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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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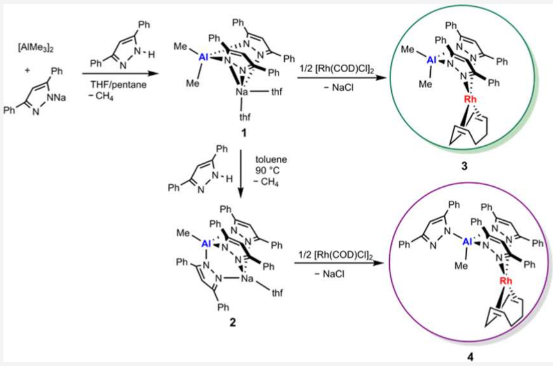

ABSTRACT: In this work, we report the transfer of alkyl bis- and tris(pyrazolyl)aluminates metalloligands to an electron-rich organotransition metal center. The 16-electron heterobimetallic complexes of rhodium [Rh(COD){Al(Ph_2pz)$_2$$Me_2$}] (**3**) and [Rh(COD){Al(Ph_2pz)$_3$Me}] (**4**) were obtained by metathesis reaction of the sodium bis- (**1**) and tris(pyrazolyl)aluminate (**2**) with [RhCl(COD)]$_2$. For **3**, ^{1}H and ^{13}C NMR in solution along with DFT calculations are consistent with a κ^2-coordination mode of the bis(pyrazolyl)aluminate to a square-planar Rh(I) center. The X-ray structure of **4** shows a similar κ^2-coordination mode of the tris(pyrazolyl)aluminate to Rh(I) with a pendant pyrazolyl moiety. The attempted synthesis of aluminate-rhodium complexes with R = CF_3, ^{t}Bu on the pyrazolate ring afforded [Rh(R_2pz)(COD)]$_2$ and [$R_2pzAlMe_2$]$_2$. Complexes **3** and **4** were investigated as homogeneous catalysts in the polymerization of phenylacetylene (PA). Both complexes showed enhanced catalytic activity compared to analogous rhodium poly(pyrazolyl)borates. Optimized gas-phase DFT geometries of **3**, **4**, [Rh(COD){B(Ph_2pz)$_2$$Me_2$}], and [Rh(COD){B($Ph_2pz$)$_3$Me}] were used to compare bite angles, while DFT geometries of **3-CO**, **4-CO**, [Rh(CO)$_2${B(Ph_2pz)$_2$$Me_2$}], and [Rh(CO)$_2${B($Ph_2pz$)$_3$Me}] were employed to probe the electronic situation of the 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 analogues 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,[1−4] very few reports of the heavier aluminum analogues are known.[5,6] 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 1970s,[7] it was not until a few years ago that one of us reported the first authenticated sodium poly(pyrazolyl)aluminate exhibiting Al−CH_3 bonds.[8] A remarkable series of poly(pyrazolyl)aluminates with Al−H bonds were also reported,[6,9] with the aim of transferring the aluminate to different metal halides. Significantly, the successful transfer of the hydrotris(pyrazolyl)aluminate [HAl(Ph_2pz)$_3$]$^-$ to a Zn center was accompanied by the undesired hydride transfer from aluminum to zinc giving [{HAl(Ph_2pz)$_3$}ZnH]. Other metal halides gave bimetallic pyrazolates [M_2X_2(Ph_2pz)$_2$(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.[9] 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.[10−17] We surmised that a better performance of the poly(pyrazolyl)aluminate ligand system toward 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, 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 [{Na(THF)$_2$}{Al(Ph_2pz)$_2$$Me_2$}] (**1**) and [{Na(THF)}{Al(Ph_2pz)$_3$Me}] (**2**) and the complexation of aluminates **1** and **2** to an electron-rich Rh(I) center to afford

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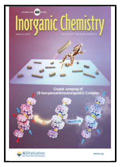

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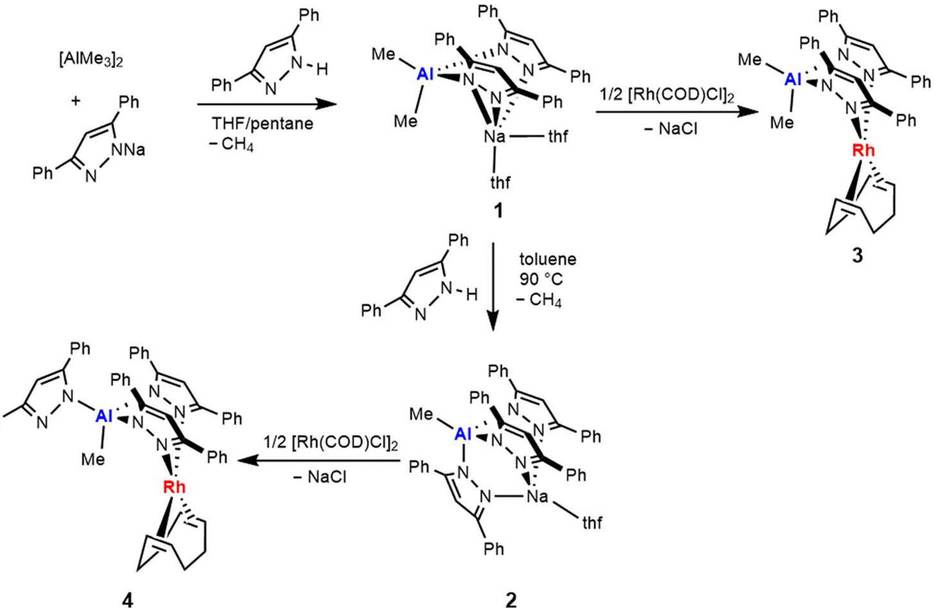
Scheme 1. New Poly(pyrazolyl)aluminate Chemistry



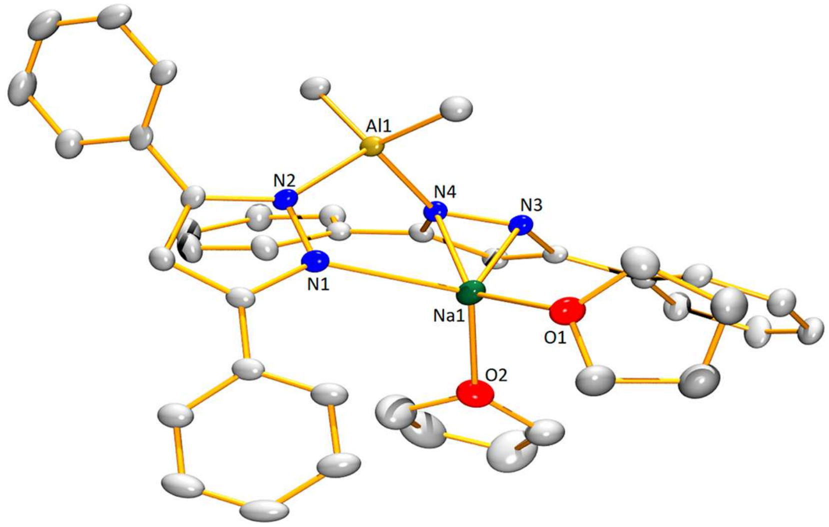


Figure 1. Perspective view of the X-ray structure of **1** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms have been removed for clarity. Relevant bond lengths (Å) and angles (deg): Na(1)−O(1) 2.277(3), Na(1)−O(2) 2.270(3), Na(1)−N(1) 2.389(3), Na(1)−N(3) 2.374(3), Na(1)−N(4) 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).

$[Rh(COD)\{Al(Ph_2pz)_2Me_2\}]$ (**3**) and $[Rh(COD)\{Al(Ph_2pz)_3Me\}]$ (**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 modeling helps rationalizing structural and reactivity differences between boron- and aluminum-based ligands.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Bis(pyrazolyl)-aluminate 1 and Tris(pyrazolyl)aluminate 2.

1 and **2** were synthesized by nucleophilic addition of $[Na(Ph_2pz)]$ to $AlMe_3$ and the stepwise addition of 1 and 2 molar equiv of Ph_2pzH (Scheme 1).[5,18,19] The bimetallic complex $[Ph_2pzAlMe_2]_2$[20,21] (^1H NMR, benzene-d_6: δ 7.42, 7.03, 6.26, −0.66) is a minor side product (~10% from ^1H 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 Ph_2pzH at 90 °C in toluene. In contrast,[18] the related aluminate $[\{Na(THF)\}\{Al(^tBu_2pz)_3Me\}]$ is formed at ambient temperature, possibly reflecting that, in the putative bridged Al−Me−Na intermediate $[Me_2Al(R_2pz)_2Na(R_2pzH)]$,[18] the bridging methyl group is less nucleophilic when R = Ph. Consistently, in the ^1H NMR spectra for **1** and **2** in benzene-d_6, the characteristic high field CH_3−Al resonances appear at δ −0.35 and −1.48, respectively, at significantly higher field than those of $[\{Na(THF)\}\{Al(^tBu_2pz)_2Me_2\}]_2$ and $[\{Na(THF)\}\{Al(^tBu_2pz)_3Me\}]$ 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 $^{13}C\{^1H\}$ NMR spectra where the methyl substituents show broad resonances at δ −6.28 and −8.98, respectively (δ −1.2 and 1.8 for $[\{Na(THF)\}\{Al(^tBu_2pz)_2Me_2\}]_2$ and $[\{Na(THF)\}\{Al(^tBu_2pz)_3Me\}]$, 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 $[\{Li(THF)_2\}\{Al(Ph_2pz)_2H_2\}]$ that exists in equilibrium with $[\{Li(THF)\}\{Al(Ph_2pz)_3H\}]$.[9]

The X-ray crystallographic studies of complexes **1** and **2** reveal mononuclear complexes. In **1**, the aluminate binds the sodium ion in a κ^3-N,N,N fashion that involves κ^1 coordination of one pyrazolyl ring (Na(1)−N(1) 2.389(3) Å) and κ^2 coordination of the second ring [Na(1)−N(3) 2.374(3) Å, 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_3 group and Na (Na···C 3.62 Å) for which typical distances are in the range of 2.569−2.873 Å.[8,18,22] The ^{t}Bu analogue of **1** also exhibits a κ^1,κ^2 coordination, but it appears as a dimer with Al-Me-Na bridges and a single THF ligand per Na.[18]

In **2** (Figure 2), the aluminate binds the sodium ion in a κ^3-N,N,N fashion that involves κ^1 coordination of the three pyrazolyl rings to the sodium ion [Na(1)−N(2) 2.433(2) Å, Na(1)−N(4) 2.377(2) Å, 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 (deg): 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 ^{t}Bu analogue of **2**, a more distorted structure is observed with one pyrazolyl ring being κ^2 coordinated to Na.

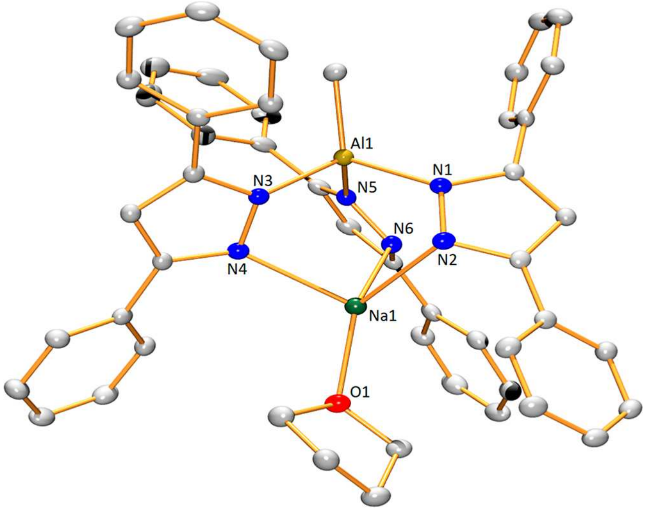
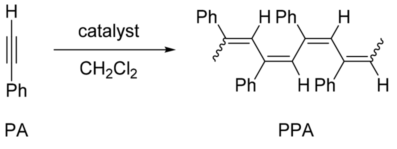


Figure 2. Perspective view of the X-ray structure of **2** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms have been removed for clarity. Relevant bond lengths (Å) and angles (deg): Na(1)−N(2) 2.433(2), Na(1)−N(4) 2.377(2), Na(1)−N(6) 2.386(2), Na(1)−O(1) 2.247(2), Al(1)−C(50) 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 $[Rh(COD)Cl]_2$ in toluene at 100 °C overnight, affording after workup the yellow 16-electron bimetallic complexes $[Rh(COD)\{Al(Ph_2pz)_2Me_2\}]$ (**3**) and $[Rh(COD)\{Al(Ph_2pz)_3Me\}]$ (**4**) in 63% and 89% yield, respectively. Complexes **3** and **4** co-crystallize with $[Rh(\mu\text{-}Ph_2pz)(COD)]_2$ in the solvents investigated; additionally, **4** also co-crystallizes with **2**. The best solvent for the extraction of **3** is toluene (93% by ^{1}H NMR, Figure S19), whereas, for **4**, it is dichloromethane (DCM) (97% by ^{1}H NMR, Figure S22). The room temperature ^{1}H and ^{13}C NMR spectra of **3** and **4** are consistent with both complexes' proposed formulation. For **3**, two distinct methyl signals for the Al-CH_3 moieties are observed in the ^{1}H and ^{13}C NMR spectra at δ 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 δ 0.41, −2.22; and −3.18, −8.51, respectively. The two most shielded resonances are attributed to the π electronic currents of two flanking phenyl rings on a CH_3 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_3 moieties are those pointing toward phenyl centroids. The ^{1}H and ^{13}C NMR of **4** show two distinct methyne resonances assigned to two pyrazolate moieties coordinated to the Rh center (^{1}H, ^{13}C NMR: δ 6.39, 107, respectively), and one unbound pyrazolate (^{1}H, ^{13}C NMR: δ 5.70, 86.19, respectively). Interestingly, the borate analogue of **4**, $Tp^{Ph,Ph}Rh(COD)$, shows an average spectrum consisting of either B ↔ C conformers in solution or fast interconverting A ↔ B ↔ C as shown in Scheme 2.[23−26] Consistent with the NMR data, the X-ray structure of **4** (Figure 4) shows a κ^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 the A-type isomer observed in $[Tp^{Ph}Rh(COD)]$,[25] $[Tp^{Ph,Me}Rh(COD)]$,[23] and in the open-diene complexes $[Tp^{tol}Rh(CH_2{=}CH_2)_2]$ and $[Tp^{tol}Rh(CH_2{=}C(Me)C(Me){=}CH_2)]$[27] (Scheme 2). The Rh−N bond lengths in **4** are comparable to those of the boron analogues that are in the range of 2.083−2.114 Å.[23]

2.3. Polymerization of Phenylacetylene by Catalysts 3 and 4. We sought to compare the catalytic activity of rhodium poly(pyrazolyl)aluminates **3** and **4** with their boron analogues $[Bp^{R,R}RhCOD]$ and $[Tp^{R,R}RhCOD]$. Published data for the latter borates are available for the polymerization of phenylacetylene (PA),[23,28,29] 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



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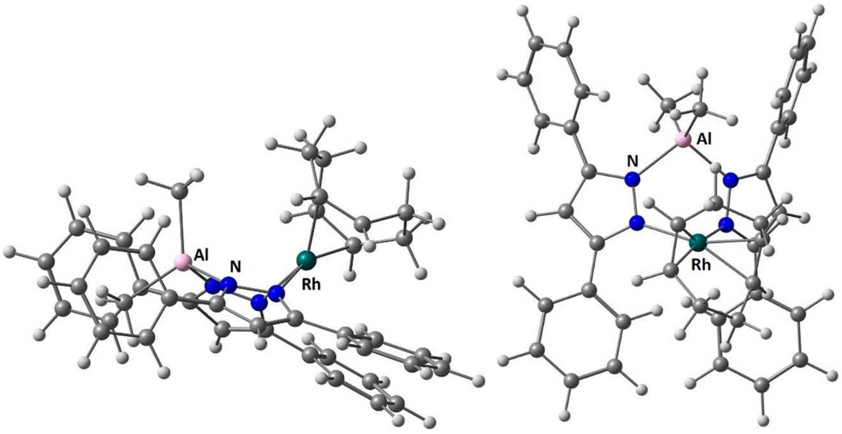
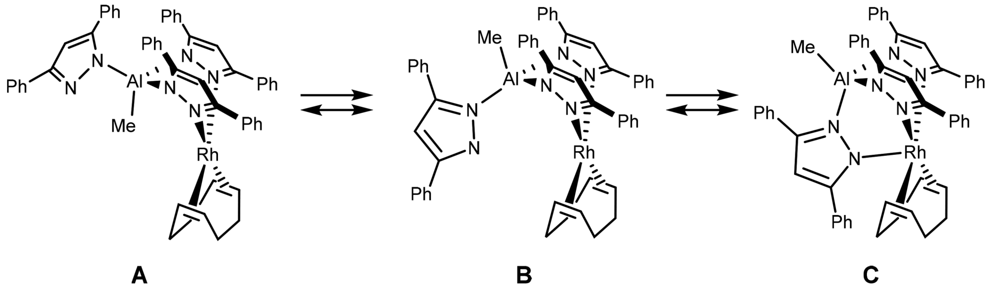


Figure 3. DFT PBE0 gas-phase structure of **3**. Relevant bond lengths (Å) and angles (deg): AlC–H 1.105, 1.105, 1.07, 1.08, 1.107, 1.107; Al–C 1.990, 1.999; Al–N 2.007, 2.008; Rh–N 2.132, 2.100; C–Al–C 121.43; C–Al–N 110.66, 109.14; N–Al–N 103.25; N–Rh–N 88.13.

Scheme 2. Possible Conformers for 4 in Solution



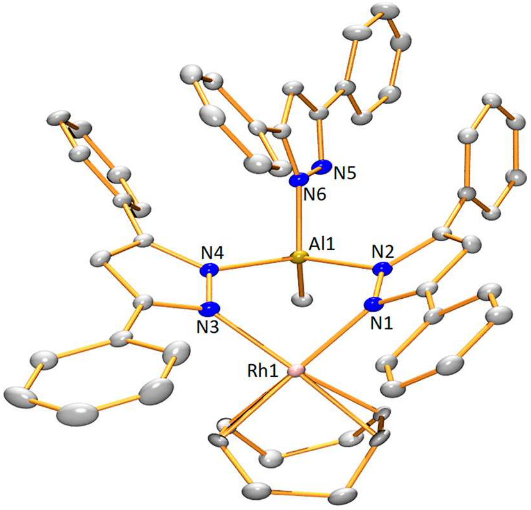


Figure 4. Perspective view of the X-ray structure of **4** showing thermal ellipsoids at the 30% probability level. Hydrogen atoms have been removed for clarity. Relevant bond lengths (Å) and angles (deg): Rh(1)–N(1) 2.095(3), Rh(1)–N(3) 2.097(3), Al(1)–N(4) 1.928(3), Al(1)–N(2) 1.933(3), Al(1)–N(6) 1.882(3), Al(1)–C(46) 1.942(4); N(1)–Rh(1)–N(3) 86.90(12), N(3)–Rh(1)–C48 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).

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 cm^{-1} and a broad one at 885 cm^{-1}. An overall highly stereoregular polymer with a *cis*-transoidal structure is inferred from a sharp singlet resonance at δ 5.84 in the ^1H NMR spectrum. Integration revealed a *cis* content higher than 90%[29−31] (Figures S7 and S8, eq S2). *Cis*-transoidal PPA was also isolated from boron analogues[23,29] 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 and 40 °C, entries 6–14]. The isolated polymers show molecular weights, M_n, ranging from 4.2×10^4 to 8.9×10^4 and *Đ* from 2.02 to 2.69. The enhanced catalytic activity of complexes **3** and **4** is ascribed to the unsaturated coordination κ^2 form. The κ^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 $[TpRh(CO)_2]$ complexes are inactive.[23,29] 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 analogues.[23,29]

Catalysts **3** and **4** were isolated with a minor content of $[Rh(Ph_2pz)(COD)]_2$. 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** are 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)[32] and electronic properties and if both factors influence the catalytic polymerization of PA. The lack of a crystal structure for **3** and

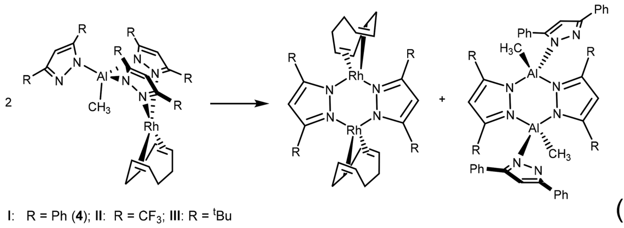
Table 1. Polymerization of PA Using Catalysts 3, 4, and$[Rh(Ph_2pz)(COD)]_2$[a]

entry	catalyst	temperature (°C)	time (min)	conversion[b] (%)	M_n[c] 10^{-4}	M_w/M_n
1	**3**	20	60	85	8.9	2.12
2	**3**	0	60	99	7.6	2.20
3	**4**	20	15	98	4.2	2.02
4	**4**	0	15	97	5.1	2.69
5	$[Rh(Ph_2pz)(COD)]_2$	20	60	0		
6[d]	$[Bp^{Me_2}Rh(COD)]$	40	1440	84	3.2	2.43
7[d]	$[Bp^{(CF_3)_2}Rh(COD)]$	40	1440	92	2.1	2.34
8[d]	$[Tp^{Ph_2}Rh(COD)]$	40	1440	98	1.5	2.48
9[d]	$[Tp^{Me_2}Rh(COD)]$	40	1440	98	1.5	2.48
10[d]	$[Tp^{iPr_2}Rh(COD)]$	40	180	99	2.7	2.32
11[e]	$[Tp^{Ph,Me}Rh(COD)]$	20	1440	96	2.0	2.38
12[e]	$[HB(3\text{-}Ph,5\text{-}Mepz)_2(3\text{-}Me,5\text{-}Phpz)Rh(COD)]$	20	1440	98	0.9	2.03
13[e]	$[HB(3\text{-}Ph,5\text{-}Mepz)_2(3,5\text{-}diEtpz)Rh(COD)]$	20	1440	100	3.4	2.48
14[d]	$[TpRh(COD)]$	40	1440	2		

[a] Catalyst loading 0.7%. [b] % of PPA determined by ^{1}H NMR in dichloromethane-d_2. [c] Determined by GPC based on polystyrene standards. [d] Reference 29. [e] Reference 23.

crystallographic data of rhodium poly(pyrazolyl)borate analogues prompted us to explore gas-phase DFT structures of **3**, **4**, and their boron counterparts $[Rh(COD)\{B(Ph_2pz)_2Me_2\}]$ and $[Rh(COD)\{B(Ph_2pz)_3Me\}]$which are shown in the Supporting Information (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**, $[Rh(CO)_2\{B(Ph_2pz)_2Me_2\}]$, and $[Rh(CO)_2\{B(Ph_2pz)_3Me\}]$ (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 $[Rh(COD)\{B(Ph_2pz)_2Me_2\}]$ and $[Rh(COD)\{B(Ph_2pz)_3Me\}]$ (84°). Bite angles for these borates are within the range of those crystallographycally characterized in entries 11−13 of Table 1 which span from 82° to 83°.[23] The symmetric and antisymmetric CO stretching modes of **3-CO** and **4-CO** are consistently 2−4 wavenumbers higher than those for $[Rh(CO)_2\{B(Ph_2pz)_2Me_2\}]$ and $[Rh(CO)_2\{B(Ph_2pz)_3Me\}]$, implying rhodium was 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 results in better performance of the catalytic active species during polymerization of PA due to wider bite angles and a more electron-deficient rhodium center.

2.4. Complexation of other Bis- and Tris(pyrazolyl)aluminates to $[Rh(COD)Cl]_2$ 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_3 and ^{t}Bu substituents on the pyrazol ring, namely, $[Rh(COD)\{Al((CF_3)_2pz)_nMe_{4-n}\}]$ and $[Rh(COD)\{Al(^tBu_2pz)_nMe_{4-n}\}]$ with $n = 2, 3$. Sodium bis(3,5-*tert*-butylpyrazolyl)aluminate, $[\{Na(THF)_2\}\{Al(^tBu_2pz)_2Me_2\}]$, was previously reported by us,[18] and the synthesis of sodium bis(3,5-trifluoromethylpyrazolyl)aluminate, $[\{Na(THF)_2\}\{Al((CF_3)_2pz)_2Me_2\}]$, is given in the SI. Whatever the nature of R, reaction of these sodium aluminates with $[Rh(COD)Cl]_2$ at ambient temperature in toluene-d_8 gave decomposition products $[Rh(R_2pz)(COD)]_2$ and $[R_2pzAlMe_2]_2$ together with unreacted $[\{Na(THF)_2\}\{Al(R_2pz)_2Me_2\}]$. Carrying out these reactions at 100 °C for R = ^{t}Bu afforded $[Rh(^tBu_2pz)(COD)]_2$ and $[^tBu_2pzAlMe_2]_2$ in a 1:1 ratio (^{1}HNMR Figure S28), whereas, for R = CF_3, only $[Rh\{(CF_3)_2pz\}(COD)]_2$ was detected in solution (^{1}H, ^{13}CNMR Figure S26). Strikingly, the ^{1}HNMR spectrum for the CF_3 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 ωB97M-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_3, respectively) are endothermic (ΔE = 7.2, 20.8 kcal mol^{-1}, respectively), whereas reaction III (R = ^{t}Bu) is almost thermoneutral. Therefore, the CF_3 derivative $[Rh(COD)\{Al(CF_3)_2pz)_3Me\}]$ 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 π−π 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 κ^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 ΔE of reaction II and the optimized geometry of $[Rh(COD)\{Al(CF_3)_2pz)_2Me_2\}]$ shown in the SI, it can be inferred that van der Waals repulsions between CF_3 substituents due to C−C bond rotation may favor the decomposition reaction II, precluding the possibility to isolate $[Rh(COD)\{Al(CF_3)_2pz)_2Me_2\}]$ and $[Rh(COD)\{Al(CF_3)_2pz)_3Me\}]$. Most probably, $[Rh(COD)\{Al(CF_3)_2pz)_2Me_2\}]$ should present even smaller van der Waals repulsions than $[Rh(COD)\{Al(CF_3)_2pz)_3Me\}]$. The fact that rhodium bis(pyrazolyl)aluminates $[Rh(COD)\{AlR_2pz)_2Me_2\}]$ with R = ^{t}Bu and CF_3 cannot be isolated under conditions reported



(2)

herein did not encourage us to attempt the synthesis of rhodium tris(pyrazolyl)aluminates. In the series of rhodium aluminates discussed so far, the ^{t}Bu derivatives $[Rh(COD)\{Al^tBu_2pz)_nMe_{4-n}\}]$ are those with the most important van der Waals repulsions, and accordingly, the decomposition pathway dominates the reaction course.

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, first, on the nature of the substituents on the pyrazolate ring that minimizes electronic repulsions and therefore suppresses bimolecular metathesis. Second, 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 homogeneous catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01434.

Experimental details and spectroscopic, polymerization, ESI-MS, SCXRD, and computational data (PDF)

Accession Codes

CCDC 2081992−2081994 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing 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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Notes

The authors declare no competing financial interest.

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