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# Cyclooctadiene Rh(I) bis and tris(pyrazolyl)aluminate complexes and their catalytic activity on the polymerization of phenylacetylene

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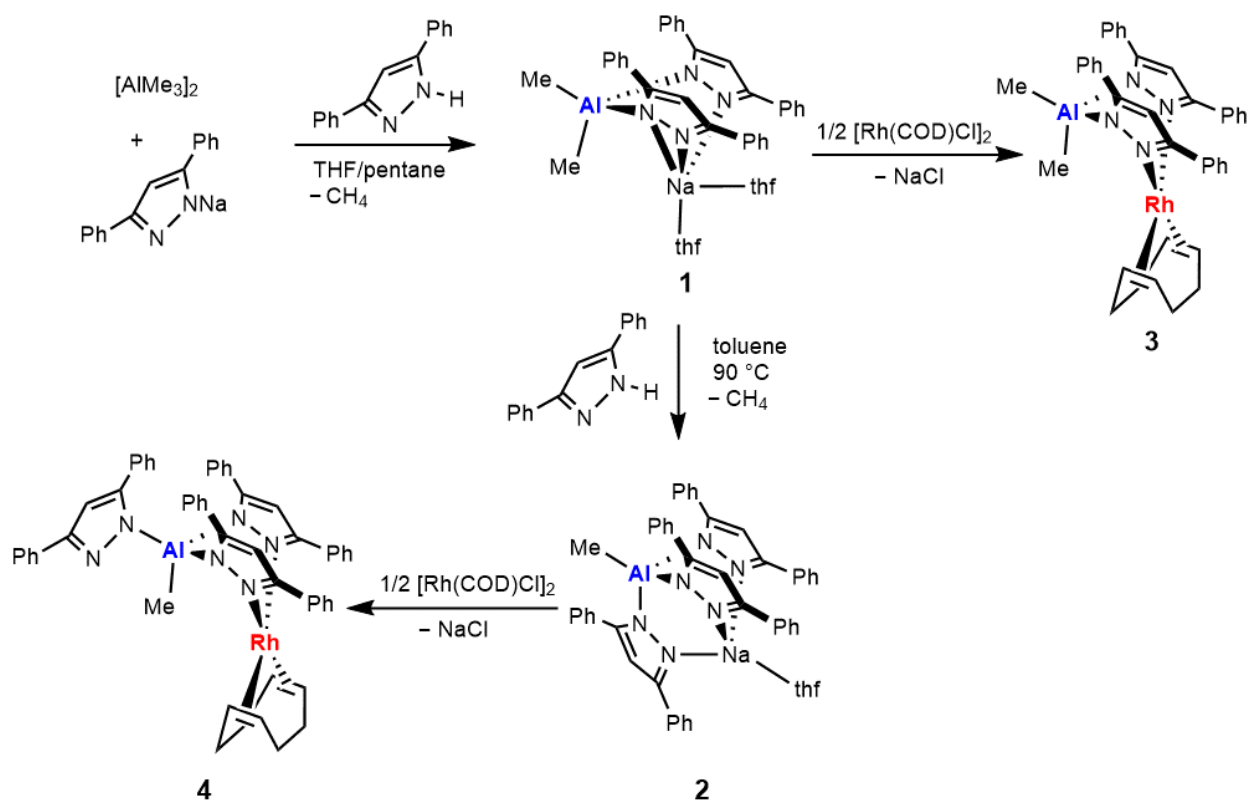
**Abstract:** In this work we report the transfer of alkyl bis and tris(pyrazolyl)aluminates metalloligands to an electron rich organotransition metal center. The 16-electron heterobimetallic complexes of rhodium  $[\text{Rh}(\text{COD})\{\text{Al}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$  (**3**) and  $[\text{Rh}(\text{COD})\{\text{Al}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  (**4**) were obtained by metathesis reaction of the sodium bis (**1**) and tris(pyrazolyl)aluminate (**2**) with  $[\text{RhCl}(\text{COD})]_2$ . For **3**, <sup>1</sup>H and <sup>13</sup>C NMR in solution along with DFT calculations are consistent with a  $\kappa^2$ -coordination mode of the bis(pyrazolyl)aluminate to a square-planar Rh(I) center. The X-ray structure of **4** shows a similar  $\kappa^2$ -coordination mode of the tris(pyrazolyl)aluminate to Rh(I) with a pendant pyrazolyl moiety. The attempted synthesis of aluminate-rhodium complexes with R = CF<sub>3</sub>, <sup>t</sup>Bu on the pyrazolate ring afforded  $[\text{Rh}(\text{R}_2\text{pz})(\text{COD})]_2$  and  $[\text{R}_2\text{pzAlMe}_2]_2$ . Complexes **3** and **4** were investigated as homogenous catalysts in the polymerization of phenylacetylene

(PA). Both complexes showed enhanced catalytic activity compared to analogous rhodium poly(pyrazolyl)borates. Optimized gas phase DFT geometries of **3**, **4**,  $[\text{Rh}(\text{COD})\{\text{B}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$ , and  $[\text{Rh}(\text{COD})\{\text{B}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  were used to compare bite angles, while DFT geometries of **3-CO**, **4-CO**,  $[\text{Rh}(\text{CO})_2\{\text{B}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$ , and  $[\text{Rh}(\text{CO})_2\{\text{B}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  were employed to probe the electronic situation of rhodium center through IR CO stretching modes. The wider bite angles and the less electron-rich rhodium center of the poly(pyrazolyl)aluminates compared with their borate analogs could be implicated in the better performance of the active catalytic species during polymerization of PA.

## 1. Introduction

In stark contrast to the ubiquitous poly(pyrazolyl)borates<sup>1-4</sup> very few reports of the heavier aluminum analogs are known<sup>5-6</sup>. In addition to easy tuning of steric and electronic properties promoted by the rich pyrazole chemistry, the change from boron to aluminum would be highly valuable due to the availability of ligands with wider bites and redox activity. Although the first report on such a ligand system dates to the seventies,<sup>7</sup> it was not until a few years ago that one of us reported the first authenticated sodium poly(pyrazolyl)aluminate exhibiting Al-CH<sub>3</sub> bonds.<sup>8</sup> A remarkable series of poly(pyrazolyl)aluminates with Al-H bonds were also reported,<sup>6,9</sup> with the aim of transferring the aluminate to different metal halides. Significantly the successful transfer of the hydrotris(pyrazolyl)aluminate  $[\text{HAl}(\text{Ph}_2\text{pz})_3]^-$  to a Zn center was accompanied by the undesired hydride transfer from aluminum to zinc giving  $[\{\text{HAl}(\text{Ph}_2\text{pz})_3\}\text{ZnH}]$ . Other metal halides gave bimetallic pyrazolates  $[\text{M}_2\text{X}_2(\text{Ph}_2\text{pz})_2(\text{THF})_3]$  with M = Mg, X = Br; M = Co; X = Cl, whereas reactions with first row transition metal halides of Mn, Fe, Ni, and Cu produced intractable powders.<sup>9</sup> These results highlight the difficulties of this chemistry and underpin the need for a better understanding of the factors that might lead to well-defined poly(pyrazolyl)aluminate

metalloligands and complexes as it has been shown for the related tris(pyridyl)aluminates.<sup>10-17</sup> We surmised that a better performance of the poly(pyrazolyl)aluminate ligand system towards its transfer to a transition metal center could be achieved using alkyl groups on the aluminum atom instead of hydrogen to prevent hydride transfer on the one hand and, on the other hand, by using a more electron rich low-valent organotransition metal center, potentially leading to more stable, less reactive complexes. Indeed, we report herein the preparation and full characterization of the new bis and tris(pyrazolyl)aluminates  $[\{\text{Na}(\text{THF})_2\}\{\text{Al}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$  (**1**) and  $[\{\text{Na}(\text{THF})\}\{\text{Al}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  (**2**) and the complexation of aluminates **1** and **2** to an electron rich Rh(I) center to afford  $[\text{Rh}(\text{COD})\{\text{Al}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$  (**3**) and  $[\text{Rh}(\text{COD})\{\text{Al}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  (**4**). This chemistry is summarized in Scheme 1. We also disclose our findings on the catalytic activity of **3** and **4** in the polymerization of phenylacetylene (PA) comparing catalytic activities with the borate counterparts. DFT modelling helps rationalizing structural and reactivity differences between boron- and aluminum-based ligands.



**Scheme 1.** New poly(pyrazolyl)aluminate chemistry.

## 2. Results and discussion

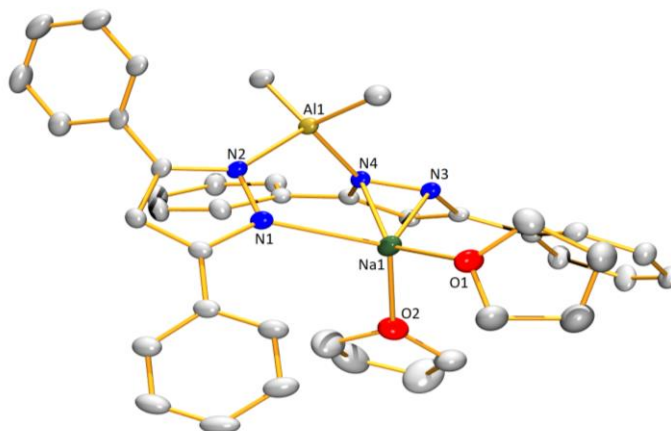
### 2.1 Synthesis and characterization of bis(pyrazolyl)aluminate **1** and tris(pyrazolyl)aluminumate

**2**

**1** and **2** were synthesized by nucleophilic addition of  $[\text{Na}(\text{Ph}_2\text{pz})]$  to  $\text{AlMe}_3$  and the stepwise addition of **1** and **2** molar equivalents of  $\text{Ph}_2\text{pzH}$  (Scheme 1).<sup>5, 18-19</sup> The bimetallic complex  $[\text{Ph}_2\text{pzAlMe}_2]_2$ <sup>20-21</sup> ( $^1\text{H NMR}$ , benzene- $d_6$ :  $\delta$  7.42, 7.03, 6.26,  $-0.66$ ) is a minor side product ( $\sim 10\%$  from  $^1\text{H NMR}$  integration) of the reaction, albeit **1** was isolated analytically pure in 75 % yield by crystallization in a 10:1 pentane-THF solution at ambient temperature. Complex **2** is readily obtained in 82 % yield by reacting **1** with  $\text{Ph}_2\text{pzH}$  at 90 °C in toluene. In contrast,<sup>18</sup> the related aluminate  $[\{\text{Na}(\text{THF})\}\{\text{Al}(\text{tBu}_2\text{pz})_3\text{Me}\}]$  is formed at ambient temperature, possibly reflecting

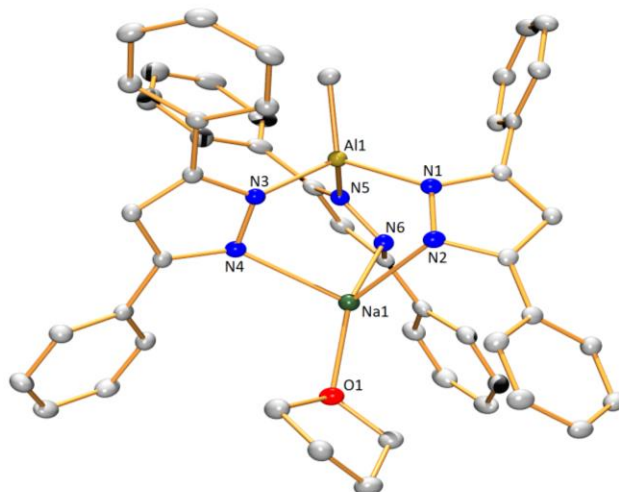
that in the putative bridged Al–Me–Na intermediate  $[\text{Me}_2\text{Al}(\text{R}_2\text{pz})_2\text{Na}(\text{R}_2\text{pzH})]$ ,<sup>18</sup> the bridging methyl group is less nucleophilic when R = Ph. Consistently, in the <sup>1</sup>H NMR spectra for **1** and **2** in benzene-*d*<sub>6</sub>, the characteristic high field CH<sub>3</sub>–Al resonances appear at δ –0.35 and –1.48, respectively, at significantly higher field than those of  $[\{\text{Na}(\text{THF})\}\{\text{Al}(\text{}^t\text{Bu}_2\text{pz})_2\text{Me}_2\}]_2$  and  $[\{\text{Na}(\text{THF})\}\{\text{Al}(\text{}^t\text{Bu}_2\text{pz})_3\text{Me}\}]$  at δ 0.11 and 0.58, respectively. This shielding may be reinforced by the ring current effect of the 3,5-phenyl group(s) on the pyrazolyl ring(s). A similar situation is observed in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra where the methyl substituents show broad resonances at δ –6.28 and –8.98, respectively (δ –1.2 and 1.8 for  $[\{\text{Na}(\text{THF})\}\{\text{Al}(\text{}^t\text{Bu}_2\text{pz})_2\text{Me}_2\}]_2$  and  $[\{\text{Na}(\text{THF})\}\{\text{Al}(\text{}^t\text{Bu}_2\text{pz})_3\text{Me}\}]$ , respectively). Reflecting their remarkable kinetic and thermodynamic stability, solutions of the bis(pyrazolyl)aluminate **1** show no trace of the tris(pyrazolyl)aluminate **2**, contrary to what is observed with the hydride version  $[\{\text{Li}(\text{THF})_2\}\{\text{Al}(\text{Ph}_2\text{pz})_2\text{H}_2\}]$  that exists in equilibrium with  $[\{\text{Li}(\text{THF})\}\{\text{Al}(\text{Ph}_2\text{pz})_3\text{H}\}]$ .<sup>9</sup>

The X-ray crystallographic studies of complexes **1** and **2** reveal mononuclear complexes. In **1** the aluminate binds the sodium ion in a κ<sup>3</sup>-N, N, N fashion that involves κ<sup>1</sup> coordination of one pyrazolyl ring [Na(1)–N(1) 2.389(3) Å] and κ<sup>2</sup> coordination of the second ring [Na(1)–N(3) 2.374(3), Na(1)–N(4) 2.747(3) Å], see Figure 1. The sodium ion completes its pseudotetrahedral coordination sphere with two THF molecules. There is no indication of any “agostic” interaction between the Al–CH<sub>3</sub> group and Na (Na⋯C 3.62 Å) for which typical distances are in the range 2.569–2.873 Å.<sup>8, 18, 22</sup> The <sup>t</sup>Bu analog of **1** also exhibits a κ<sup>1</sup>, κ<sup>2</sup> coordination, but it appears as a dimer with Al–Me–Na bridges and a single THF ligand per Na.<sup>18</sup>



**Figure 1.** Perspective view of the X-ray structure of **1** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms have been removed for clarity. Relevant bond lengths (Å) and angles (deg): Na(1)–O(1) 2.277(3), Na(1)–O(2) 2.270(3), Na(1)–N(1) 2.389(3), Na(1)–N(3) 2.374(3), Na(1)–N(4) 2.747(3), Al(1)–C(31) 1.951(4), Al(1)–C(32) 1.972(4); N(1)–Na(1)–N(3) 105.95(10), N(1)–Na(1)–N(4) 77.11(8), O(1)–Na(1)–O(2) 101.56(10), C(31)–Al(1)–C(32) 119.96(16).

In **2** (Figure 2), the aluminate binds the sodium ion in a  $\kappa^3$ -N, N, N fashion that involves  $\kappa^1$  coordination of the three pyrazolyl rings to the sodium ion [Na(1)–N(2) 2.433(2), Na(1)–N(4) 2.377(2), Na(1)–N(6) 2.386(2) Å]. The sodium ion completes its coordination sphere with one molecule of THF [Na(1)–O(1) 2.247(2) Å]. The sodium ion is only slightly out (0.69 Å) of the plane defined by the atoms O(1)–N(4)–N(6). The overall structure is highly distorted as judged by the N–Al–N angles and the torsion angles involving Na, Al, and the two N atoms of a given pyrazole ring. These atoms are far from being coplanar with a propeller shape being adopted around the Al...Na axis [torsion angles (°): Na(1)–N(2)–N(1)–Al(1) 38, Na(1)–N(4)–N(3)–Al(1) 49, Na(1)–N(6)–N(5)–Al(1) 52]. In the <sup>t</sup>Bu analog of **2**, a more distorted structure is observed with one pyrazolyl ring being  $\kappa^2$  coordinated to Na.



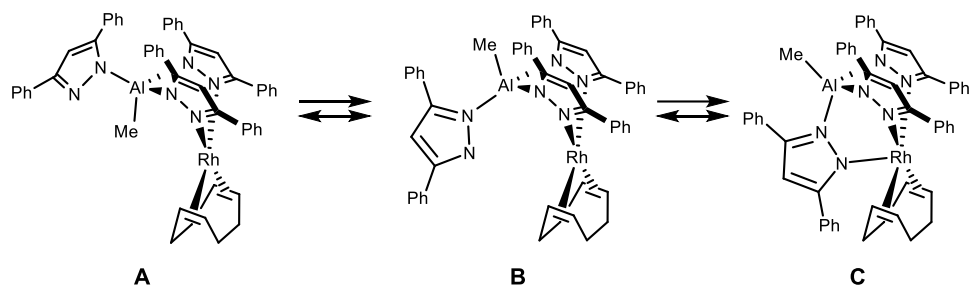
**Figure 2.** Perspective view of the X-ray structure of **2** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms have been removed for clarity. Relevant bond lengths (Å) and angles (deg): Na(1)-N(2) 2.433(2), Na(1)-N(4) 2.377(2), Na(1)-N(6) 2.386(2), Na(1)-O(1) 2.247(2), Al(1)-C(50) 1.948(2); O(1)-Na(1)-N(2) 125.18(7), O(1)-Na(1)-N(4) 112.14(7), O(1)-Na(1)-N(6) 139.47(8), N(4)-Na(1)-N(6) 90.15(7), N(4)-Na(1)-N(2) 96.73(7), N(6)-Na(1)-N(2) 82.38(7), N(1)-Al(1)-N(3) 107.50(9), N(1)-Al(1)-N(5) 98.71(9), N(3)-Al(1)-N(5) 102.11(9).

## 2.2 Synthesis and characterization of bis(pyrazolyl)aluminate rhodium complex **3** and tris(pyrazolyl)aluminate rhodium complex **4**

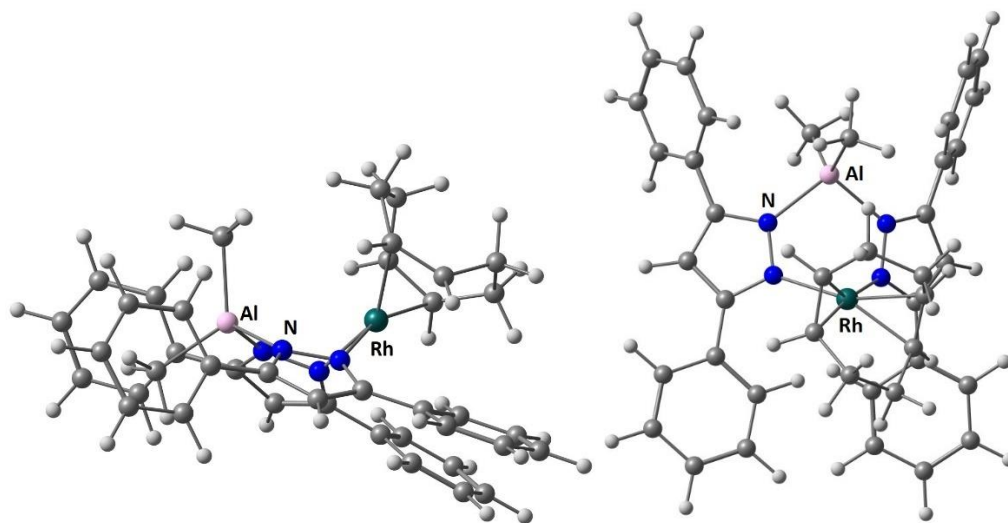
We accomplished a metathesis reaction to transfer aluminates **1** and **2** to the rhodium center by treating **1** and **2** with  $[\text{Rh}(\text{COD})\text{Cl}]_2$  in toluene at 100 °C overnight affording after workup the yellow 16-electron bimetallic complexes  $[\text{Rh}(\text{COD})\{\text{Al}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$  (**3**) and  $[\text{Rh}(\text{COD})\{\text{Al}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  (**4**) in 63 and 89 % yield, respectively. Complexes **3** and **4** co-crystallize with  $[\text{Rh}(\mu\text{-Ph}_2\text{pz})(\text{COD})]_2$  in the solvents investigated, additionally; **4** also co-crystallizes with **2**. The best solvent for the extraction of **3** is toluene (93% by  $^1\text{H}$  NMR, Figure S19), while for **4** it is dichloromethane (DCM) (97% by  $^1\text{H}$  NMR, Figure S22). The room



temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** and **4** are consistent with both complexes proposed formulation. For **3**, two distinct methyl signals for the Al-CH<sub>3</sub> moieties are observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra at  $\delta$  0.36, -2.15; and -4.26, -7.52, respectively. These values are in reasonable agreement with the computed chemical shifts of the DCM solvated structure of **3** at  $\delta$  0.41, -2.22; and -3.18, -8.51, respectively. The two most shielded resonances are attributed to the  $\pi$  electronic currents of two flanking phenyl rings on a CH<sub>3</sub> substituent on Al (Figure 3). The DFT calculated gas-phase structure seen in Figure 3 shows that the shortest carbon-hydrogen bond distances (1.10 Å) in the Al-CH<sub>3</sub> moieties are those pointing towards phenyl centroids. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR of **4** show two distinct methyne resonances assigned to two pyrazolate moieties coordinated to the Rh center ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR:  $\delta$  6.39, 107, respectively), and one unbound pyrazolate ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR:  $\delta$  5.70, 86.19, respectively). Interestingly the borate analog of **4**,  $\text{Tp}^{\text{Ph,Ph}}\text{Rh}(\text{COD})$  shows an average spectrum consisting of either B  $\leftrightarrow$  C conformers in solution or fast interconverting A  $\leftrightarrow$  B  $\leftrightarrow$  C as shown in Scheme 2.<sup>23-26</sup> Consistent with the NMR data, the X-ray structure of **4** (Figure 4) shows a  $\kappa^2$ -coordination mode of the tris(pyrazolyl)aluminate to a square-planar Rh(I) center. The unbound pyrazolyl substituent adopts an equatorial position resembling that of A-type isomer observed in  $[\text{Tp}^{\text{Ph}}\text{Rh}(\text{COD})]^{25}$ ,  $[\text{Tp}^{\text{Ph,Me}}\text{Rh}(\text{COD})]^{23}$  and in the open-diene complexes  $[\text{Tp}^{\text{tol}}\text{Rh}(\text{CH}_2=\text{CH}_2)_2]$  and  $[\text{Tp}^{\text{tol}}\text{Rh}(\text{CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)]^{27}$  (Scheme 2). The Rh-N bond lengths in **4** are comparable to those of the boron analogs that are in the range 2.083-2.114 Å.<sup>23</sup>

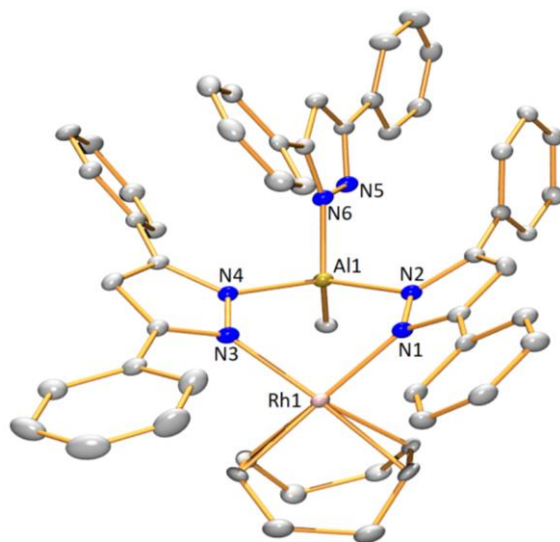


**Scheme 2.** Possible conformers for **4** in solution.



**Figure 3.** DFT PBE0 gas phase structure of **3**. Relevant bond lengths ( $\text{\AA}$ ) and angles (deg):

Al-C 1.105, 1.105, 1.07, 1.08, 1.107, 1.107, Al-C 1.990, 1.999; Al-N 2.007, 2.008; Rh-N 2.132, 2.100; C-Al-C 121.43, C-Al-N 110.66, 109.14; N-Al-N 103.25; N-Rh-N 88.13.



**Figure 4.** Perspective view of the X-ray structure of **4** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms have been removed for clarity. Relevant bond lengths (Å) and angles (deg): Rh(1)-N(1) 2.095(3), Rh(1)-N(3) 2.097(3), Al(1)-N(4) 1.928(3), Al(1)-N(2) 1.933(3), Al(1)-N(6) 1.882(3), Al(1)-C(46) 1.942(4); N(1)-Rh(1)-N(3) 86.90(12), N(3)-Rh(1)-C(48) 92.94(14), N(1)-Rh(1)-C(52) 89.85(14), N(4)-Al(1)-N(2) 105.67(13), N(6)-Al(1)-N(4) 102.69(14), N6-Al1-N2 102.45(14), N6-Al1-C46 116.85(16); N4-Al1-C46 112.81(16); N2-Al1-C46 114.91(16).

### 2.3 Polymerization of phenylacetylene by catalysts **3** and **4**

We sought to compare the catalytic activity of rhodium polypyrazoliluminates **3** and **4** with their boron analogs [Bp<sup>R,R</sup>RhCOD] and [Tp<sup>R,R</sup>RhCOD]. Published data for the latter borates are available for the polymerization of phenylacetylene (PA)<sup>23, 28-29</sup>, Eq 1, and Table 1.

Consequently, we proceeded to carry out the polymerization of PA with **3** and **4** in DCM using a catalyst loading of 0.7% and in conditions given in Table 1. The IR spectra of isolated yellow polyphenylacetylene (PPA) from **3** and **4** show *cis*-PPA according to two strong absorptions at

755 and 738  $\text{cm}^{-1}$  and a broad one at 885  $\text{cm}^{-1}$ . An overall highly stereoregular polymer with *cis*-transoidal structure is inferred from a sharp singlet resonance at  $\delta$  5.84 in the  $^1\text{H}$  NMR spectrum. Integration revealed a *cis* content higher than 90%<sup>29-31</sup> (Figures S7, S8, and Eq S2). *Cis*-transoidal PPA was also isolated from boron analogs<sup>23, 29</sup> of **3** and **4**. Remarkably complexes **3** and **4** polymerize PA considerably faster [15-60 min at 0 °C, entries 1-4] than their boron counterparts [hours between 20 to 40°C, entries 6-14]. The isolated polymers show molecular weights,  $M_n$ , ranging from  $4.2 \times 10^4$  to  $8.9 \times 10^4$  and  $D$  from 2.02 to 2.69. The enhanced catalytic activity of complexes **3** and **4** is ascribed to the unsaturated coordination  $\kappa^2$  form. The  $\kappa^2$  form is favored with large substituents on the pyrazolyl rings and with complexes having COD as a ligand instead of NBD. Indeed, some [TpRhNBD] complexes show modest catalytic activity and [TpRh(CO)<sub>2</sub>] complexes are inactive.<sup>23, 29</sup> According to the NMR data of the polymerization reactions before quenching, there is no significant degradation of complexes **3** and **4** (Figures S2, and S4), suggesting dissociation of the diene is most likely not the event that initiates polymerization, as is the case with [TpRhCOD] borate analogs<sup>23, 29</sup>.

Catalysts **3** and **4** were isolated with a minor content of [Rh(Ph<sub>2</sub>pz)(COD)]<sub>2</sub>. The latter was tested under the same reaction conditions for PA polymerization as **3** and **4** with no noticeable formation of PPA during reaction time, and after workup, only unreacted PA was isolated.

Obvious questions for complexes **3** and **4** is how the aluminate ligand system compares to the borate ligands in terms of bite angle (taken from measured N-Rh-N angles in a similar manner as P-M-P bite angles for phosphines),<sup>32</sup> and electronic properties and if both factors influence the catalytic polymerization of PA. The lack of a crystal structure for **3** and crystallographic data of rhodium poly(pyrazolyl)borate analogs prompted us to explore gas phase DFT structures of **3**, **4**, and their boron counterparts [Rh(COD){B(Ph<sub>2</sub>pz)<sub>2</sub>Me<sub>2</sub>}], and [Rh(COD){B(Ph<sub>2</sub>pz)<sub>3</sub>Me}] which

are shown in the SI. The electronic situation of the rhodium center in **3** and **4** compared to analogous borates was probed indirectly by the IR CO stretching modes of optimized **3-CO**, **4-CO**,  $[\text{Rh}(\text{CO})_2\{\text{B}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$ , and  $[\text{Rh}(\text{CO})_2\{\text{B}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  (Table S4). The COD derivatives show wider bite angles for **3** and **4**, (88 and 89°, respectively). The same angle in the solid state structure of **4** is 87°, than for complexes  $[\text{Rh}(\text{COD})\{\text{B}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$  and  $[\text{Rh}(\text{COD})\{\text{B}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  (84°). Bite angles for these borates are within the range of those crystallographically characterized in entries 11 to 13 of Table 1 which span from 82 to 83°. <sup>23</sup> The symmetric and antisymmetric CO stretching modes of **3-CO** and **4-CO** are consistently 2 to 4 wavenumbers higher than for  $[\text{Rh}(\text{CO})_2\{\text{B}(\text{Ph}_2\text{pz})_2\text{Me}_2\}]$ , and  $[\text{Rh}(\text{CO})_2\{\text{B}(\text{Ph}_2\text{pz})_3\text{Me}\}]$  implying rhodium been slightly less electron-rich in the rhodium-aluminate complexes. Therefore, current data available highlight that replacing B for Al in Bp and Tp complexes of Rh result in better performance of the catalytic active species during polymerization of PA due to wider bite angles and a more electron-deficient rhodium center.

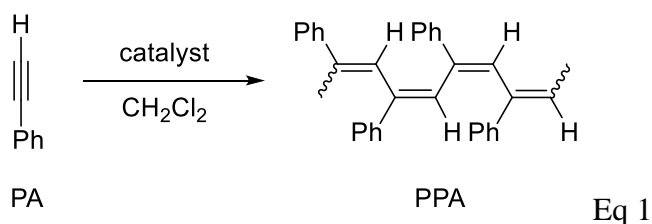


Table 1. Polymerization of PA using catalysts **3**, **4**, and  $[\text{Rh}(\text{Ph}_2\text{pz})(\text{COD})]_2$ .<sup>a</sup>

Entry	Catalyst	Temperature (°C)	Time (min)	Conversion <sup>b</sup> (%)	$M_n^c$ 10 <sup>-4</sup>	$M_w/M_n$
1	<b>3</b>	20	60	85	8.9	2.12
2	<b>3</b>	0	60	99	7.6	2.20
3	<b>4</b>	20	15	98	4.2	2.02
4	<b>4</b>	0	15	97	5.1	2.69
5	$[\text{Rh}(\text{Ph}_2\text{pz})(\text{COD})]_2$	20	60	0	–	–
6 <sup>c</sup>	$[\text{Bp}^{\text{Me}_2}\text{Rh}(\text{COD})]$	40	1440	84	3.2	2.43

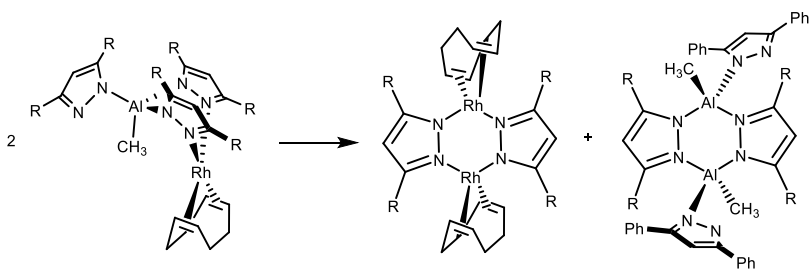
7 <sup>d</sup>	[Bp <sup>(CF<sub>3</sub>)<sub>2</sub></sup> Rh(COD)]	40	1440	92	2.1	2.34
8 <sup>d</sup>	[Tp <sup>Ph<sub>2</sub></sup> Rh(COD)]	40	1440	98	1.5	2.48
9 <sup>d</sup>	[Tp <sup>Me<sub>2</sub></sup> Rh(COD)]	40	1440	98	1.5	2.48
10 <sup>d</sup>	[Tp <sup>iPr<sub>2</sub></sup> Rh(COD)]	40	180	99	2.7	2.32
11 <sup>e</sup>	[Tp <sup>Ph,Me</sup> Rh(COD)]	20	1440	96	2.0	2.38
12 <sup>e</sup>	[HB(3-Ph,5-Mepz) <sub>2</sub> (3-Me,5-Phpz)Rh(COD)]	20	1440	98	0.9	2.03
13 <sup>e</sup>	[HB(3-Ph,5-Mepz) <sub>2</sub> (3,5-diEtpz)Rh(COD)]	20	1440	100	3.4	2.48
14 <sup>d</sup>	[TpRh(COD)]	40	1440	2	–	–

<sup>a</sup> Catalyst loading 0.7%. <sup>b</sup> % of PPA determined by <sup>1</sup>H NMR in dichloromethane-*d*<sub>2</sub>. <sup>c</sup> Determined by GPC based on polystyrene standards. References 29<sup>d</sup> and 23<sup>e</sup>, respectively.

#### 2.4 Complexation of other bis and tris (pyrazolyl)aluminates to [Rh(COD)Cl]<sub>2</sub> and decomposition reaction energetics of bis and tris(pyrazolyl)aluminate rhodium complexes by DFT computations

Having at hand phenyl substituted complexes **3** and **4**, we sought to synthesize other rhodium-aluminate derivatives with R = CF<sub>3</sub> and <sup>t</sup>Bu substituents on the pyrazol ring namely [Rh(COD){Al((CF<sub>3</sub>)<sub>2</sub>pz)<sub>n</sub>Me<sub>4-n</sub>}] and [Rh(COD){Al(<sup>t</sup>Bu<sub>2</sub>pz)<sub>n</sub>Me<sub>4-n</sub>}] with n = 2, 3. Sodium bis(3,5-tert-butylpyrazolyl)aluminate, [Na(THF)<sub>2</sub>]{Al(<sup>t</sup>Bu<sub>2</sub>pz)<sub>2</sub>Me<sub>2</sub>}, was previously reported by us<sup>18</sup> and the synthesis of sodium bis(3,5-trifluoromethylpyrazolyl)aluminate, [Na(THF)<sub>2</sub>]{Al((CF<sub>3</sub>)<sub>2</sub>pz)<sub>2</sub>Me<sub>2</sub>}, is given in the SI. Whatever the nature of R, reaction of these sodium aluminates with [Rh(COD)Cl]<sub>2</sub> at ambient temperature in toluene-*d*<sub>8</sub> gave decomposition products [Rh(R<sub>2</sub>pz)(COD)]<sub>2</sub> and [R<sub>2</sub>pzAlMe<sub>2</sub>]<sub>2</sub> together with unreacted [Na(THF)<sub>2</sub>]{Al(R<sub>2</sub>pz)<sub>2</sub>Me<sub>2</sub>}. Carrying out these reactions at 100 °C for R = <sup>t</sup>Bu afforded [Rh(<sup>t</sup>Bu<sub>2</sub>pz)(COD)]<sub>2</sub> and [<sup>t</sup>Bu<sub>2</sub>pzAlMe<sub>2</sub>]<sub>2</sub> in a 1:1 ratio (<sup>1</sup>H NMR Figure S28), whereas for R = CF<sub>3</sub> only [Rh((CF<sub>3</sub>)<sub>2</sub>pz)(COD)]<sub>2</sub> was detected in solution (<sup>1</sup>H, <sup>13</sup>C NMR Figure S26). Strikingly, the <sup>1</sup>H NMR spectrum for the CF<sub>3</sub> derivative also showed the presence of methane (δ 0.18) implying the formation of a sodium alkyl aluminate or an alkyl aluminum compound that

eventually decomposed. Before attempting the synthesis of rhodium tris(pyrazolyl)aluminates, we performed DFT calculations at the  $\omega$ B97M-V/def2-TZVPP level of theory to estimate the differences in energies of the coveted rhodium tris(pyrazolyl)aluminates and their possible decomposition products in bimolecular metathesis reactions as shown in Eq 2 and Table S3. Reactions I and II (R = Ph, CF<sub>3</sub>, respectively) are endothermic ( $\Delta E = 7.2, 20.8 \text{ kcal mol}^{-1}$ , respectively), while reaction III (R = <sup>t</sup>Bu) is almost thermoneutral. Therefore, the CF<sub>3</sub> derivative [Rh(COD){Al(CF<sub>3</sub>)<sub>2</sub>pz)<sub>3</sub>Me}] would be the species most likely to be isolated on thermodynamic grounds, with the next most likely being **4**. It can be seen from the crystal structure of **4** (Figure 4) and its optimized geometry in the gas phase shown in the SI that  $\pi$ - $\pi$  contacts (X-ray: 3.48 and 3.79 Å; DFT: 3.88 and 3.92 Å) of the loose pyrazolate flanked with phenyl rings from the  $\kappa^2$ -pyrazolates play an important role in the overall stabilization of the complex by restricting the C–C rotation of phenyl rings and consequently diminishing Van der Waals repulsions. From the  $\Delta E$  of reaction II and the optimized geometry of [Rh(COD){Al(CF<sub>3</sub>)<sub>2</sub>pz)<sub>2</sub>Me<sub>2</sub>}] shown in the SI, it can be inferred that Van der Waals repulsions between CF<sub>3</sub> substituents due to C-C bond rotation may favor the decomposition reaction II, precluding the possibility to isolate [Rh(COD){Al(CF<sub>3</sub>)<sub>2</sub>pz)<sub>2</sub>Me<sub>2</sub>}] and [Rh(COD){Al(CF<sub>3</sub>)<sub>2</sub>pz)<sub>3</sub>Me}]. Most probably [Rh(COD){Al(CF<sub>3</sub>)<sub>2</sub>pz)<sub>2</sub>Me<sub>2</sub>}] should present even smaller Van der Waals repulsions than [Rh(COD){Al(CF<sub>3</sub>)<sub>2</sub>pz)<sub>3</sub>Me}]. The fact that rhodium bis(pyrazolyl)aluminates [Rh(COD){AlR<sub>2</sub>pz)<sub>2</sub>Me<sub>2</sub>}] with R = <sup>t</sup>Bu and CF<sub>3</sub> cannot be isolated under conditions reported herein did not encourage us to attempt the synthesis of rhodium tris(pyrazolyl)aluminates. In the series of rhodium aluminates discussed so far, the <sup>t</sup>Bu derivatives [Rh(COD){Al<sup>t</sup>Bu<sub>2</sub>pz)<sub>n</sub>Me<sub>4-n</sub>}] are those with the most important Van der Waals repulsions, and accordingly, the decomposition pathway dominates the reaction course.



I: R = Ph (4); II: R = CF<sub>3</sub>; III: R = <sup>t</sup>Bu

Eq 2

### 3. Conclusion

Complexes **3** and **4** are the first examples of the successful transfer of a poly(pyrazolyl)aluminate to a transition metal center. The isolation of bimetallic poly(pyrazolyl)aluminate-TM complexes relies firstly on the nature of the substituents on the pyrazolate ring that minimizes electronic repulsions and therefore suppresses bimolecular metathesis. Secondly, having alkyls instead of hydrides substituents on the aluminate metalloligand suppresses undesirable substituent transfer to the TM center. Regarding the better performance of the poly(pyrazolyl)aluminate ligand system in the catalytic polymerization of PA by rhodium complexes compared to the poly(pyrazolyl)borates, it may be attributed to the wider bite angles and more electron-deficient rhodium center of the aluminate complexes. Ongoing research aims to expand the transfer of other poly(pyrazolyl)aluminates to transition metal centers for their use in homogenous catalysis.

### Associated Content

### Supporting Information



The Supporting Information is available free of charge at <https://pubs.acs.org/>. It contains experimental details and, spectroscopic, polymerization, ESI-MS, SCXRD and computational data.

### Accession codes

CCDC 2081992-2081994 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### References

- (1) Trofimenko, S., *Scorpionates – The Coordination Chemistry of Polypyrazolylborate Ligands*. Imperial College Press: London, 1999.
- (2) Trofimenko, S., Recent advances in poly(pyrazolyl)borate (scorpionate) chemistry. *Chem. Rev.* **1993**, *93*, 943-980.
- (3) Pettinari, C., *Scorpionates II: Chelating Borate Ligands*. 2008.
- (4) Trofimenko, S., Scorpionates: genesis, milestones, prognosis. *Polyhedron* **2004**, *23*, 197-203.
- (5) Muñoz-Hernández, M. A.; Montiel-Palma, V., Polypyrazolates of the heavier group 13 and 14 elements: A review. *Inorg. Chim. Acta* **2009**, *362*, 4328-4339.
- (6) Sambade, D.; Parkin, G., Synthesis and structural characterization of tris(pyrazolyl)hydroaluminate and tris(pyrazolyl)hydrogallate lithium compounds. *Polyhedron* **2017**, *125*, 219-229.
- (7) Breakell, K. R.; Patmore, D. J.; Storr, A., Synthesis of pyrazolyl-borate, -aluminate, -gallate, and -indate ligands, and their chelating properties towards cobalt(II), nickel(II), copper(II), and zinc(II). *J. Chem. Soc., Dalton Trans.* **1975**, 749-754.
- (8) Cortes-Llamas, S.; Velázquez-Carmona, M. A.; Muñoz-Hernández, M. A., Isolation and authentication of a sodium bispyrazolylaluminate. *Inorg. Chem. Commun.* **2005**, *8*, 155-158.

- (9) Snyder, C. J.; Heeg, M. J.; Winter, C. H., Poly(pyrazolyl)aluminate Complexes Containing Aluminum–Hydrogen Bonds. *Inorg. Chem.* **2011**, *50*, 9210-9212.
- (10) Plajer, A. J.; Kopf, S.; Colebatch, A. L.; Bond, A. D.; Wright, D. S.; García-Rodríguez, R., Deprotonation, insertion and isomerisation in the post-functionalisation of tris-pyridyl aluminates. *Dalton Trans.* **2019**, *48*, 5692-5697.
- (11) García-Romero, Á.; Plajer, A. J.; Álvarez-Miguel, L.; Bond, A. D.; Wright, D. S.; García-Rodríguez, R., Postfunctionalization of Tris(pyridyl) Aluminate Ligands: Chirality, Coordination, and Supramolecular Chemistry. *Chem. Eur. J.* **2018**, *24*, 17019-17026.
- (12) García-Rodríguez, R.; Simmonds, H. R.; Wright, D. S., Formation of a Heterometallic AlIII/SmIII Complex Involving a Novel [EtAl(2-py)2O]2– Ligand (2-py = 2-Pyridyl). *Organometallics* **2014**, *33*, 7113-7117.
- (13) Bullock, T. H.; Chan, W. T. K.; Eisler, D. J.; Streib, M.; Wright, D. S., Metal and ligand substitution of the aluminium tris-pyridyl ligands [RAI(2-py[prime or minute])3]- (R = Et, nBu, sBu, tBu; 2-py[prime or minute] = 2-pyridyl, 3-methyl-2-pyridyl, 5-methyl-2-pyridyl, 6-methyl-2-pyridyl). *Dalton Trans.* **2009**, 1046-1054.
- (14) Garcia, F.; Hopkins, A. D.; Kowenicki, R. A.; McPartlin, M.; Silvia, J. S.; Rawson, J. M.; Rogers, M. C.; Wright, D. S., Pyridyl 'ring-flipping' in the dimers [Me2E(2-py)]2 (E = B, Al, Ga; 2-py = 2-pyridyl). *Chem. Commun.* **2007**, 586-588.
- (15) García, F.; Hopkins, A. D.; Kowenicki, R. A.; McPartlin, M.; Rogers, M. C.; Silvia, J. S.; Wright, D. S., Syntheses and Structure of Heterometallic Complexes Containing Tripodal Group 13 Ligands [RE(2-py)3]- (E = Al, In). *Organometallics* **2006**, *25*, 2561-2568.
- (16) Alvarez, C. S.; Garcia, F.; Humphrey, S. M.; Hopkins, A. D.; Kowenicki, R. A.; McPartlin, M.; Layfield, R. A.; Raja, R.; Rogers, M. C.; Woods, A. D.; Wright, D. S., Highly selective epoxidation of styrene using a transition metal-aluminium(III) complex containing the [MeAl(2-py)3]- anion (2-py = 2-pyridyl). *Chem. Commun.* **2005**, 198-200.
- (17) García, F.; Hopkins, A. D.; Kowenicki, R. A.; McPartlin, M.; Rogers, M. C.; Wright, D. S., Synthesis of the [MeAl(2-py)3]- Anion and Its Application as a Stable and Mild Pyridyl-Transfer Reagent (2-py = 2-Pyridyl). *Organometallics* **2004**, *23*, 3884-3890.
- (18) Cortes-Llamas, S. A.; Muñoz-Hernández, M. Á., Sodium polypyrazolylaluminates: Synthesis, characterization, and isolation of a reaction intermediate of a trispyrazolylaluminate. *Organometallics* **2007**, *26*, 6844-6851.
- (19) Yu, Z. K.; Wittbrodt, J. M.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H., Unusually stable pyrazolate-bridged dialuminum complexes containing bridging methyl groups. *J. Am. Chem. Soc.* **2000**, *122*, 9338-9339.
- (20) Lewiński, J.; Zachara, J.; Goś, P.; Grabska, E.; Kopeć, T.; Madura, I.; Marciniak, W.; Prowotorow, I., Reactivity of Various Four-Coordinate Aluminum Alkyls towards Dioxygen: Evidence for Spatial Requirements in the Insertion of an Oxygen Molecule into the Al–C Bond. *Chem. Eur. J.* **2000**, *6*, 3215-3227.
- (21) Kosuru, S. R.; Sun, T.-H.; Wang, L.-F.; Vandavasi, J. K.; Lu, W.-Y.; Lai, Y.-C.; Hsu, S. C. N.; Chiang, M. Y.; Chen, H.-Y., Enhanced Catalytic Activity of Aluminum Complexes for the Ring-Opening Polymerization of  $\epsilon$ -Caprolactone. *Inorg. Chem.* **2017**, *56*, 7998-8006.
- (22) Andrikopoulos, P. C.; Armstrong, D. R.; Barley, H. R. L.; Clegg, W.; Dale, S. H.; Hevia, E.; Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E., Sodium dialkyl-amidozincates: Alkyl or amido bases? An experimental and theoretical case study. *J. Am. Chem. Soc.* **2005**, *127*, 6184-6185.
- (23) Ruman, T.; Ciunik, Z.; Trzeciak, A. M.; Wołowicz, S.; Ziólkowski, J. J., Complexes of Heteroscorpionate Trispyrazolylborate Ligands. Part 10. Structures and Fluxional Behavior of Rhodium(I) Complexes with Heteroscorpionate Trispyrazolylborate Ligands, Tp' 'Rh(LL) (LL = (CO)2 or COD). *Organometallics* **2003**, *22*, 1072-1080.
- (24) Bucher, U. E.; Currao, A.; Nesper, R.; Rueegger, H.; Venanzi, L. M.; Younger, E., .kappa.2-.kappa.3 Isomerism in Rhodium(I) Tris(pyrazolyl)borate Complexes of the Type Tp3R,4R,5RRh(LL) (LL

- = 2CO, COD, and NBD) and Their Dynamic Behavior in Solution. X-ray Crystal Structure of TpMeRh(NBD). *Inorg. Chem.* **1995**, *34*, 66-74.
- (25) Sanz, D.; Santa María, M. D.; Claramunt, R. M.; Cano, M.; Heras, J. V.; Campo, J. A.; Ruíz, F. A.; Pinilla, E.; Monge, A., Regular paper. *J. Organomet. Chem.* **1996**, *526*, 341-350.
- (26) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y., Synthesis and Structure Determination of Rh–diene Complexes with the Hydridotris(3,5-diisopropylpyrazolyl)borate Ligand, TpiPrRh(diene) (diene = cod, nbd): Dependence of the  $\nu(\text{B-H})$  Values on the Hapticity of the TpiPr Ligand ( $\kappa^2$  vs  $\kappa^3$ ). *Organometallics* **1997**, *16*, 4121-4128.
- (27) Conejero, S.; Esqueda, A. C.; Valpuesta, J. E. V.; Álvarez, E.; Maya, C.; Carmona, E., Different coordination modes of an aryl-substituted hydrotris(pyrazolyl)borate ligand in rhodium and iridium complexes. *Inorg. Chim. Acta* **2011**, *369*, 165-172.
- (28) Casado, M. A.; Fazal, A.; Oro, L. A., Rhodium-Catalyzed Polymerization of Phenylacetylene and its Derivatives. *Arab. J. Sci. Eng.* **2013**, *38*, 1631-1646.
- (29) Katayama, H.; Yamamura, K.; Miyaki, Y.; Ozawa, F., Stereoregular Polymerization of Phenylacetylenes Catalyzed by [Hydridotris(pyrazolyl)borato]rhodium(I) Complexes. *Organometallics* **1997**, *16*, 4497-4500.
- (30) Furlani, A.; Licoccia, S.; Russo, M. V.; Camus, A.; Marsich, N., Rhodium and platinum complexes as catalysts for the polymerization of phenylacetylene. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 991-1005.
- (31) Simionescu, C. I.; Percec, V.; Dumitrescu, S., Polymerization of acetylenic derivatives. XXX. Isomers of polyphenylacetylene. *J. Polym. Sci.: Polym. Chem. Ed.* **1977**, *15*, 2497-2509.
- (32) Dierkes, P.; Leeuwen, P. W. N. M. v., The bite angle makes the difference: a practical ligand parameter for diphosphine ligands. *J. Chem. Soc., Dalton Trans.* **1999**, 1519-1529.