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Use of pyrazolyl ligands for the formation of a bimetallic cobalt-ruthenium complex

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Dedicated with pleasure to Uwe Rosenthal on the occasion of his 60th birthday.

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ABSTRACT

A straightforward route to $Ru(pyz)_2(Hpyz)_4$ (Hpyz = pyrazole) has been developed. This has been found to react readily with a modified Co(pyrazolylborate)Cl complex in the presence of triethylamine as an HCl acceptor to yield a bimetallic cobalt–ruthenium complex, in which the two metals are each six-coordinate, and bridged by three pyrazolyl anions. Both species have been characterized structurally, as has a modified Co(pyrazolylborate)₂ complex.

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POLYHEDRON

1. Introduction

The construction of molecules containing di- and poly-metallic units has been a topic of great interest for some time. Such species have attracted attention as they may be characterized by interesting metal-metal bonding interactions, mixed valency, complex electronic and magnetic properties, and could potentially lead to useful cooperative chemical reactivity. In the latter area, there has been specific interest in the preparation of molecular cobaltruthenium complexes, given these metals' Fischer–Tropsch activities, and the fact that ruthenium is used commercially to improve the activities of cobalt catalysts [1]. While the incorporation of the ruthenium is at least initially non-selective, migration to the cobalt domains occurs and leads to significant improvement in catalyst properties.

Although a more selective "redox targeting" approach has been developed [2], in which cobalt is selectively delivered to ruthenium oxide on various supports, much use has also been made of ligands which can bridge two metal centers in close proximity. Excluding compounds containing potentially deleterious species such as other metals, metalloids, or phosphorus, cobalt–ruthenium bime-tallics have readily been accessed using ligands such as cyanides [3] or poly(cyclopentadienyls) [4], or others which can at least support the formation of bi- and poly-metallic clusters, and have been definitively characterized structurally [5]. In general, these ligands such as CO [6–8], may still require significant effort for

* Corresponding author. *E-mail address:* ernst@chem.utah.edu (R.D. Ernst). the preparation of the desired Co–Ru species, which often occurs in relatively low yield. Additional approaches have led to bimetallic salts, in which one metal occurs in the cation, the other in the anion [5c,9]. In one report, pyrazolyl ligands have been used to link cobalt and ruthenium, as well as other metal combinations, in organometallic complexes [10]. Herein we extend this approach, in order to link cobalt and ruthenium simultaneously in a nonorganometallic environment. Other heterobimetallic combinations linked by the simple pyrazole ligand have been prepared, most [11] but not all [12] being organometallic or carbonyl complexes. One can certainly expect that this approach can be expanded to the preparations of a much wider variety of bi- and poly-metallic complexes.

2. Experimental

All reactions were carried out in Schlenk apparatus under a nitrogen atmosphere. C_6D_6 and THF were dried and deoxygenated by distillation from sodium or sodium benzophenone ketyl under a nitrogen atmosphere, while other solvents were passed through activated alumina columns under a nitrogen atmosphere. Analytical data were obtained from E&R Microanalytical and Desert Analytics Laboratories.

2.1. K[HB(3-ⁱPr-4-Br-pyz)₃]

A modification of previously reported syntheses was used to prepare this species [13]. First, 3-^{*i*}Pr-pyrazole, an air-stable and colorless liquid, was prepared in a two-step reaction. Twenty milliliters of ethyl formate was added to 10.8 g (0.20 mol) of sodium methoxide in 100 mL of toluene. While being stirred, the colorless



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solution was combined with 21.4 mL (0.20 mol) of 3-methyl-2butanone. An exothermic reaction ensued and the mixture turned vellow immediately. After 30 min, 100 mL of distilled water was added and the mixture was kept stirring for another 20 min. In another flask, 10 g (0.20 mol) of hydrazine monohydrate was added to 100 mL of 2 M HCl carefully, and the solution was cooled to room temperature with a cold bath. Then, the mixture from the first reaction was transferred to a separatory funnel, from which the yellow aqueous phase was dripped into the hydrazine hydrochloride solution. The reaction mixture was stirred for 15 min while an amber oil appeared. KOH (7.0 g) was added to yield a basic solution. The orange product was extracted with 40 mL of ether and dried with magnesium sulfate. After the ether was removed with a rotoevaporator, the mixture was heated to 150 °C and the product 3-^{*i*}Pr-Hpyz was distilled under dynamic vacuum (BP: 59 °C at 10⁻³ torr). Yield: 10.8 g (49%).

In the next step, 5.0 mL (0.097 mol) of bromine was added to a suspension of 10.8 g (0.097 mol) 3-ⁱPr-Hpyz in 125 mL of water in a flask cooled by a cold bath. After 30 min, the solution was neutralized with 4.1 g (0.10 mol) of NaOH, yielding a yellow oil. It was extracted with 20 mL of CH₂Cl₂ and dried with magnesium sulfate. The concentrated product was heated to 160 °C slowly (overheating causes decomposition) and distilled under dynamic vacuum (BP: 75 °C at 10^{-3} torr). Yield: 11.8 g (62%). 3-ⁱPr-4-bromopyrazole is an air-stable, colorless liquid, but often is contaminated with some light yellow impurity.

Subsequently, 0.54 g (0.010 mol) of KBH₄ powder was added to 9.5 g (0.050 mol) of the above-prepared 3-ⁱPr-4-Br-Hpyz, and thereafter stirred at 125 °C for 5 h, during which time about 100 mL of hydrogen gas was generated. The temperature of the mixture was raised to 180 °C and the reaction continued for 10 h or until another 600 mL of hydrogen was evolved. After being cooled down, the flask was carefully evacuated and the residual pyrazole was distilled at 185 °C under dynamic vacuum. The crude product was cooled and mixed with 30 mL of hexane. It was stirred until the white solid was well dispersed. The product was collected by filtration and washed with hexane. Yield: 2.9 g (46%). KHB(3-ⁱPr-4-Br-pyz)₃ is an air-stable, white solid that dissolves easily in THF.

The distillations in the first two steps were very important, because the impurities are extremely hard to separate from the thick oily product by other means. In the third step, the reaction progress can be difficult to control, leading to some bis- or tetrakis-(pyrazolyl)borate salt as minor byproducts. These may be separated by crystallization or filtration.

2.2. $K[B(^{i}Pr-Br-pyz)_{4}]$

The potassium salt of the tetrapyrazolylborate ligand was prepared similar to Trofimenko's [13c] method for other polypyrazolylborate ligands. Under nitrogen, 0.61 g (11 mmol) of potassium borohydride was suspended in 12.5 g (66 mmol) of distilled 3-isopropyl-4-bromopyrazole (see Section 2.1). With vigorous stirring, the mixture was heated to 120 °C with the evolved hydrogen gas being passed through a -78 °C cold trap to a wet-test meter. In the reaction mixture, borohydride started to dissolve into the pyrazole. The slurry was kept at 120 °C for 3 h and then the temperature was raised to 180 °C and the reaction continued for another 12 h or until 750 mL of hydrogen gas, as monitored by the wet-test meter, was generated. To eliminate all unsaturated side products, the temperature was ultimately kept at 210 °C for two further hours. Once cooled to below 70 °C, the flask was carefully evacuated and the unreacted pyrazole was distilled at 180 °C and 0.3 Torr. The remaining material was mixed with 40 mL of hexane and sonicated until it became well dispersed. A white solid was collected by filtration on a frit, washed with hexane, and dried. It is stable in air and can be further purified by recrystallization from THF. Yield: 3.94 g, 45%.

2.3. Ru(pyz)₂(Hpyz)₄, 2

To 0.50 g (1.8 mmol) of $[Ru(COD)Cl_2]_x$ [14] in 10 ml of methanol under nitrogen were added 0.80 g (12 mmol) of pyrazole and 0.80 g (7.5 mmol) of ground Na₂CO₃ in a heavy-wall borosilicate glass tube. The mixture was stirred under 3 bar of hydrogen at 50 °C for 40 h. The color of the solution changed from dark red to orange. After cooling to room temperature, the slurry was transferred to a Schlenk flask. Fifteen milliliter of CH₂Cl₂ was used to extract the product from the last trace of Na₂CO₃ left in the reaction tube. After all the solvent was removed in vacuo, the residue was extracted with 30 mL of CH₂Cl₂ and filtered through a frit with a Celite pad. The filtrate was dried in vacuo and washed with two 10 mL portions of ether and one 5 mL portion of acetone. Excess pyrazole was removed by sublimation at 60 °C under vacuum. The crude product often had a reddish tinge, though the pure product should be yellow. However, NMR analysis showed that it was pure enough for further reactions. Yield: 0.55 g, 60%. The solid product appeared stable in the air for a short period of time. However in solution, it underwent decomposition on contact with oxygen to give an uncharacterized oily product. It changed slowly to a deep red color even in an inert environment. Crystals suitable for an X-ray diffraction study were obtained by cooling a concentrated CH_2Cl_2 solution to -30 °C overnight.

Anal. Calc. for C₁₈H₂₂N₁₂Ru: C, 42.60; H, 4.34. Found: C, 42.04; H, 3.86%.

¹H NMR (300 MHz, CD_2Cl_2 , ppm): 7.79 (d, 6H, J = 2.4 Hz, H1,1',4,4',7,7'), 6.68 (d, 6H, J = 1.9 Hz, H3,3',6,6',9,9'), 6.18 (dd, 6H, J = 2.3, 2.0 Hz, H2,2',5,5',8,8'). ¹³C{¹H} NMR (75 MHz, CDCl₃, ppm): 143.4 (C1,4,7), 132.5 (C3,6,9), 105.6 (C2,5,8).

2.4. Ru(Hpyz)₃(μ-pyz)₃Co(ⁱPr-Br-pyz)₃BH, **4**

To a slurry of 0.20 g (0.39 mmol) of $Ru(pyz)_2(Hpyz)_4$ in 15 ml of CH₂Cl₂ at -78 °C was added 0.26 g (0.39 mmol) of CoCl[HB(^{*i*}Pr-Brpyz)₃] [13a] in 5 mL of CH₂Cl₂ under nitrogen. The green mixture was stirred for several minutes, at which time 55 µL of NEt₃ (0.39 mmol) was added dropwise, while all solids dissolved to produce a red solution. The flask was allowed to warm to room temperature over the course of 2 h, during which time much orange solid precipitated out and the solution changed to a lighter color. All volatiles were removed in vacuo. The powder was washed with two 8 mL aliquots of ether, and then was extracted with 25 ml of toluene with sonication, which was required to help dissolution. The solution was filtered through a medium frit with a Celite pad and the solvent was removed in vacuo. The product was collected as an orange powder. Yield: 0.32 g, 71%. Crystals suitable for an X-ray diffraction study were grown by evaporating an ether solution in an H-tube to CH₂Ph₂.

Anal. Calc. for C₃₆H₄₆BBr₃N₁₈RuCo: C, 37.85; H, 4.03; N, 22.08. Found: C, 38.82; H, 3.98; N, 21.16%.

2.5. Co[(ⁱPr-Br-pyz)₂B(ⁱPr-Br-pyz)₂]₂, 5

To 8 mL of an aqueous solution containing 0.75 g (2.6 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ and 0.77 g (10.0 mmol) of KCl was added an equal volume of methanol, followed by 0.82 g (1.0 mmol) of KB(^{*i*}Pr-Br-pyz)₄ in 8 mL of THF. The color of the solution changed to purple immediately. After several minutes, it was diluted to twice its original volume with water, which resulted in precipitation of a purple solid, while the solution changed back to orange-red. The mixture was filtered though a medium frit, washed with two 15 mL aliquots of toluene, followed by 10 mL of CH₂Cl₂, yielding

0.66 g (42%) of purple solid. The product is air stable, soluble in CH₂Cl₂ and sparingly soluble in toluene. Crystals suitable for an X-ray diffraction study were obtained by slowly evaporating a concentrated CH₂Cl₂ solution from one side of an H-shaped tube to CH₂Ph₂ in the other side.

Anal. Calc. for $C_{48}H_{64}B_2Br_8N_{16}$ Co: C, 36.24; H, 4.04; N, 14.14. Found: C, 36.09; H, 3.90; N, 14.05%.

2.6. Crystallographic studies

Single crystals for the diffraction studies were attached to glass fibers using Paratone oil, and then transferred to a Nonius Kappa CCD diffractometer, where they were maintained at 150(1) K for unit cell determination and data collection. The structures were solved using direct methods and Fourier programs in sIR-97, and thereafter further refined using the SHELXL-97 program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **2** were refined isotropically, while for **4** and **5**, the hydrogen atoms were allowed to ride on their attached atoms. Pertinent crystal and data collection parameters are provided in Table 1.

2.7. TPR studies of supported Ru/CO species

Two FTS catalysts were prepared in the same way except for their metal sources. One catalyst precursor was compound **2**, while the other was a mixture of $Ru(acac)_3$ and $Co(NO_3)_2$ · $6H_2O$ in a 1:1 M ratio, used in an amount designed to give the same metal content as obtained from the bimetallic complex. They were loaded separately onto alumina supports by solution phase (bimetallic in toluene; others in THF) and calcined at 300 °C.

3. Results and discussion

As $[RuCl_2(1,5-COD)]_n$ (COD = cyclooctadiene) has been shown to be a useful reagent for the formation of $RuCl_2(tmeda)_2$ (tmeda = tetramethylethylenediamine) under hydrogenation conditions [15], an analogous reaction was attempted using pyrazole (Hpyz, **1**), in the presence of Na_2CO_3 which could serve to neutralize any HCl that might be generated. Indeed, under these condi-

Table 1

 $Crystallographic parameters for Ru(pyz)_2(Hpyz)_4, HB(3-i-C_3H_7-4-Br-C_3N_2H)_3Co(C_3N_2H_3)_3Ru(C_3N_2H_4)_3, and Co[\kappa^2-(3-i-C_3H_7-4-Br-C_3N_2H)_4B]_2.$

Formula	$C_{18}H_{22}N_{12}Ru$	C36H46BBr3CoN18Ru	C48H64B2Br8CoN16
Formula weight	507.55	1141.5	1585
Temperature (K)	150(1)	150(1)	150(1)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	cubic	monoclinic
Space group	Pnaa	P213	C2/c
Unit cell dimensions			
a (Å)	7.4189(2)	16.9893(5)	25.9481(6)
b (Å)	16.6616(3)	16.9893(5)	11.3503(3)
c (Å)	17.0220(5)	16.9893(5)	21.3567(3)
β (°)	90	90	98.0603(12)
Volume (Å ³)	2104.10(9)	4903.7(2)	6227.8(2)
Z	4	4	4
D _{calc}	1.602	1.546	1.69
Absorption coefficient (cm ⁻¹)	7.79	31.37	54.55
θ Range (°)	3.4-27.5	2.7-27.5	2-27.5
Limiting indices	$-9 \leqslant h \leqslant 9$	$-22\leqslant h\leqslant 22$	$-33 \leqslant h \leqslant 33$
	$-21 \leqslant k \leqslant 21$	$-15 \leqslant k \leqslant 15$	$-14 \leqslant k \leqslant 13$
	$-21 \leqslant l \leqslant 22$	$-14 \leqslant l \leqslant 14$	$-27 \leqslant l \leqslant 27$
Number of reflections collected	4442	3607	12147
Number of independent reflections $[I > 2\sigma(I)]$	2418; 2	3607; 2	7133; 2
R(F)	0.0238	0.0682	0.0472
$R_w(F^2)$	0.0588	0.171	0.1075
Maximum/minimum differences Fourier peak ($e Å^{-3}$)	0.31, -0.73	1.12, -0.75	0.70, -1.14
Data completeness	99.80%	98.30%	99.60%

tions, six pyrazoles were incorporated, two of which were deprotonated, to yield *trans*-Ru(pyz)₂(Hpyz)₄ (**2**).



The structure of $Ru(pyz)_2(Hpyz)_4$, **2**, is presented in Fig. 1, while pertinent bonding parameters are provided in Table 2. The complex has crystallographically imposed inversion symmetry. As no disorder between the Hpyz and pyz ligands was observed, this necessitates a *trans* orientation of the two pyrazolyl anions. The Ru–N distances for their coordinated nitrogen atoms (N1) can be seen to be longer than those for the Hpyz ligands, 2.1155(14) versus 2.0838(14) and 2.0891(14) Å. The N-N distance for the anionic pyz ligands, 1.384(2) Å, is longer than those for the neutral ligands, which average 1.357(1) Å. The angles between the Hpyz and pyz ligands are all quite close to expectation, falling within 0.13(5)° of 90°, while the *cis* angles between the Hpyz ligands alternate between 87.83(6)° and 92.17(6)°. An interesting distortion is observed about the coordinated nitrogen atoms, such that the Ru-N-N' angles (122.57(10)°, 123.51(11)°, 122.89(11)°) are significantly smaller than the Ru–N–C angles (130.11(12)°, 131.51(12)°, 132.39(12)°).





Fig. 1. The structure of Ru(pyz)₂(Hpyz)₄.

Table 2				
Selected	bonding	parameters	for	Ru(pyz) ₂ (Hpyz) ₄ .

Bond distances (Å)			
Ru–N1	2.1155(14)	N1-N2	1.384(2)
Ru–N3	2.0838(14)	N3-N4	1.355(2)
Ru-N5	2.0891(14)	N5-N6	1.359(2)
Bond angles (°)			
N1-Ru-N3	90.13(5)	N1-Ru-N3'	89.87(5)
N1-Ru-N5	89.91(5)	N1-Ru-N5'	90.09(5)
N3-Ru-N5	92.17(6)	N3-Ru-N5'	87.83(6)
Ru-N1-N2	122.57(10)	Ru-N1-C1	130.11(12)
Ru-N3-N4	123.51(11)	Ru-N3-C4	131.51(12)
Ru-N5-N6	122.89(11)	Ru-N5-C7	132.39(12)



The CoCl[$(3-i-C_3H_7-4-Br-C_3N_2H)_3BH$] complex (**3**) appeared to be an ideal candidate for reaction with **2**, as **3** had been previously used to prepare an organobimetallic cobalt–ruthenium complex [10]. The bromo and isopropyl substituents prevent incorporation of two κ^3 pyrazolylborates into the cobalt coordination sphere, while perhaps allowing for subsequent incorporation of three simple, bridging pyrazolyl ligands. Indeed, the combination of **2** and **3** in CH₂Cl₂, in the presence of triethylamine, led to the formation of the desired bimetallic, **4**, in good yield.



Fig. 2. The structure of the HB(3-i-C_3H_7-4-Br-C_3N_2H)_3Co(C_3N_2H_3)_3Ru(C_3N_2H_4)_3 complex.



The structure of the bimetallic complex may be seen in Fig. 2, while pertinent bonding parameters are listed in Table 3. The complex lies along a C₃ axis of symmetry, resulting in one unique pyrazole ligand, and two unique pyrazolyl ligands, one bridging the two metals, the other bridging the cobalt and boron centers. The metal ions are linked by three bridging pyrazolyl ligands, and for cobalt the pseudo octahedral coordination sphere is completed by the anionic pyrazolylborate ligand, while for ruthenium, there are three additional pyrazole ligands. This is consistent with the expected presence of Co(II) and Ru(II) centers. The Co-Ru distance of 3.666(2) Å is sufficiently long that one can discount the presence of significantly favorable Co-Ru bonding. For other bonding comparisons, reference can be made to the parameters set out in Scheme 1. Regarding the distances, one can observe that the Co-N distances to the boron-attached ring are substantially longer than those to the ruthenium-attached ring, indicative of the particularly strong interaction of nitrogen with the electropositive boron atom. For ruthenium, the distances to the neutral pyrazole ligands appear to be slightly shorter than those for the bridging pyrazolyl ligands, consistent with the results for $Ru(pyz)_2(Hpyz)_4$ (vide supra). All Co-N distances are longer than the Ru-N distances, due to the former metal ion's high spin d⁷ configuration, and the latter's low spin d⁶ configuration.

Table 3 Selected bonding parameters for HB(3-i-C_3H_7-4-Br-C_3N_2H)_3Co(C_3N_2H_3)_3Ru(C_3N_2H_4)_3.

Bond distances (Å)			
Ru-N1	2.060(7)	Ru-N3	2.080(7)
Co-N4	2.102(8)	Co-N5	2.233(7)
B-N6	1.544(9)	N1-N2	1.328(13)
N3-N4	1.333(10)	N5-N6	1.358(10)
Co-Ru	3.666(2)		
Bond angles (°)			
N1-Ru-N1'	92.8(3)	N4-Co-N4'	91.6(3)
N1-Ru-N3	86.0(3)	N4-Co-N5	175.6(3)
N1-Ru-N3'	89.2(3)	N4-Co-N5'	90.8(3)
N1-Ru-N3''	177.7(3)	N4-Co-N5"	92.0(3)
N3-Ru-N3'	91.9(3)	N5-Co-N5'	85.4(3)
Ru-N1-N2	119.0(6)	Co-N4-N3	123.3(5)
Ru-N3-N4	123.9(5)	Co-N5-N6	115.8(5)
Ru-N1-C1	136.8(7)	Co-N4-C6	127.2(6)
Ru-N3-C4	127.7(6)	Co-N5-C7	135.5(6)
N6-B-N6′	109.4(6)		



Scheme 1. Pertinent bonding parameters for the bimetallic Ru-Co complex.

The coordination angles around the metals show slight distortions. The N–Co–N angles involving the pyrazolylborate ligand are 85.4(3)°, which likely leads to an expansion of the N–Co–N angles for the other three nitrogen atoms, to 91.6(3)°. A similar difference arises around ruthenium, whose N–Ru–N angles involving the nitrogen atoms of the bridging pyrazolyl ligands are 91.9(3)°, close to the value of cobalt, while the corresponding angles for the nonchelating pyrazole ligands are 92.8(3)°.



Fig. 3. The structure of $Co[(3-i-C_3H_7-4-Br-C_3N_2H)_4B]_2$.

Not surprisingly, significant distortion of the bond angles about the nitrogen donor centers in the pyrazolylborate ligand occurs, in order to optimize the B–N and Co–N interactions. Thus, the Co–N5–N6 angle of $115.8(5)^{\circ}$ is much smaller than the Co–N5– C7 angle, $135.5(6)^{\circ}$. For these two angles to become more similar, without further angular distortion, the Co–N bonds would need to be lengthened. There is also a smaller distortion of the angles about N6, which prevented an even greater difference in angles about N5. Interestingly, while there is little such distortion for the bridging pyrazolyl ligands, the neutral pyrazole ligands show a significant difference in the respective Ru–N1–N2 and Ru–N1–C1 angles, $119.0(6)^{\circ}$ versus $136.8(7)^{\circ}$.

Although the presence of bromo and isopropyl substituents on the pyrazole ligand may prevent the incorporation of two tridentate ligands in a metal coordination sphere, it has been found that with two equivalents of these disubstituted pyrazolyl ligands, both may be incorporated as bidentate ligands. The structure of the resulting species, $Co[(3-i-C_3H_7-4-Br-C_3N_2H)_4B]_2$ (5) can be seen in Fig. 3, with pertinent bonding parameters presented in Table 4. The complex has crystallographically imposed C₂ symmetry, leading to pseudo-tetrahedral coordination as a result of the κ^2 coordination by each ligand. Clearly the presence of the $i-C_3H_7$, and perhaps Br, substituents has prevented $bis(\kappa^3)$ coordination for the complex. The two unique Co-N distances are similar, averaging 1.984(2) Å. The chelating N1-Co-N3 angle is naturally the smallest observed, at 99.24(12)°, with the four non-chelating N-Co-N angles coming at 108.72(19)°, 112.02(12)° (two), and 125.28(19)°. Nonetheless, the N1-Co-N3 angle is significantly larger than its counterparts in the bimetallic complex, and is accompanied by a larger N2–B–N4 angle, 113.4(3)°. As in complex 4, some angular distortion about the Co-bound nitrogen centers is observed. Thus, the Co-N1-N2 and Co-N3-N4 angles are again smaller, at 118.3(2)° and 123.4(2)°, while the Co-N1-C1 and Co-N3-C7 angles are 131.4(3)° and 128.4(3)°, respectively. The lesser difference in this case seems then to lead to less distortion about N2 and N4.



Temperature Programmed Reduction (TPR) was performed on two mixed Co/Ru samples supported on alumina, one prepared from bimetallic complex **4**, while the other was prepared by load-

Table 4	
Selected bonding parameters for $Co[\kappa^2-(3-i-C_3H_7-4-Br-C_3N_2H)_4B]_2$.	

Bond distances (Å)			
Co-N1	1.978(3)	Co-N3	1.990(3)
B-N2	1.547(5)	B-N4	1.552(5)
B-N5	1.520(5)	B-N7	1.513(6)
N1-N2	1.374(4)	N3-N4	1.374(4)
N5-N6	1.375(5)	N7-N8	1.368(5)
Bond angles (°)			
N1-Co-N1'	125.3(2)	N3-Co-N3'	108.7(2)
N1-Co-N3	99.2(1)	N1-Co-N3'	112.0(1)
Co-N1-N2	118.3(2)	Co-N3-N4	123.4(2)
B-N5-N6	118.3(3)	B-N7-N8	119.7(3)
Co-N1-C1	131.4(3)	Co-N3-C7	128.4(3)
B-N5-C13	128.7(4)	B-N7-C19	129.4(3)



Fig. 4. TPR of physically mixed and bimetallic catalysts.

ing the two metals from separate sources. The TPR results are shown in Fig. 4. Four stages of reduction were observed at 180 °C, 310 °C, 420 °C and 620 °C for the bimetallic catalyst, while only one reduction step occurred, at a temperature around 210 °C, for the physically mixed catalyst. The former showed some promising advantages because its starting reduction temperature was lower, and the overall hydrogen consumption was higher, thus leading to higher reducibility of both ruthenium and cobalt contents, which might be caused by the bimetallic interactions. The unique properties could translate to a longer catalyst lifetime and higher percentage of active sites for FTS catalysis with the same metal loading.

4. Conclusions

The pyrazolyl ligand has been shown to provide an effective means to link cobalt and ruthenium together in a coordination complex. This may offer advantages compared to organometallic or phosphorus-containing alternatives. As demonstrated by TPR data, the nature of bimetallic catalysts prepared with bridging pyrazolyl ligands may differ dramatically from what is obtained through random incorporation.

The Ru(pyz)₂(Hpyz)₄ complex appears ideal for the formation of numerous other heterobimetallic species. The two anionic ligands offer two readily available donor sites for other metal centers, and obviously from the results reported herein, others can become available via deprotonation. In fact, this means it should be possible to link the ruthenium center to at least a second additional metal. Furthermore, a variety of other $M(pyz)_x(Hpyz)_{6-x}$ complexes should be accessible, perhaps quite promisingly from deprotonation of known cationic M(Hprz)₆ species [16] and thus this approach could ultimately lead to numerous other bimetallics.

The negative charge carried by the pyrazolyl ligand appears to greatly facilitate the formation of bimetallics, as compared to potential alternatives such as pyridazine or 1,8-naphthyridine, though these neutral species should yield shorter metal-metal contacts in any bimetallics they form, due to their differing geometries.

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Appendix A. Supplementary data

CCDC 813861, 813862 and 813863 contains the supplementary crystallographic data for compounds 2, 4, and 5. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] M.E. Dry, in: A.P. Steynberg, M.E. Dry (Eds.), "Fischer-Tropsch Technology" Studies in Surface Science and Catalysis, vol. 152, Elsevier, New York, 2004, p. 560
- R.D. Ernst, E.M. Eyring, G.C. Turpin, B.C. Dunn, Methods of Selectively [2] Incorporating Metals onto Substrates, US Patent, 2008 7, 429,404.
- [3] (a) Y. Kim, K.-T. Youm, M.-J. Jun, Bull. Korean Chem. Soc. 19 (1998) 1023;
 (b) Z.N. Chen, R. Appelt, H. Vahrenkamp, Inorg. Chim. Acta 309 (2000) 65; (c) S.M. Contakes, M.L. Kuhlman, M. Ramesh, S.R. Wilson, T.B. Rauchfuss, Proc. Natl. Acad. Sci. USA 99 (2002) 4889;
 - (d) D. Yoshioka, M. Mikuriya, M. Handa, Chem. Lett. (2002) 1044;
 - (e) S.C.N. Hsu, M. Ramesh, J.H. Espenson, T.B. Rauchfuss, Angew. Chem., Int. Ed. 42 (2003) 2663:
 - (f) M.L. Kuhlman, T.B. Rauchfuss, J. Am. Chem. Soc. 125 (2003) 10084;
 - (g) M.L. Kuhlman, T.B. Rauchfuss, Inorg. Chem. 43 (2004) 430;
 - (h) M. Ramesh, T.B. Rauchfuss, J. Organomet. Chem. 689 (2004) 1425;

(i) P.V. Bernhardt, F. Bozoglian, B.P. Macpherson, M. Martinez, J. Chem. Soc., Dalton Trans. (2004) 2582:

(j) A.L. Reiff, E.M. Garcia-Frutos, J.M. Gil, O.P. Anderson, L.S. Hegedus, Inorg. Chem. 44 (2005) 9162;

(k) W.-F. Yeung, P.-H. Lau, T.-C. Lau, H.-Y. Wei, H.-L. Sun, S. Gao, Z.-D. Chen, W.-T. Wong, Inorg. Chem. 44 (2005) 6579;

(1) L.M. Toma, L.D. Toma, F.S. Delgado, C. Ruiz-Pérez, J. Sletten, J. Cano, J.M. Clemente-Juan, F. Lloret, M. Julve, Coord. Chem. Rev. 250 (2006) 2176;

(m) P.V. Bernhardt, F. Bozoglian, M. Font-Bardia, M. Martinez, A.P. Meacham, B. Sienra, X. Solans, Eur. J. Inorg. Chem. (2007) 5270;

(n) K. Halbauer, H. Görls, T. Fodler, W. Imhof, J. Organomet. Chem. 692 (2007) 1898.

- (o) J.L. Boyer, H. Yao, M.L. Kuhlman, T.B. Rauchfuss, S. Wilson, Eur. J. Inorg. Chem. (2007) 2721
- [4] (a) P. Jaitner, H. Schottenberger, S. Gamper, D. Obendorf, J. Organomet. Chem. 475 (1994) 113:

(b) H. Schottenberger, M. Buchmeiser, C. Rieker, P. Jaitner, K. Wurst, J. Organomet, Chem, 541 (1997) 249:

- (c) G. Laus, C.E. Strasser, K. Wurst, H. Schottenberger, Z. Krist. 221 (2006) 103. [5] (a) C.M. Elliott, J.K. Arnette, R.R. Krebs, J. Am. Chem. Soc. 107 (1985) 4904;
 - (b) R. Hotzelmann, K. Wieghardt, J. Ensling, H. Romstedt, P. Gütlich, E. Bill, U. Flörke, H.-J. Haupt, J. Am. Chem. Soc. 114 (1992) 9470; (c) M. Jakonen, P. Hirva, T. Nivajärvi, M. Kallinen, M. Haukka, Eur. J. Inorg.

Chem. (2007) 3497. [6] (a) For bimetallic examples, see: R. Zoet, G. Van Koten, A.L.J. Van der Panne, P.

- Versloot, K. Vrieze, C.H. Stam, Inorg. Chim. Acta 149 (1988) 177; (b) O.C.P. Beers, M.M. Bouman, A.E. Komen, K. Vrieze, C.J. Elsevier, E. Horn, A.L. Spek, Organometallics 12 (1993) 315; (c) H. Matsuzaka, K. Ichikawa, T. Ishioka, H. Sato, T. Okubo, T. Ishii, M. Yamashita, M. Kondo, S. Kitagawa, J. Organomet. Chem. 596 (2000) 121; (d) J.N.L. Dennett, J. Jacke, G. Nilsson, A. Rosborough, M.J. Ferguson, M. Wang, R. McDonald, J. Takats, Organometallics 23 (2004) 4478.
- [7] (a) For trimetallic examples, see: E. Roland, H. Vahrenkamp, Organometallics 2 (1983) 1048:
 - (b) P. Braunstein, J. Rose, O. Bars, J. Organomet. Chem. 252 (1983) C101;
 - (c) E. Roland, W. Bernhardt, H. Vahrenkamp, Chem. Ber. 118 (1985) 2858;
 - (d) S.-H. Han, J.-S. Song, P.D. Macklin, S.T. Nguyen, G.L. Geoffroy, A.L. Rheingold, Organometallics 8 (1989) 2127;
 - (e) H. Bantel, A.K. Powell, H. Vahrenkamp, Chem. Ber. 123 (1990) 661
 - (f) W. Bernhardt, H. Vahrenkamp, J. Organomet. Chem. 383 (1990) 357
 - (g) T. Nakajima, I. Shimizu, K. Kobayashi, Y. Wakatsuki, Organometallics 17 (1998) 262
 - (h) T.M. Räsänen, S. Jääskeläinen, T.A. Pakkanen, J. Organomet. Chem. 554 (1998) 129;

(i) R.C. Cordiner, D. Corcoran, D.S. Yufit, A.E. Goeta, J.A.K. Howard, P.J. Low, J. Chem. Soc., Dalton Trans. (2003) 3541;

(j) N. Nakagawa, T. Yamada, M. Murata, M. Sugimoto, H. Nishihara, Inorg. Chem. 45 (2006) 14:

- (k) J.-M. Yang, B. Hu, C.-G. Xia, J. Clust. Sci. 19 (2008) 615;
- (1) E. Roland, H. Vahrenkamp, Chem. Ber. 118 (1985) 1133;
- (m) E. Roland, H. Vahrenkamp, Chem. Ber. 119 (1986) 12566;
- (n) P. Braunstein, F.Y. Jiao, J. Rosé, P. Granger, F. Balegroune, O. Bars, D. Grandjean, J. Chem. Soc., Dalton Trans. (1992) 2543;
- (o) E.N.-M. Ho, Z. Lin, W.-T. Wong, Eur. J. Inorg. Chem. (2001) 1321.
- [8] (a) For tetrametallic and larger species, see references 71-o, and: P.C. Steinhardt, W.L. Gladfelter, A.D. Harley, J.R. Fox, G.L. Geoffroy, Inorg. Chem. 19 (1980) 332;

(b) M. Hidai, M. Orisaku, M. Ue, Y. Koyasu, T. Kodama, Y. Uchida, Organometallics 2 (1983) 292;

(c) E. Roland, H. Vahrenkamp, Organometallics 2 (1983) 183;

(d) O. Benali-Baitich, J.-C. Daran, Y. Jeanin, J. Organomet. Chem. 344 (1988) 393;

(e) L.J. Farrugia, Acta Crystallogr., Sect. C. 44 (1988) 219;

(f) S. Rossi, J. Pursiainen, M. Ahlgren, T.A. Pakkanen, Organometallics 9 (1990) 475:

(g) S. Rossi, J. Pursiainen, M. Ahlgren, T.A. Pakkanen, J. Organomet. Chem. 393 (1990) 403;

(h) S. Rossi, J. Pursiainen, T.A. Pakkanen, J. Organomet. Chem. 397 (1990) 81;

(i) S. Rossi, J. Pursiainen, T.A. Pakkanen, Organometallics 10 (1991) 1390;

(j) J. Pursiainen, P. Hirra, T.A. Pakkanen, J. Organomet. Chem. 419 (1991) 193;

(k) P. Braunstein, L. Mourey, J. Rosé, P. Granger, T. Richert, F. Balegroune, D. Grandjean, Organometallics 11 (1992) 2628;

(I) S. Rossi, J. Pursiainen, T.A. Pakkanen, J. Organomet. Chem. 436 (1992) 55;
 (m) K.J. Adams, J.J. Barker, P.H. Charmant, C. Ganter, G. Klatt, S.A.R. Knox, A.G.

Orpen, S. Ruile, J. Chem. Soc., Dalton Trans. (1994) 477; (n) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, Polyhedron 14 (1995) 2647:

(o) P.J. Low, K.A. Udachin, G.D. Enright, A.J. Carty, J. Organomet. Chem. 578 (1999) 103;

(p) X.-N. Chen, J. Zhang, Y.-Q. Yin, W.-L. Wang, Chem. Lett. (1999) 583;

(q) H. Wadepohl, S. Gebert, R. Merkel, H. Pritzkow, Eur. J. Inorg. Chem. (2000) 783;

(r) P.J. Dyson, A.K. Hearley, B.F.G. Johnson, T. Khimyak, J.S. McIndoe, P.R.R. Langridge-Smith, Organometallics 20 (2001) 3970;

(s) E.N.-M. Ho, Z. Lin, W.-T. Wong, Chem. Eur. J. (2001) 258;

(t) E.N.-M. Ho, W.-T. Wong, J. Organomet. Chem. 626 (2001) 125;

(u) C. Evans, B.K. Nicholson, J. Organomet. Chem. 645 (2002) 281;

(v) M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, J. Clust. Sci. 13 (2002) 235;

(w) W.H. Watson, J.-C. Wang, M.G. Richmond, J. Chem. Cryst. 33 (2003) 957;

(x) A. Choualeb, J. Rosé, P. Braunstein, R. Welter, Organometallics 22 (2003) 2688;

(y) A. Choualeb, P. Braunstein, J. Rosé, R. Welter, Inorg. Chem. 43 (2004) 57;

(z) C. Moreno, M.-L. Marcos, M.-J. Macazaga, J. Gómez-González, R. Gracia, F. Benito-López, E. Martinez-Gimeno, A. Arnanz, M.-E. Medina, C. Pastor, J. González-Velasco, R.-M. Medina, Organometallics 26 (2007) 5199.

[9] (a) K.-D. Plitzko, B. Rapko, B. Gollas, G. Wehrle, T. Weakley, D.T. Pierce, W.E. Geiger Jr., R.C. Haddon, V. Boekelheide, J. Am. Chem. Soc. 112 (1990) 6545;
 (b) H. Tamura, N. Ikeda, T. Iguro, T. Ohno, G.-E. Matsubayashi, Acta Crystallogr., Sect. C 52 (1996) 1394;

(c) M.-L. Zhu, L.-P. Lu, Y. Pin, Chin. J. Struct. Chem. 21 (2002) 396;

(d) S. Derossi, H. Adams, M.D. Ward, J. Chem. Soc., Dalton Trans. (2007) 33;

- (e) J. Mola, E. Mas-Marza, X. Sala, I. Romero, M. Rodriguez, C. Viñas, T. Parella, A. Llobet, Angew. Chem., Int. Ed. 47 (2008) 5830.
- [10] D. Carmona, F.J. Lahoz, R. Atencio, A.J. Edwards, L.A. Oro, M.P. Lamata, M. Esteban, S. Trofimenko, Inorg. Chem. 35 (1996) 2549.

[11] (a) S.R. Stobart, K.R. Dixon, D.T. Eadie, J.L. Atwood, M.D. Zaworotko, Angew. Chem., Int. Ed. 19 (1980) 931;

(b) F.H. Cano, D. Foces-Foces, L.A. Oro, M.T. Pinillos, C. Tejel, Inorg. Chim. Acta 128 (1987) 75;

(c) M.T. Pinillos, C. Tejel, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Chem. Soc., Dalton Trans. (1989) 1133;

(d) D. Carmona, F.J. Lahoz, L.A. Oro, J. Reyes, M.P. Lamata, J. Chem. Soc., Dalton Trans. (1990) 3551;

(e) D. Carmona, F.J. Lahoz, L.A. Oro, M.P. Lamata, S. Buzarra, Organometallics 10 (1991) 3123;

(f) D. Carmona, J. Ferrer, A. Mendoza, F.J. Lahoz, J. Reyes, L.A. Oro, Angew. Chem., Int. Ed. 30 (1991) 1171;

(g) A. Elduque, L.À. Oro, M.T. Pinillos, C. Tejel, A. Tiripicchio, F. Ugozzoli, J. Chem. Soc., Dalton Trans. (1991) 2807;

(h) D. Carmona, M.P. Lamata, J. Ferrer, J. Modrego, M. Perales, F.J. Lahoz, R. Atencio, L.A. Oro, J. Chem. Soc., Chem. Commun. (1994) 575;

(i) M. Scotti, M. Valderrama, R. Moreno, R. López, D. Boys, Inorg. Chim. Acta 219 (1994) 67;

(j) M.T. Pinillos, A. Elduque, E. Martin, N. Favarro, F.J. Lahoz, J.A. Lopez, L.A. Oro, Inorg. Chem. 34 (1995) 111;

(k) R. Atencio, C. Bohanna, M.A. Esteruelas, F.J. Lahoz, L.A. Oro, J. Chem. Soc., Dalton Trans. (1995) 2171;

(I) D. Carmona, J. Ferrer, R. Atencio, F.J. Lahoz, L.A. Oro, Organometallics 14 (1995) 2057;

(m) M.T. Pinillos, A. Elduque, E. Martin, N. Navarro, L.A. Oro, A. Tiripicchio, F. Ugozzoli, Inorg. Chem. 34 (1995) 3105;

(n) M. Valderrama, J. Cuevas, D. Boys, D. Carmona, M.P. Lamata, F. Viguri, R. Atencio, F.J. Lahoz, L.A. Oro, J. Chem. Soc., Dalton Trans. (1996) 2877;

(o) D. Carmona, J. Ferrer, F.J. Lahoz, L.A. Oro, M.P. Lamata, Organometallics 15 (1996) 5175;

(p) C. Pettinari, F. Marchetti, A. Cingolani, S.I. Troyanov, A. Drozdov, J. Chem. Soc., Dalton Trans. (1998) 3335;

(q) G.A. Ardizzoia, G. La Monica, A. Maspero, N. Masciocchi, M. Moret, Eur. J. Inorg. Chem. (1999) 1301;

(r) D. Carmona, J. Ferrer, J.M. Arilla, J. Reyes, F.J. Lahoz, S. Elipe, J. Modrego, L.A. Oro, Eur. J. Inorg. Chem. (2000) 159;
(s) D. Carmona, J. Ferrer, J.M. Arilla, J. Reyes, F.J. Lahoz, S. Elipe, F.J. Modrego,

L.A. Oro, Organometallics 19 (2000) 798.

- [12] A. Schneider, E. Freisinger, B. Beck, B. Lippert, J. Chem. Soc., Dalton Trans. (2000) 837.
- [13] (a) S. Trofimenko, J.C. Calabrese, P.J. Domaille, J.S. Thompson, Inorg. Chem. 28 (1989) 1091;

(b) S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842;

(c) S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3170.

[14] M.O. Albers, T.V. Ashworth, H.E. Oosthuizen, E. Singleton, Inorg. Syn. 26 (1989) 68.

[15] (a) J. Gomez, C. Gernel, C. Slugovc, E. Wozniac, R. Schmid, K. Kirchner, Monatsch. Chem. 132 (2001) 1137;
(b) M.E. Morilla, G. Morfes, M.C. Nicasio, T.R. Belderrain, M.M. Díaz-Requejo, C. Graiff, A. Tíripicchio, R. Sánchez-Delgado, P.J. Pérez, Chem. Commun. (2002) 1848.

[16] (a) C.W. Reimann, A. Santoro, A.D. Mighell, Acta Crystallogr., Sect. B 26 (1970) 521;

(b) R.W.M. ten Hoedt, W.L. Driessen, G.C. Verschoor, Acta Crystallogr., Sect. C C39 (1983) 71;

(c) P.O. Lumme, E. Lindell, P.-R. Kivimäki, Thermochim. Acta 126 (1988) 187;
(d) P.O. Lumme, E. Lindell, I. Mutikainen, Acta Crystallogr., Sect. C 44 (1988) 967;

(e) D. Collison, M. Helliwell, V.M. Jones, F.E. Mabbs, E.J.L. McInnes, P.C. Riedi, G.M. Smith, R.G. Pritchard, W.I. Cross, J. Chem. Soc., Faraday Trans. 94 (1998) 3019;

(f) T. Otieno, J.R. Blanton, M.J. Hatfield, S.L. Asher, S. Parkin, Acta Crystallogr., Sect. C 58 (2002) m182.