1-yl)borate (=L*) is a new type of $[\text{R}_2\text{B}(\text{pz})_2]^-$ ligand in which the R_2 groups form part of a rigid bicyclic system and in the complexes of which the pseudoaxial bridgehead hydrogen is forced into close proximity to the metal. The complexes ML^*_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}$), $\text{ML}^*(\eta^3\text{-CH}_2\text{CRCH}_2)(\text{CO})_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{H}, \text{Me}, \text{Ph}$), and $\text{PdL}^*(\eta^3\text{-CH}_2\text{CRCH}_2)$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$) were synthesized. The agostic interaction was confirmed in $\text{ML}^*(\eta^3\text{-CH}_2\text{CRCH}_2)(\text{CO})_2$ complexes by IR and NMR spectroscopy and by an X-ray structure determination of CoL^*_2 . There was no agostic interaction in the mixed complex $\text{CoL}^*(\text{HB}(3\text{-}i\text{-Pr-4-Br-pz})_3)$, the bridgehead hydrogen being 2.62 Å from the Co atom. The complex $\text{Co}(\text{L}^*)_2$ crystallizes in the space group $P\bar{1}$ with 1 molecule per unit cell of dimensions $a = 7.665$ (1) Å, $b = 9.301$ (2) Å, $c = 10.551$ (3) Å, $\alpha = 88.56$ (2)°, $\beta = 80.27$ (2)°, $\gamma = 66.26$ (2)° at -70 °C. Least-squares refinement of 178 variables led to a value of the conventional R index (on F) of 0.046 and $R_w = 0.066$ for reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to four pyrazolyl nitrogen atoms from two L* ligands and two H atoms from the borabicyclononane ring systems, is pseudooctahedral with the pyrazolyl nitrogen atoms in a planar arrangement and the agostic hydrogen atoms in axial positions. The complex $\text{CoL}^*(\text{HB}(3\text{-}i\text{-Pr-4-Br-pz})_3)$ crystallizes in the space group $P\bar{1}$ with 4 molecules per unit cell of dimensions $a = 10.075$ (2) Å, $b = 20.640$ (10) Å, $c = 20.700$ (10) Å, $\alpha = 99.09$ (4)°, $\beta = 102.91$ °, and $\gamma = 97.98$ (2)° at -70 °C. Least-squares refinement of 917 variables led to a value of the conventional R index (on F) of 0.055 and $R_w = 0.057$ for reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to five pyrazolyl nitrogen atoms from two different polypyrazolylborate ligands, is square pyramidal.

Introduction

Over the years since their introduction, the polypyrazolylborates¹ have been viewed in a dichotomous way: either as tridentate ligands (when $[\text{RB}(\text{pz}^*)_3]^-$) analogous to the cyclopentadienyl anion or as bidentate ligands (when $[\text{R}_2\text{B}(\text{pz}^*)_2]^-$) similar to β -diketonates. As the area was explored more thoroughly, it became more and more apparent that the two structures mentioned above are in reality members of a continuum within one family, since instances are known where $[\text{RB}(\text{pz}^*)_3]^-$ functions as a bidentate ligand and, conversely, $[\text{R}_2\text{B}(\text{pz}^*)_2]^-$ may coordinate in a tridentate fashion.

The unifying feature in all polypyrazolylborate complexes is the six-membered ring $\text{M}(\text{RR}'\text{B}(\mu\text{-pz}^*)_2)$, where M may contain additional ligands and where R, R' can be H, alkyl, aryl, NR_2 , ArS, or pz^* ($\text{pz}^* = 1\text{-pyrazolyl}$ or substituted 1-pyrazolyl). Because of the bond angles and distances involved, this ring has almost always a boat structure of varying depth. In such a structure the pseudoaxial group R is curled toward the metal and may bond to or interact with it.²



We can distinguish two categories of polypyrazolylborate ligands: those where the pseudoaxial $\text{R} = \text{pz}^*$ and those where the coordinating pseudoaxial R is anything but pz^* ; it can, however,

- (2) On the basis of their structural features and coordinative behavior it is very tempting to call the geminal polypyrazolyl ligands, and polypyrazolylborates in particular, "scorpionates", as the scorpion is the only species whose prey-attacking behavior resembles that of polypyrazolylborate coordination to metal ions. The two identical pz^* groups, symmetrically coordinated to the metal are the "claws", while the pseudoaxial substituent R, arching toward the metal ion, is the "sting". While the "claws" always grab the metal ion, an attack by the sting is an option, which may or may not be exercised, depending on a variety of factors pertaining to the structural features of the ligand and the metal.

(1) Trofimenko S. J. *Am. Chem.* 1966, 88, 1842-1844.