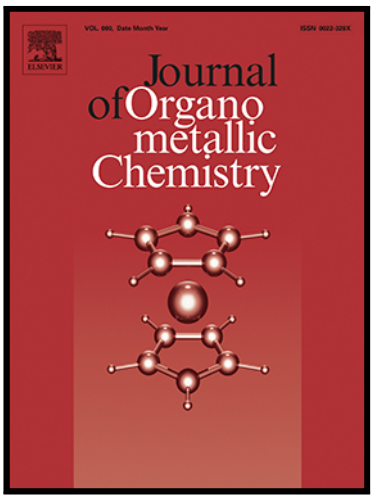

Tris(pyrazolyl)borate rhodium complexes. Application for reductive amination and esterification of aldehydes in the presence of carbon monoxide

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Highlights

- Tris(pyrazolyl)borate rhodium complexes were synthesized.
- They effectively catalyze reductive amination and esterification of aldehydes in the presence of carbon monoxide.
- The catalytic activity is dependent on the nature of auxiliary ligands.
- Primary and secondary amines with aromatic and aliphatic substituents are suitable for the reductive amination.

Tris(pyrazolyl)borate rhodium complexes. Application for reductive amination and esterification of aldehydes in the presence of carbon monoxide

Vladimir B. Kharitonov,[a] Vladimir S. Ostrovskii,[a] Yulia V. Nelyubina,[a] Dmitry V. Muratov,[a] Denis Chusov,[a] Dmitry A. Loginov*[a]

Abstract

The halide complexes $TpRhCl_2(MeOH)$ and $Tp^{Me2}RhI_2(CO)$ (Tp = hydrotris-(pyrazolyl)borate; Tp^{Me2} = hydrotris-(3,5-dimethylpyrazolyl)borate) were synthesized by reactions of $RhCl_3$ with K[Tp] in methanol and $Tp^{Me2}Rh(CO)_2$ with iodine, respectively. Reactions of $Tp^{Me2}RhCl_2(MeOH)$ and $Tp^{Me2}RhI_2(CO)$ with 1,10-phenanthroline afford the phenanthroline derivatives $[Tp^{Me2}Rh(phen)X]^+$ (X = Cl, I). The structures of $TpRhCl_2(MeOH)$ and $TpRhI_2(CO)$ were determined by X-ray diffraction. Tris(pyrazolyl)borate rhodium complexes effectively catalyze the reductive amination and the reductive esterification of aldehydes in the presence of carbon monoxide.

Keywords: Amines; Carbon monoxide; Hydridotris(pyrazolyl)borate complexes; Reductive amination; Rhodium

1. Introduction

It is well known that the easy flexibility of the supporting ligand in the catalyst can considerably increase its catalytic activity. In particular, we have recently found that indenyl rhodium complexes show high catalytic activity in the reductive amination of aldehydes and ketones in the presence of carbon monoxide.[1] It is an atom- and step-economical approach to amines, which are of importance for the electronic and pharmaceutical industry.[2] The enhanced catalytic activity of indenyl complexes is attributed to the easy generation of an additional free coordination site at the metal atom as a result of the slippage of indenyl ligand from η^5 to η^3 coordination mode.[3]

Tris(pyrazolyl)borate anions (Tp) are well-known ligands,[4] whose metal complexes easily undergo $k^3 – k^2$ isomerization with the release of a free coordination site at the metal atom. So, the Tp ligand can be coordinated in a bidentate or tridentate fashion.[5] This flexibility should

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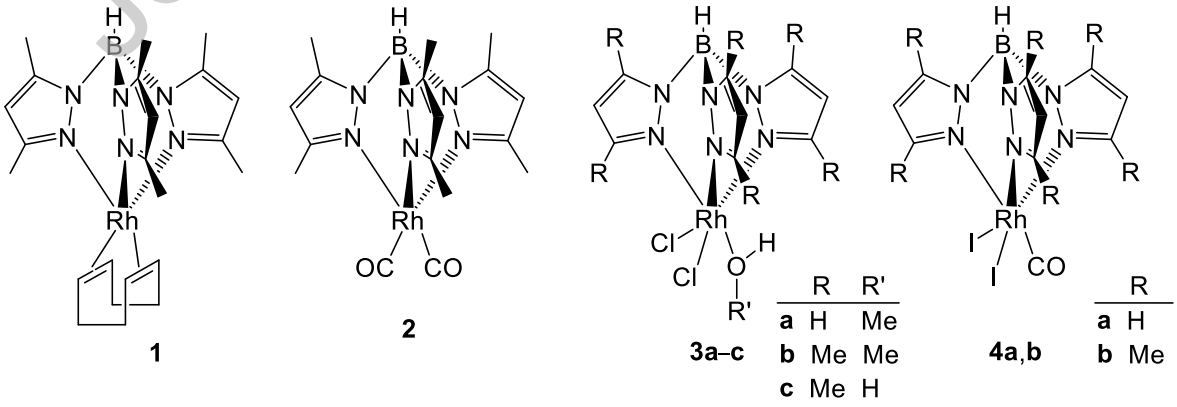
enhance the catalytic activity of tris(pyrazolyl)borate metal complexes as compared with cyclopentadienyl analogs. However, even in the case of rhodium, which is a typical catalytic metal, only a few examples of the successful application of Tp complexes in catalysis are known.[6] In particular, bis(ethylene) and cyclooctadiene derivatives, $TpRh(C_2H_4)_2$ and TpRh(COD), have proved to be effective catalysts for the stereoregular polymerization of *para*-substituted phenylacetylenes,[7] hydrogenation of quinoline,[8] the addition of amines to alkynes,[9] the substitution of allylic carbonates by organolithium reagents,[10] as well as di- and trimerization of alkynes.[11] Recently, Jones with co-workers have demonstrated the activation of the E–H bonds (E = B, C, Si, N) with phosphine and isocyanide complexes.[12]

Herein, we report the first example of the application of tris(pyrazolyl)borate rhodium complexes as catalysts for the reductive amination and the reductive esterification of aldehydes in the presence of carbon monoxide. For catalyst screening, we used both rhodium(I) and rhodium(III) complexes.

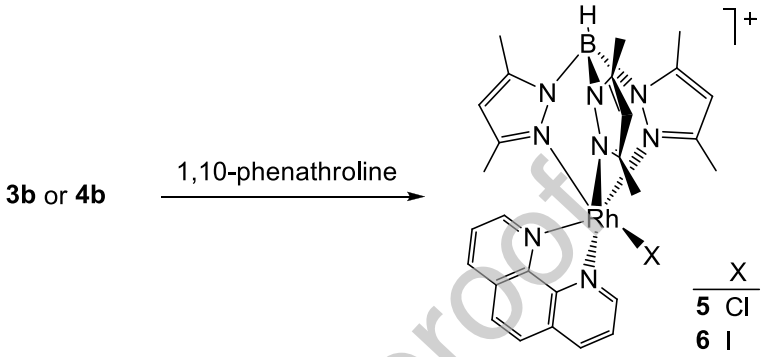
2. Results and Discussion

Tris(pyrazolyl)borate rhodium complexes with labile COD and CO ligands $Tp^{Me2}Rh(COD)$ (**1**) and $Tp^{Me2}Rh(CO)_2$ (**2**) (Tp^{Me2} = hydrotris-(3,5-dimethylpyrazolyl)borate) as well as derivatives with halide ligands $Tp^{Me2}RhCl_2(MeOH)$ (**3b**) and $TpRhI_2(CO)$ (**4a**) were synthesized by known procedures (Scheme 1).[13,14] Complexes $TpRhCl_2(MeOH)$ (**3a**) and $Tp^{Me2}RhI_2(CO)$ (**4b**) were prepared analogously to the methods employed by Powell, Venanzi, and Cocivera for the synthesis of **3b** and **4a**.[14] It was shown that in wet solvents (such as dichloromethane and acetone) the methanol ligand in **3b** is replaced by water to give $Tp^{Me2}RhCl_2(H_2O)$ (**3c**) in almost quantitative yield.



Scheme 1. Tris(pyrazolyl)borate rhodium complexes studied in this work.

We found that one of the halide anions in **3b** and **4b** is also labile and can be easily displaced. In particular, reactions with 1,10-phenanthroline lead to the cationic complexes $[Tp^{Me2}Rh(phen)Cl]^+$ (**5**) and $[Tp^{Me2}Rh(phen)I]^+$ (**6**) (Scheme 2). In the case of chlorine derivative, the reaction is also accompanied by the formation of a sparingly soluble salt **5**$[Tp^{Me2}RhCl_3]$. Earlier, Powell with co-workers showed that a similar reaction of **3b** with 2,2'-bipyridyl leads to the attachment of two tris(pyrazolyl)borate rhodium moieties to bipyridyl as a result of the replacement of methanol only,[14c] which can be explained by greater structural flexibility of bipyridyl as compared with phenanthroline.



Scheme 2. Reactions of **3b** and **4b** with 1,10-phenanthroline.

The structures of **3a** and **4a** were elucidated by X-ray diffraction (Figs. 1 and 2). As expected, in both compounds the rhodium atom adopts distorted octahedral coordination and the tris(pyrazolyl)borate ligand is coordinated in a tridentate fashion. In **4a**, the CO ligand and the iodine atoms are disordered by three positions around the three-fold axis passing through the boron and the rhodium atoms, which precludes any detailed discussion of the Rh–I and Rh–C distances. The Rh–N and Rh–Cl distances in **3a** are close to those in other related tris(pyrazolyl)borate rhodium complexes.[14a,15] At the same time, the Rh–N bonds in **3a** (1.991–2.026 Å, av. 2.006 Å) are shorter than in the carbene derivative $TpRhCl_2[C(SMe)_2]$ (2.020–2.107 Å, av. 2.051 Å),[16] which can be explained by strong π-back-donation of the carbene ligand.[17]

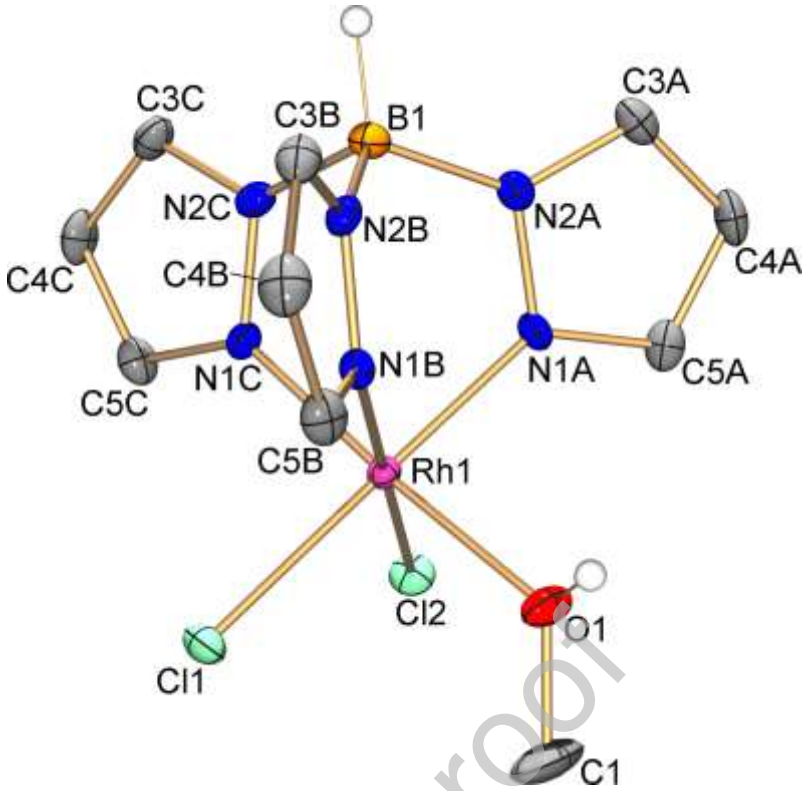


Figure 1. General view of compound **3a** with atoms shown as thermal ellipsoids at the 50% probability level. The solvate methanol molecule and hydrogen atoms except those of the BH and OH groups are omitted for clarity. Selected bond lengths (Å): Rh1–Cl1 2.3469(12), Rh1–Cl2 2.3492(14), Rh1–O1 2.065(3), Rh1–N1a 2.001(4), Rh1–N1b 2.026(4), Rh1–N1c 1.991(4).

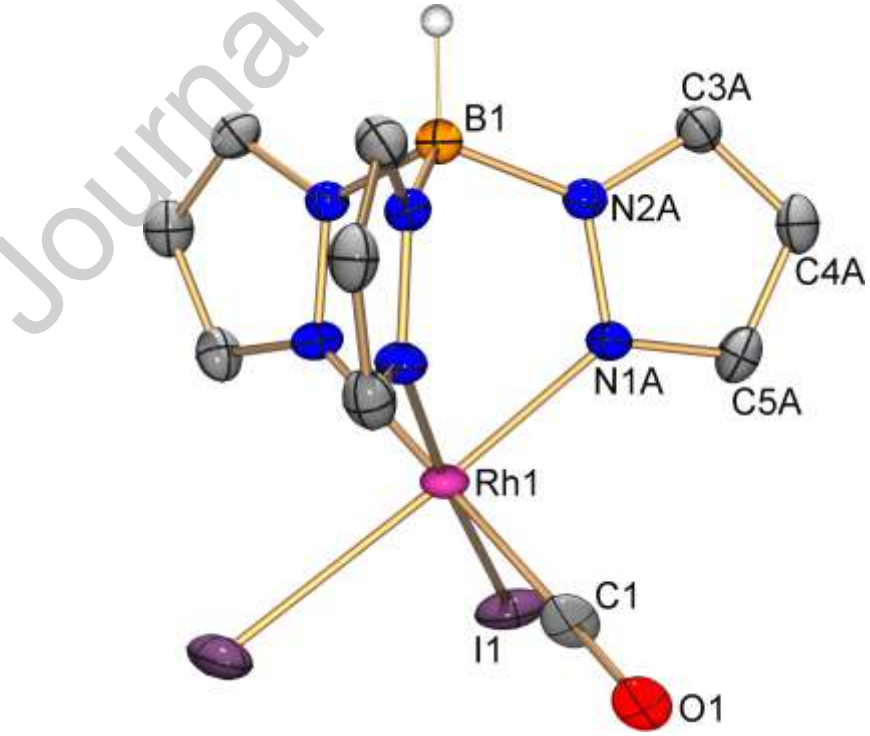
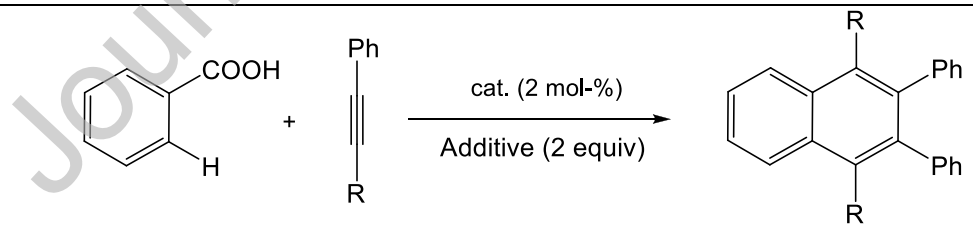


Figure 2. General view of compound **4a** with atoms shown as thermal ellipsoids at the 50% probability level. Only one component of the CO ligand and the iodine atoms, which are

disordered by three positions around the three-fold axis passing through the boron and the rhodium atoms, is shown. Hydrogen atoms except one of the BH group are omitted for clarity, and labels are given only for symmetry-independent atoms. Selected bond lengths (Å): Rh1–I1 2.6476(14), Rh1–C1 1.86(2), Rh1–N1a 2.069(4).

Taking into account the close relation of the rhodium(III) halide complexes **3a**,**b** and **4a**,**b** to $[Cp^*RhCl_2]_2$ and $Cp^*Co(CO)I_2$, which are well-known catalysts for CH activation,[18] we tested the catalytic ability of the new complexes in the oxidative coupling of benzoic acid with diphenylacetylene in *o*-xylene at 150 ºC (Table 1).[19] Unfortunately, our attempts were unsuccessful and all complexes showed very low catalytic activity, giving substituted naphthalene as the only product. The best yield of 1,2,3,4-tetraphenylnaphthalene (35%) was achieved using iodide **4a** as a catalyst (Table 1, entry 2). Noteworthy, the chloride derivatives **3a**,**b** proved to be almost inactive (entries 3, 4, and 8). The low activity of the tris(pyrazolyl)borate rhodium complexes may be explained by the presence in their structure of the tris(pyrazolyl)borate anion, which is a strong donor nitrogen ligand. Earlier, we have found that N, N′-ligands (such as 2,2'-bipyridyl and 1,10-phenanthroline) can considerably change the reaction pathway of CH activation.[20] The use of methanol as a solvent and more donor 1-phenyl-1-propyne as a coupling partner as well as the decrease of the reaction temperature to 80 ºC did not give any positive impact (entries 6–8).

Table 1. The catalytic activity of the tris(pyrazolyl)borate rhodium complexes in the oxidative coupling of benzoic acid with internal alkynes.



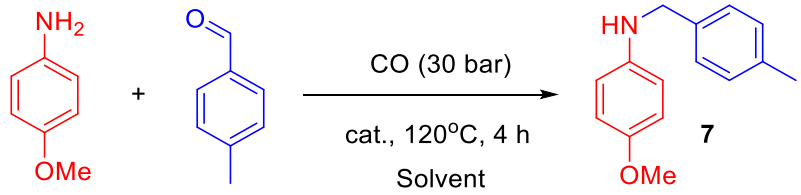
Entry	Catalyst	Additive	Solvent and temperature, ºC	Time	R	Yield,[a] %
1	$TpRhI_2(CO)$, **4a**	AgOAc	*o*-xylene, 150	10	Ph	16
2	$TpRhI_2(CO)$, **4a**	AgOAc	*o*-xylene, 150	24	Ph	35
3	$Tp^{Me2}RhCl_2(MeOH)$, **3b**	AgOAc	*o*-xylene, 150	10	Ph	Nd
4[b]	$Tp^{Me2}RhCl_2(MeOH)$, **3b**	$Cu(OAc)_2$	*o*-xylene, 150	10	Ph	Nd
5[c]	$Tp^{Me2}RhI_2(CO)$, **4b**	$Cu(OAc)_2$	*o*-xylene, 150	10	Ph	12
6[c]	$TpRhI_2(CO)$, **4a**	AgOAc	*o*-xylene, 150	10	Me	2

7	$TpRhI_2(CO)$, **4a**	AgOAc	MeOH, 80	10	Me	Nd
8	$TpRhCl_2(MeOH)$, **3a**	AgOAc	MeOH, 80	10	Me	Nd

[a] Yields are given for the isolated product. Nd = not detected.

The reductive amination of aldehydes catalyzed by the tris(pyrazolyl)borate rhodium complexes was more successful. Amines are an irreplaceable class of organic compounds, and reductive amination[21] is widely used for the synthesis of industrially important amines[22]. The reductive amination without an external hydrogen source provides unique selectivity for this approach. Carbon monoxide is using as a deoxygenating agent that provides the target amine and carbon dioxide.[23] As model substrates, we chose p-anisidine and 4-tolualdehyde. The catalytic activity with 1 mol% of the catalysts was very high to find the difference between the complexes (Table 2, entries 1–3). Therefore, we decided to decrease the catalyst loading to 0.5 mol% (Table 2, entries 4–9). All tris(pyrazolyl)borate rhodium complexes showed higher catalytic activity compared to $Cp_2Rh_2(CO)_3$ complex (entries 4–8 *vs*. 9). The rhodium(I) complex **1** based on the cyclooctadiene ligand turned out to be less active than the carbonyl derivative **2** (entry 4 *vs*. 5), which can be explained by a stronger binding of rhodium with COD as compared with CO. The rhodium(III) iodide **4b** also showed low activity (entry 8). Nevertheless, complex **1** can be used for this transformation in ethanol with 1 mol% catalyst loading (entry 10). However, for the complex **4b,** even 1 mol% of the catalyst loading is not enough to get a satisfactory yield (entry 12). At the same time, the rhodium(III) chlorides **3b** and **3c** led to the product with a yield of more than 90%, even in water (entries 6 and 7). When the catalyst loading is decreased to 0.2 mol%, only traces of the product were detected (entries 13–15). Such a dramatic effect may be explained by impurities in the starting organic materials, which deactivate catalytic species. The yield of the product drops dramatically when the pressure was decreased (entries 16–18). At the same time, the reaction with carbon monoxide at 20 bar under prolonged reaction time can proceed with preparative yield (entry 16).

Table 2. The catalytic activity of tris(pyrazolyl)borate rhodium complexes in the reductive amination

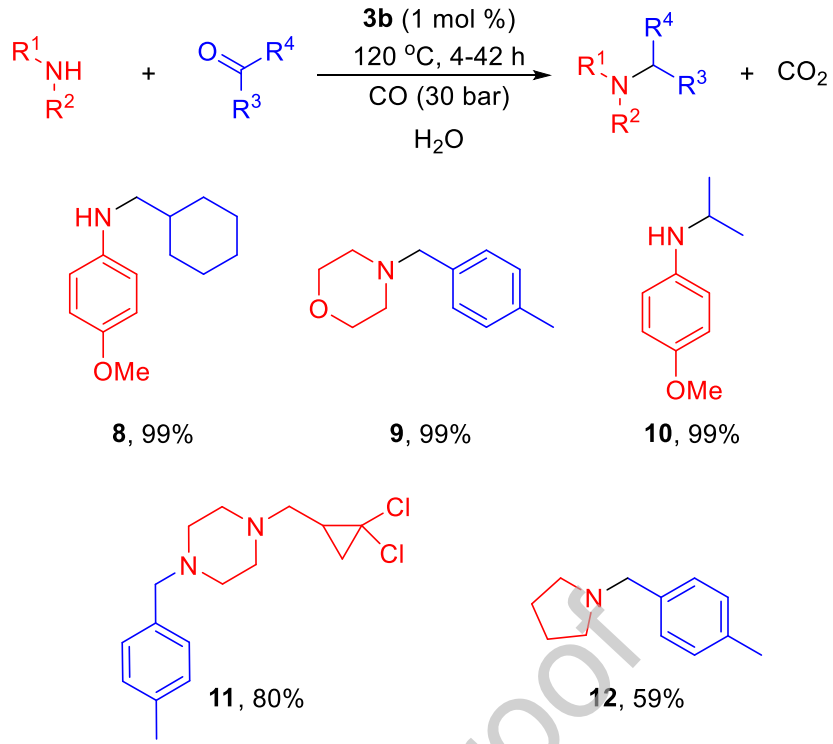


Entry	catalyst	Loading catalyst, mol %	Solvent	Yield[b] of **7**
1	$Tp^{Me2}Rh(CO)_2$, **2**	1	H_2O	99%
2	$TpRhCl_2(MeOH)$, **3a**	1	H_2O	99%

3	$Tp^{Me2}RhI_2(CO)$, **4b**	1	H_2O	92%
4	$Tp^{Me2}Rh(COD)$, **1**	0.5	H_2O	26%
5	$Tp^{Me2}Rh(CO)_2$, **2**	0.5	H_2O	94%
6	$Tp^{Me2}RhCl_2(MeOH)$, **3b**	0.5	H_2O	95%
7	$Tp^{Me2}RhCl_2(H_2O)$, **3c**	0.5	H_2O	92%
8	$Tp^{Me2}RhI_2(CO)$, **4b**	0.5	H_2O	50%
9	$Cp_2Rh_2(CO)_3$	0.5	H_2O	10%
10	$Tp^{Me2}Rh(COD)$, **1**	1	EtOH	99%
11	$Tp^{Me2}Rh(CO)_2$, **2**	1	EtOH	99%
12	$Tp^{Me2}RhI_2(CO)$, **4b**	1	EtOH	15%
13	$Tp^{Me2}Rh(CO)_2$, **2**	0.2	H_2O	traces
14	$Tp^{Me2}RhCl_2(MeOH)$, **3b**	0.2	H_2O	0%
15	$Tp^{Me2}RhCl_2(H_2O)$, **3c**	0.2	H_2O	traces
16[c]	$Tp^{Me2}RhCl_2(MeOH)$, **3b**	0.5 (20 bar, 20 h)	H_2O	66%[d]
17[e]	$Tp^{Me2}RhCl_2(MeOH)$, **3b**	0.5 (10 bar, 20 h)	H_2O	26%[d]
18[f]	$Tp^{Me2}RhCl_2(MeOH)$, **3b**	0.5 (5 bar, 20 h)	H_2O	3%[d]

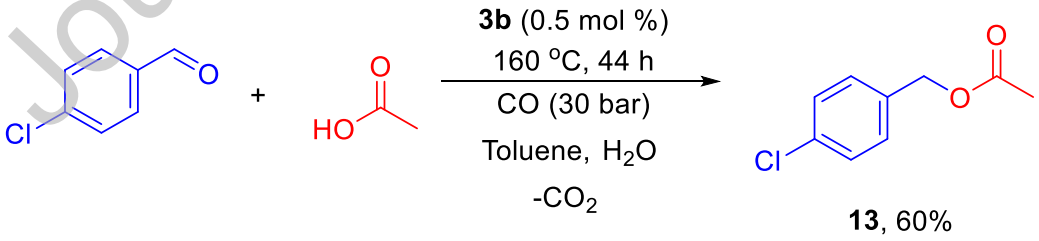
[a] 40.6 mg (0.33 mmol) p-anisidine, 26 μL (0.22 mmol) 4-tolualdehyde, 200 μL of solvent. [b] Yields were determined by NMR. [c] 20 bar of CO, 20 h. [d] The average yield of two experiments. [e] 10 bar of CO, 20 h. [f] 5 bar of CO, 20 h.

With optimal conditions in hand, we checked the general applicability of different amines and carbonyl compounds (Scheme 3). The reaction proceeds well with primary and secondary amines, with aromatic and aliphatic amines, with aldehydes and ketones. The cyclopropyl moiety and aliphatic chlorides are suitable for the reaction. The only limitation is the combination of pyrrolidine with aromatic aldehydes. In this case, besides the main product **12**, a significant number of by-products were observed. Even when the catalyst loading was decreased to 0.5 mol% and the reaction time was decreased to 4 hours, only 59% of the product was formed, while the conversion was 98%.



Scheme 3. The substrate scope of the reductive amination using CO as a reducing agent and **3b** as a catalyst.

Finally, we found that the catalytic system can also be applied for the reductive esterification.[24] In the case of **3b**, the reductive esterification of 4-chlorobenzaldehyde with acetic acid led to a 60% yield of **13** (Scheme 4). This result is comparable to the best catalytic system for this reaction. The activity of **3b** is 120 TON while the best ruthenium-based catalyst has TON 71 per ruthenium atom,[24a] and the best rhodium catalyst shows TON 70.[24b]



Scheme 4. The reductive esterification of 4-chlorobenzaldehyde with acetic acid using CO as a reducing agent and **3b** as a catalyst.

3. Conclusion

In conclusion, the tris(pyrazolyl)borate rhodium complexes were synthesized by simple procedures starting with rhodium trichloride. Their full characterization was provided. The trends of the catalytic activity of tris(pyrazolyl)borate rhodium complexes in the reductive

amination and the reductive esterification without an external hydrogen source were studied. The developed catalytic system can be used for the synthesis of secondary and tertiary amines from aldehydes and ketones. The complex **3b** also showed the highest catalytic activity in the reductive esterification of chlorobenzaldehyde with acetic acid.

4. Experimental section

The reactions were carried out under an inert atmosphere in dry solvents. The isolation of products was conducted in the air. The starting materials **2**[13] and **3b**[14c] were prepared as described in the literature. All other reagents were purchased from Acros or Aldrich and used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 400.13 and 100.61 MHz, respectively. Chemical shifts are reported in ppm using the residual signals of the solvents as internal standards. The signals with the apostrophe (′) correspond to the pyrazolyl ring, which is in the *trans*-position to the additional auxiliary ligand (H_2O, MeOH, CO, etc.).

*4.1. Synthesis of TpRhCl$_2$(MeOH) (**3a**)*

A solution of K[Tp] (478 mg; 1.89 mmol) in MeOH (5 ml) was slowly added to a suspension of $RhCl_3{\cdot}3H_2O$ (500 mg; 1.9 mmol) in MeOH (1.25 ml). The reaction is quite exothermic, the red solution turns yellow and then becomes black due to a small amount of rhodium metal formed. The reaction mixture was refluxed for 4 h. Rhodium was centrifuged off, the solution was concentrated *in vacuo* until a precipitate began to form. The solution was left overnight at −30 ºC. The obtained orange crystals were filtered off, crushed and dried *in vacuo*. Compound **3a** was obtained as a yellow solid (436 mg, 55%). ^{1}H NMR (dmso-d_6): δ = 8.14 (d, 2H, H5, J=2.4), 8.04 (d, 1H, H5′, J=2.4), 7.96 (q, 1H, CH_3OH, J=4.0), 7.86 (d, 2H, H3, J=1.6), 7.68 (d, 1H, H3′, J=1.6), 6.49 (t, 2H, H4, J=2.4), 6.38 (t, 2H, H4′, J=2.4), 3.44 (d, 3H, CH_3OH, J=4.0). ^{13}C{^{1}H} NMR (dmso-d_6): δ = 145.45 (s, C3), 143.06 (s, C3′), 137.54 (s, C5), 137.36 (s, C5′), 107.61 (s, C4), 107.5 (s, C4′), 53.01 (s, CH_3OH). HRMS (ESI): calc. for $C_9H_{14}N_7BCl_2Rh$ $[M-MeOH+NH_4]^+$ = 403.9832. Found: 403.9831.

*4.2. Synthesis of Tp^{Me2}RhCl$_2$(H$_2$O) (**3c**)*

A suspension of **3b** complex (50 mg, 0.1 mmol) in wet CH_2Cl_2 (3 ml) was stirred overnight (an inert atmosphere is not necessary). The precipitate was centrifuged off and washed with an additional amount of CH_2Cl_2. Compound **3c** was obtained as a colorless solid (46 mg, 95%). ^{1}H NMR (dmso-d_6): δ = 6.60 (s, 2H, H_2O), 5.93 (s, 2H, H4), 5.87 (s, 1H, H4′), 2.47 (s, 3H, CH_3 at C3′), 2.45 (s, 6H, CH_3 at C3), 2.36 (s, 3H, CH_3 at C5′), 2.35 (s, 6H, CH_3 at C5). ^{13}C{^{1}H} NMR

(dmso-d_6): δ = 155.34 (s, C3′), 153.71 (s, C3), 144.89 (s, C5’), 144.62 (s, C5), 108.99 (s, C4), 108.73 (s, C4’), 16.08 (s, CH_3), 14.56 (s, CH_3), 12.67 (s, CH_3), 12.44 (s, CH_3). HRMS (ESI): calc. for $C_{15}H_{26}N_7BCl_2Rh$ $[M-H_2O+NH_4]^+$ = 488.0772. Found: 488.0756.

*4.3. Synthesis of $Tp^{Me2}RhI_2(CO)$ (**4b**)*

A solution of I_2 (109 mg, 0.42 mmol) in ether (8 ml) was added dropwise to a stirred solution of 2 (190 mg, 0.42 mmol) in dichloromethane (9 ml). The reaction mixture was stirred overnight. The solvent was removed *in vacuo*. The red residue was washed with water and reprecipitated from CH_2Cl_2 with petroleum ether and dried *in vacuo*. Compound **4b** was obtained as a dark-red solid (235 mg, 82%). IR (KBr, cm^{-1}): ν(BH) = 2533, ν(CO) = 2088. ^{1}H NMR ($CDCl_3$): δ = 5.94 (s, 1H, H4′), 5.85 (s, 2H, H4), 2.93 (s, 3H, CH_3 at C3′), 2.66 (s, 6H, CH_3 at C3), 2.43 (s, 3H, CH_3 at C5′), 2.36 (s, 6H, CH_3 at C5). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 153.19 (s, C3), 145.25 (s, C3′), 144.63 (s, C5), 136.55 (s, C5′), 109.23 (s, C4), 108.70 (s, C4′), 21.31 (s, CH_3), 18.29 (s, CH_3), 12.92 (s, CH_3). The signal of CO was not observed in ^{13}C{^{1}H} NMR due to its low intensity. HRMS (ESI): calc. for $C_{19}H_{28}N_8BIRh$ $[M-CO-I^-+2MeCN]^+$ = 609.0628. Found: 609.0631.

*4.4. Synthesis of $[Tp^{Me2}Rh(phen)Cl]PF_6$ (**5**PF_6) and $[Tp^{Me2}Rh(phen)Cl][Tp^{Me2}RhCl_3]$ (**5**$[Tp^{Me2}RhCl_3]$)*

Benzene (3 ml) was added to a mixture of **3b** (50 mg, 0.1 mmol) and 1,10-phenanthroline (20 mg, 0.11 mmol). The reaction mixture was refluxed for 6 h. The solvent was removed in *vacuo*. The residue was extracted with methanol. The insoluble residue was washed with acetone and dried *in vacuo* to give **5**$[Tp^{Me2}RhCl_3]$ as a colorless solid (33 mg, 59%). An excess of an aqueous KPF_6 solution was added to the solution. The resulting pale pink precipitate was centrifuged off, washed with water, dried *in vacuo*, and reprecipitated from acetone with ether to give **5**PF_6 (20 mg, 26%).

5PF_6: ^{1}H NMR (acetone-d_6): δ = 9.20 (d, 2H, phen, J=8.2), 9.09 (d, 2H, phen, J=5.2), 8.52 (s, 2H, phen), 8.32 (q, 2H, phen, J=5.2), 6.20 (s, 2H, C4), 5.80 (s, 1H, C4′), 2.57 (s, 6H, CH_3 at C3), 2.51 (s, 3H, CH_3 at C3′), 2.46 (s, 6H, CH_3 at C5), 0.13 (s, 3H, CH_3 at C5′). ^{13}C{^{1}H} NMR (acetone-d_6): δ = 154.85 (s, phen), 153.99 (s), 152.36 (s), 149.21 (s), 146.75 (s), 146.39 (s), 141.40 (s, phen), 131.66 (s), 128.48 (s, phen), 126.41 (s, phen), 110.46 (s, C4), 110.27 (C4′), 15.59 (s, CH_3), 11.89 (s, CH_3), 11.93 (s, CH_3), 10.35 (s, CH_3). HRMS (ESI): calc. for $C_{27}H_{30}N_8BClRh$ $[M]^+$ = 615.1429. Found: 615.1442.

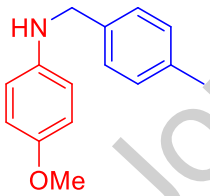
5$[Tp^{Me2}RhCl_3]$: ^{1}H NMR (dmso-d_6): δ = 9.17(d, 2H, phen, J=8.0), 8.96 (m, 2H, phen), 8.49 (s, 2H, phen), 8.18 (m, 2H, phen), 6.29 (s, 2H, C4), 5.85 (s, 1H, C4’), 5.81 (s, 3H, C4), 2.59 (s, 9H, CH_3), 2.54 (s, 6H, CH_3 at C3), 2.45 (s, 3H, CH_3 at C3′), 2.38 (s, 6H, CH_3 at C5), 2.35 (s, 9H,

CH_3), 0.01 (s, 3H, CH_3 at C5′). $^{13}C\{^1H\}$ NMR (dmso-d_6): δ = 155.08 (s, phen), 154.35 (s), 153.63 (s), 152.03 (s), 148.48 (s), 146.69 (s), 146.54 (s), 143.38 (s), 141.56 (s, phen), 131.16 (s), 128.51 (s, phen), 126.72 (s, phen), 110.58 (s, C4), 110.00 (s, C4'), 108.32 (s, C4), 16.21 (s, CH_3), 15.89 (s, CH_3), 12.83 (s, CH_3), 12.67 (s, CH_3), 12.56 (s, CH_3), 10.81 (s, CH_3). Anal. Calcd for $C_{42}H_{352}N_{14}B_2Cl_4Rh_2$: C, 44.95; H, 4.67; N, 17.47. Found: C, 44.44; H, 4.80; N, 17.04.

*4.5. Synthesis of [Tp^{Me2}Rh(phen)I]PF$_6$ (**6**PF$_6$)*

Benzene (3 ml) was added to a mixture of **4b** (70 mg, 0.1 mmol) and 1,10-phenanthroline (20 mg, 0.11 mmol). The reaction mixture was refluxed under vigorous stirring for 6 h. The solvent was removed *in vacuo*. The residue was extracted with methanol. Then, an excess of aqueous KPF_6 solution was added. The resulting brown precipitate was centrifuged off, washed with water, dried *in vacuo*, and reprecipitated from CH_2Cl_2 with ether. Complex **6**PF_6 was obtained as a brown solid (42 mg, 48%). ^1H NMR (acetone-d_6): δ = 9.20 (dd, 2H, phen, J=8.2), 9.07 (d, 2H, phen, J=5.2), 8.51 (s, 2H, phen), 8.33 (q, 2H, phen, J=5.2), 6.26 (s, 2H, C4), 5.75 (s, 1H, C4′), 2.62 (s, 6H, CH_3 at C3), 2.60 (s, 3H, CH_3 at C3′), 2.49 (s, 6H, CH_3 at C5), 0.04 (s, 3H, CH_3 at C5′). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ = 155.55 (s, phen), 154.78 (s), 151.84 (s), 150.79 (s), 147.43 (s), 145.78 (s), 141.43 (s, phen), 131.43 (s, phen), 128.55 (s, phen), 126.70 (s, phen), 110.74 (s, C4), 110.27 (s, C4′), 20.47 (s, CH_3), 12.61 (s, CH_3), 12.12 (s, CH_3), 10.10 (s, CH_3). Anal. Calcd for $C_{28}H_{30}N_8BF_6IPRh$: C, 38.89; H, 3.50; N, 13.01. Found: C, 39.14; H, 3.88; N, 12.25.

*4.6. Synthesis of 4-methoxy-N-(4-methylbenzyl)aniline (**7**)*

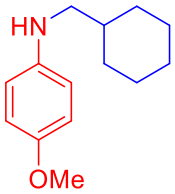


Rhodium catalyst **3b** (0.56 mg, 0.5 mol%, 1.1 µmol), p-anisidine (40.6 mg, 150 mol %, 0.33 mmol) and p-tolualdehyde (26 µL, 100 mol %, 0.22 mmol) were charged into a glass vial in a 10 ml stainless steel autoclave. 0.2 ml of H_2O was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar of CO. The reactor was placed into an oil bath preheated to 120 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2×1 ml); the product was extracted with dichloromethane (3×1 ml), the combined organic layers were filtered through a silica gel pad, the solvent was removed on a rotary evaporator. 95% yield by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 4.25 (s, 2H), 3.76 (s, 3H), 2.37 (s, 3H).

NMR spectra are in agreement with the literature data.[1c]

*4.7. Synthesis of N-(cyclohexylmethyl)-4-methoxyaniline (**8**)*

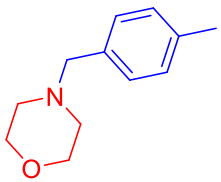


Rhodium catalyst **3b** (1.35 mg, 1.2 mol%, 2.6 µmol), *p*-anisidine (40.6 mg, 150 mol %, 0.33 mmol) and cyclohexanecarboxaldehyde (24.6 mg, 100 mol %, 0.22 mmol) were charged into a glass vial in a 10 ml stainless steel autoclave. 0.2 ml of water was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar of CO. The reactor was placed into an oil bath preheated to 120 °C. After 42 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2×1 ml); the product was extracted with dichloromethane (3×1 ml), the combined organic layers were dried with magnesium sulfate and filtered through a silica gel pad, the solvent was removed on a rotary evaporator. 99 % yield by NMR.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.80 (d, J = 8.9 Hz, 2H), 6.58 (d, J = 8.9 Hz, 2H), 3.75 (s, 3H), 3.50 – 3.20 (br s, 1H), 2.93 (d, J = 6.6 Hz, 2H), 1.90 – 1.80 (d, J = 11.6 Hz, 2H), 1.80 – 1.60 (m, 3H), 1.65 – 1.50 (m, 1H), 1.34 – 1.14 (m, 3H), 1.11 – 0,94 (m, 2H).

NMR spectra are in agreement with the literature data.[1c]

*4.8. Synthesis of 4-(4-methylbenzyl)morpholine (**9**)*



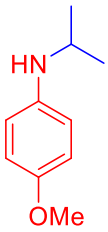
Rhodium catalyst **3b** (1.12 mg, 1 mol %, 2.2 µmol), morpholine (28.8 µL, 150 mol %, 0.33 mmol) and *p*-tolylaldehyde (22 µL, 100 mol %, 0.18 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 ml of water was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar of CO. The reactor was placed into an oil bath preheated to 120 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was

washed with dichloromethane (2×1 ml); the product was extracted with dichloromethane (3×1 ml), the combined organic layers were dried with magnesium sulfate and filtered through a silica gel pad, the solvent was removed on a rotary evaporator. 99% yield by NMR (average of two experiments).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (d, J = 7.6 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 3.75-3.65 (m, 4H), 3.46 (s, 2H), 2.48-2.37 (m, 4H), 2.34 (s, 3H).

NMR spectra are in agreement with the literature data.[1c]

*4.9. Synthesis of N-isopropyl-4-methoxyaniline (**10**)*

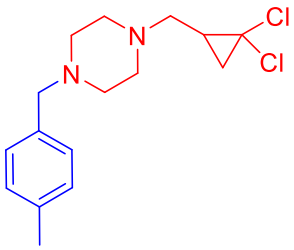


Rhodium catalyst **3b** (1.12 mg, 1 mol%, 2.2 µmol), *p*-anisidine (40.6 mg, 150 mol %, 0.33 mmol) and acetone (16 µL, 100mol%, 0.22 mmol) were charged into a glass vial in a 10 ml stainless steel autoclave. 0.2 ml of water was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar of CO. The reactor was placed into an oil bath preheated to 120 °C. After 42 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2×1 ml); the product was extracted with dichloromethane (3×1 ml), the combined organic layers were filtered through a silica gel pad, the solvent was removed on a rotary evaporator. 99 % yield by NMR.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.77 (d, J = 8.9 Hz, 2H), 6.58 (d, J = 8.9 Hz, 2H), 3.75 (s, 3H), 3.55 (sept, J = 6.2 Hz, 1H), 3.20 – 2.96 (br s, 1H), 1.19 (d, J = 6.2 Hz, 6H).

NMR spectra are in agreement with the literature data.[1c]

*4.10. Synthesis of 1-((2,2-dichlorocyclopropyl)methyl)-4-(4-methylbenzyl)piperazine (**11**)*



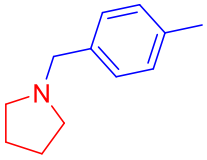
Rhodium catalyst **3b** (1.12 mg, 1 mol%, 2.2 µmol), 1-((2,2-dichlorocyclopropyl)methyl)piperazine (69 mg, 100 mol %, 0.33 mmol) and p-tolualdehyde(26

µL, 100 mol %, 0.22 mmol) were charged into a glass vial in a 10 ml stainless steel autoclave. 0.2 ml of H_2O was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar of CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2×1 ml); the product was extracted with dichloromethane (3×1 ml), the combined organic layers were filtered through a silica gel pad, the solvent was removed on a rotary evaporator. 80 % yield by NMR (average of two experiments).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, J = 7.7 Hz, 2H), 7.12 (d, J = 7.7 Hz, 2H), 3.48 (s, 2H), 2.67-2.58 (m, 6H) 2.55-2.45 (m, 4H), 2.33 (s, 3H), 1.80-1.72 (m, 1H), 1.66-1.62 (m, 1H), 1.13-1.09 (m, 1H).

NMR spectra are in agreement with the literature data.[1b]

*4.11. Synthesis of 1-(4-methylbenzyl)pyrrolidine (**12**)*

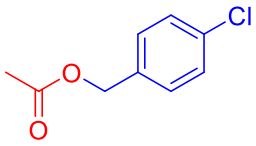


Rhodium catalyst **3b** (0.56 mg, 0.5 mol%, 1.1 µmol), pyrrolidine (27 µL, 150 mol %, 0.33 mmol) and *p*-tolylaldehyde (26 µL, 100 mol %, 0.22 mmol) were charged into a glass vial in a 10 ml stainless steel autoclave. 0.2 ml of water was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar of CO. The reactor was placed into an oil bath preheated to 120 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2×1 ml); the product was extracted with dichloromethane (3×1 ml), the combined organic layers were dried with magnesium sulfate and filtered through a silica gel pad, the solvent was removed on a rotary evaporator. 59% yield by NMR (average of two experiments).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 3.60 (s, 2H), 2.56 – 2.44 (m, 4H), 2.35 (s, 3H), 1.84 – 1.75 (m, 4H).

NMR spectra are in agreement with the literature data[25].

*4.12. Synthesis of 4-Chlorobenzyl Acetate (**13**)*



Rhodium catalyst **3b** (2.52 mg, 0.5 mol%, 5.0 μmol), 4-chlorobenzaldehyde (70.28 mg, 100 mol %, 0.50 mmol) acetic acid (143 μL, 500 mol%, 2.50 mmol) and water (45 μL, 500 mol %, 2.50 mmol) were charged into a glass vial in a 10 ml stainless steel autoclave. 0.17 ml of toluene was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar of CO. The reactor was placed into an oil bath preheated to 160 °C. After 44 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2×1 ml); the product was extracted with dichloromethane (3×1 ml), the combined organic layers were dried with magnesium sulfate and filtered through a silica gel pad, the solvent was removed on a rotary evaporator. 60% yield by NMR.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (two apparent d, J = 8.2 Hz, appears as dd, 4H), 5.04 (s, 2H), 2.07 (s, 3H).

NMR spectra are in agreement with the literature data.[24b]

4.13. X-ray crystallography

Crystals of **3a**·MeOH were obtained by slow evaporation of its methanol solution. Crystals of **4a** were obtained by slow diffusion in a two-layer system, a mixture of petroleum ether / solution of complex in dichloromethane. X-ray diffraction data were collected at 120 K with APEX2 DUO CCD diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). Using Olex2,[26] the structures were solved with the ShelXT structure solution program[27] using Intrinsic Phasing and refined with the XL refinement package[28] using Least Squares minimization. Hydrogen atoms of the OH and BH groups were located from a difference Fourier synthesis, positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation within the riding model. Crystallographic data and structure refinement parameters for **3a** and **4a** are listed in Table 3.

Table 3

Crystallographic data and structure refinement parameters for **3a**·MeOH and **4a**.

Compound	**3a**·MeOH	**4a**
Empirical formula	$C_{11}H_{18}BCl_2N_6O_2Rh$	$C_{10}H_{10}BI_2N_6ORh$
Molecular weight	450.93	597.76
Crystal system	Orthorhombic	Trigonal
Space group	*Pna*2$_1$	*P-3*

a (Å)	17.5961(14)	11.538(5)
b (Å)	7.7777(6)	11.538(5)
c (Å)	12.6395(10)	8.392(3)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	120
V (Å^3)	1729.8(2)	967.5(9)
Z	4	2
D_{calcd} (g cm^{-3})	1.732	2.052
$2\theta_{max}$ (deg)	58	58
μ(Mo-*K*α) (cm^{-3})	13.12	40.78
Collected reflections	20300	12161
Independent reflections	4595 (R_{int} = 0.0524)	1733 (R_{int} = 0.0576)
Observed reflections ($I > 2\sigma(I)$)	4078	1530
Parameters	210	74
R_1 (on *F* for obs. refls)	0.0305	0.0420
wR_2 (on F^2 for all refls)	0.0609	0.1073
F(000)	904	552
GOF	1.042	1.045
Largest diff. peak and hole (e Å^{-3})	0.935 and −0.723	1.197 and −1.096

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Appendix A. Supplementary material

Copies of NMR spectra for the tris(pyrazolyl)borate rhodium complexes.

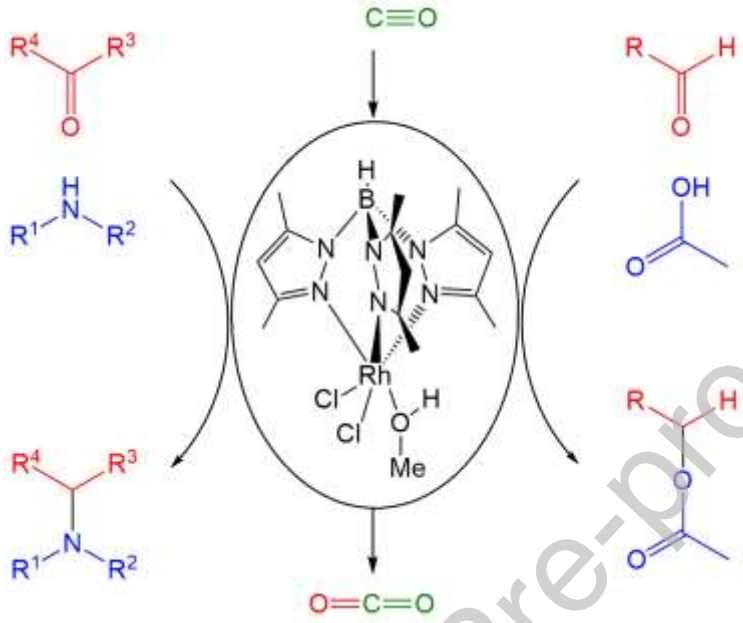
CCDC 2000123 and 2000124 contain the supplementary crystallographic data for **3a**·MeOH and **4a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Declaration of interests

X☐The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

GRAPHICAL ABSTRACT



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