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Ortho-substituted aryl diamido complexes of zirconium: observation of rotameric isomers†

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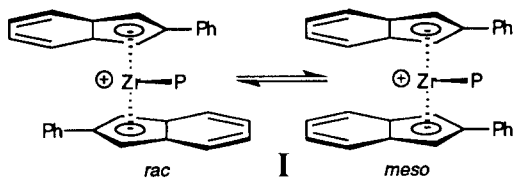
Abstract—Zirconium complexes bearing a series of ortho-substituted aryl diamido ligands [2,6-$(RNCH_2)_2NC_5H_3]^{2-}$ (R = 2-PhC_6H_4 (BPhP); 2-$^iPrC_6H_4$ (BMPP); 2-$^tBuC_6H_4$ (BMBP), 2-^{i}Pr-6-MeC_6H_3 (MPPP)) have been synthesized. The mixed amide complexes [2,6-$(RNCH_2)_2NC_5H_3$]$Zr(NMe_2)_2$ are prepared in high yield from 2,6-$(RHNCH_2)_2NC_5H_3$ and $Zr(NMe_2)_4$. The mixed amides react with excess $ClSiMe_3$ to afford the dichlorides [2,6-$(RNCH_2)_2NC_5H_3$]$ZrCl_2$ in nearly quantitative yield. Dimethyl complexes are prepared from [2,6-$(RNCH_2)_2NC_5H_3$]$ZrCl_2$ and 2 equiv. of MeMgCl. NMR spectroscopy has been used to identify rotameric isomers derived from restricted rotation about the N—C_{ipso} bond of the ligand. The aryl groups in (BPhP)ZrX_2 complexes freely rotate at all temperatures (−80 to +80°C) while (BMPP)ZrX_2 (X = NMe_2, Cl, Me) derivatives adopt *meso* and *rac* rotamers at low temperatures. In contrast, (BMBP)ZrX_2 and (MPPP)ZrX_2 (X = NMe_2, Cl, Me) compounds are locked at all temperatures. (BMBP)$ZrCl_2$ is isolated as a single isomer, likely the *meso* rotamer, while (MPPP)$ZrCl_2$ is a near statistical mixture of *meso* and *rac* isomers.

Keywords: zirconium complexes; isomer; rotamer.

Tremendous progress has been made over the past 15 years on the design and preparation of single-site group 4 catalysts for the polymerization of α-olefins [1–3]. Efforts in this area have been concerned with the way in which the catalytic activity and stereoregularity can be altered with changes to the ancillary ligands. For example, the ingeniously designed C_2-symmetric compound *rac*-ethylenebis(η^5-tetrahydroindenyl) $ZrCl_2$ [4] and the left/right C_s-symmetric derivative isopropyl(η^5-Cp-1-η^5-fluorenyl)$ZrCl_2$ [5] are catalyst precursors for the isospecific and syndiospecific polymerization of propylene, respectively. Building upon the structure/property relationship in metallocene complexes, Waymouth and Coates recently reported the details of a new zirconium catalyst that takes advantage of an 'oscillating' ligand environment [6]. The putative cationic complex $[(2\text{-Ph-indenyl})_2ZrP]^+$ (**I**) (P = polymer chain) can adopt one of two possible isomeric structures; a *rac* species which polymerizes propylene in an isospecific manner or a *meso* complex



I

which gives rise to blocks of atactic polypropylene. The interconversion of these species on the polymerization time scale affords stereoblock polypropylene, a thermoplastic elastomer.

Although the metallocene class of compounds have been successful, there is a growing interest in alternative ligand systems; in particular, attention has focused on nitrogen-based ligands [7–13]. For example, chelating diamide complexes of titanium serve as precursors for the highly active [14] and living [15] polymerization of α-olefins. In addition, pyridine diamide complexes of zirconium are active catalysts for the polymerization of ethylene [16]. With the oscillating catalyst tenet in hand, we set out to prepare diamide ligands bearing potentially oscillating aryl substituents at nitrogen. Herein we describe the syn-

† Dedicated to Professor D. C. Bradley on the occasion of his 73rd birthday.

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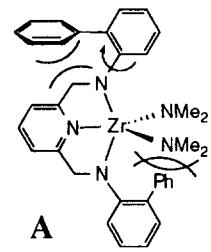
thesis and fluxional behavior of ortho-substituted aryl diamido complexes of zirconium.

RESULTS AND DISCUSSION

2,6-Bis(bromomethyl)pyridine [17] reacts with 2 equiv. of LiNHR (R = 2-PhC_6H_4; 2-$^iPrC_6H_4$; 2-$^tBuC_6H_4$, 2-^{i}Pr-6-MeC_6H_3) in THF at -78°C to afford the pyridine diamine ligands (**1a–d**) in 63–93% yield (Scheme 1).

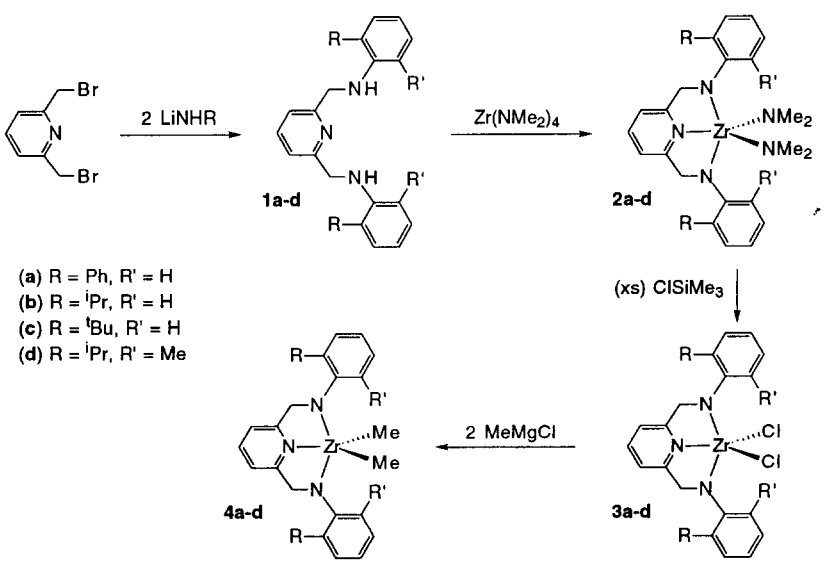
The ligands are white crystalline solids, except **1a** which was isolated as a yellow oil. We have previously reported [16,18] that amine elimination reactions [19] are an excellent method for appending bulky chelating diamide ligands to zirconium. The pyridine diamine ligands **1a–d** react cleanly with $Zr(NMe_2)_4$ [20] at 23°C to afford the mixed amide complexes (**2a–d**) in nearly quantitative yield as evidenced by ^{1}H NMR spectroscopy. The reaction between $Zr(NMe_2)_4$ and the 2-*tert*-butyl substituted ligand **1c** is fast at -80°C, as no intermediates are observed by ^{1}H NMR spectroscopy. These aminolysis reactions are unaffected by the presence of excess dimethylamine [21], hence we observe only the kinetic products. The amide complexes **2a–c** are isolated as yellow solids in >90% yield, however, the high solubility of compound **2d** in hexanes limits its isolation.

The temperature invariant proton NMR spectrum of complex **2a** exhibits a single sharp resonance for the methylene protons of the ligand (CH_2N) and a singlet for the dimethylamido groups. These resonances are consistent with some degree of free rotation about the N—C_{ipso} bond which yields a structure with local C_{2v}-symmetry. Using the X-ray coordinates [16] of $[(RNCH_2)_2NC_5H_3]ZrMe_2$ (R = 2,6-$Et_2C_6H_3$) as a starting point, modelling studies [22] on derivative **2a** predict a large barrier to rotation about the N—C_{ipso} bond when the *o*-phenyl groups pass by the dimethylamido groups (**A**). Therefore, the spectroscopically observed C_{2v}-symmetry likely arises from the *o*-phenyl groups passing by the methylene protons of the ligand backbone. Furthermore, these calculations suggest that the ease of rotation decreases in the following way: *o*-Ph > *o*-^{i}Pr > *o*-^{t}Bu (*vide infra*).



A

The room temperature ^{1}H NMR spectrum of complex **2b** exhibits a single sharp resonance for the methylene protons of the ligand (CH_2N) and a single doublet for the isopropyl methyl groups. Again these resonances are consistent with some degree of free rotation about the N—C_{ipso} bond (C_{2v}-symmetry). The low temperature (-80°C) limiting ^{1}H NMR spectrum of compound **2b** in d_8-toluene shows three $N(CH_3)_2$ resonances in a ratio of 1 : 1 : 1.2. In addition, overlapping resonances are observed for the methylene protons of the ligand (CH_2N—two AB quartets), the isopropyl methyls ($CHMe_2$—four doublets), and the isopropyl methines ($CHMe_2$—two septets). These resonances are in agreement with about a 1.67 : 1 mixture of the C_s-symmetric *meso* and C_2-symmetric *rac* rotameric isomers in solution at -80°C (Fig. 1). The above resonances coalesce at -40°C



Scheme 1.

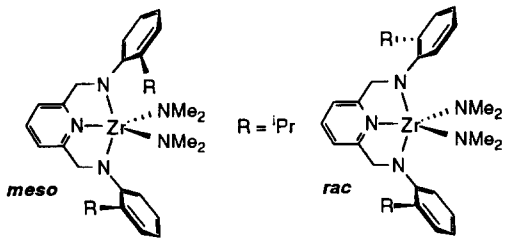


Fig. 1.

yielding a barrier to rotation of the aryl groups of $\Delta G\ddagger = 11.2$ (5) kcal mol^{-1}.

In contrast to both **2a** and **2b**, the room temperature ^{1}H NMR spectrum of compound **2c** shows resonances for two distinct species whose relative intensities do not change from -80°C to $+80$°C. Consistent with the presence of the *rac* isomer is an AB quartet for the ligand methylene protons (CH_2N), a single sharp resonance for the chemically equivalent dimethylamido groups, and a singlet for the equivalent ^{t}Bu groups. In addition to these resonances, the *meso* isomer displays a separate singlet for the ligand methylene protons, two inequivalent dimethylamido resonances, and a singlet for the *tert*-butyl group. Although an AB pattern is expected for the ligand methylene protons, if the chemical shift difference between H_A and H_B is small ($\Delta\nu \leqslant 0.4$ Hz), an apparent singlet is observed [23]. Integration of the $N(CH_3)_2$ groups indicates a *meso*/*rac* ratio of about 2.6 : 1. As noted above, this ratio is unaffected by added dimethylamine. The carbon NMR spectrum of **2c** also shows two species in about a 2.6 : 1 ratio.

Jordan has reported [21] that the reaction of $(EBI)H_2$ [EBI = 1,2-bis(1-indenyl)ethane] with Zr $(NMe_2)_4$ yields $(EBI)Zr(NMe_2)_2$ in a *meso*/*rac* ratio of 1 : 13. However, the reaction of $Me_2Si(C_5H_4$-3-^{t}Bu$)_2$ and $Zr(NMe_2)_4$ yields $[Me_2Si(C_5H_3$-3-^{t}Bu$)_2]Zr(NMe_2)_2$ in a *meso*/*rac* ratio of 2 : 1 [24]. In the latter example the higher *meso* preference is assigned to a lateral deformation of the *ansa* ligand system. We speculate that a similar 'deformation' may occur in these systems whereby the metal adopts a square-based pyramidal (sbp) geometry instead of a trigonal bipyramidal (tbp) confirmation, thus relieving the steric strain associated with the *meso* isomer relative to the *rac* (Fig. 2).

The energy difference between sbp and tbp geometries is expected to be quite small given the d^0 electronic configuration of zirconium. In fact, this change in hybridization has been observed for other

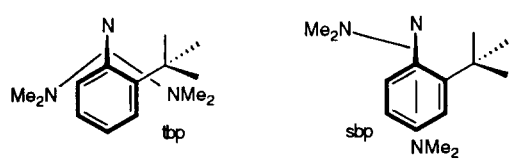


Fig. 2.

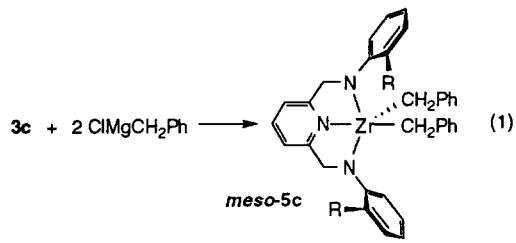
d^0 group 4 complexes bearing the pyridine diamide ligand. The mononeophyl complex $[2,6\text{-}(RNCH_2)_2NC_5H_3]TiBr(CH_2CMe_2Ph)$ (R = 2,6-$Me_2C_6H_3$) [25] displays a sbp geometry in the solid state with the largest group ($-CH_2CMe_2Ph$) occupying the apical position. This geometry minimizes the interaction between the orthomethyl groups of the aryl and the bulky neophyl ligand. We should add that it is not possible to distinguish between the proposed sbp and tbp complexes by NMR spectroscopy since both compounds possess C_s-symmetry.

The proton NMR spectrum of compound **2d**, which bears an isopropyl group in the 2-position and a methyl moiety in the 6-position of the aryl, shows resonances for two rotameric isomers. In this case, there is a slight bias for the *rac* isomer (*meso*/*rac*, 1 : 1.13). The near 1 : 1 correspondence between these species is also observed in the carbon NMR spectrum of **2d**. Given that these species do not interconvert (from -80°C to $+80$°C), even in the presence of excess dimethylamine, suggests that during the aminolysis reaction the aryl groups have little influence on one another; in other words, a near statistical distribution of isomers is produced.

The mixed amide complexes **2a–d** react with excess $ClSiMe_3$ to afford the dichloride derivatives (**3a–d**) in 80–96% isolated yield (Scheme 1). Upon addition of $ClSiMe_3$ the solutions turn black which we attribute to minor impurities given the high isolated yields. The orthophenyl substituted complex **3a** displays limited solubility in common organic solvents. The ^{1}H NMR spectrum of **3a** shows a sharp singlet for the ligand methylene protons (CH_2N), consistent with rapid rotation about the N—C_{ipso} bond. The proton NMR spectrum of **3b** at 23°C shows broad featureless resonances for the methylene (CH_2N), the isopropyl methine, and the isopropyl methyl protons of the ligand. At temperatures above $+60$°C the spectrum is consistent with rapid rotation of the aryl group. The low temperature (-60°C) limiting spectrum of **3b** displays resonances for the two rotamers in a ratio of about 2 : 3, however, it is not possible to discern which isomer predominates since the spectra of C_s- and C_2-symmetric compounds are indistinguishable (requires NMR active groups in the equatorial plane of a tbp). In this case the barrier to aryl group rotation is $\Delta G\ddagger = 13.8$ (5) kcal mol^{-1}.

The *meso*/*rac* ratio in the mixed amide complex **2c** is 2.6 : 1. Interestingly, upon reaction with excess $ClSiMe_3$ a single isomer of the dichloride complex **3c** is formed. We have followed this reaction by ^{1}H NMR spectroscopy and found that no other products are formed. It is not possible to determine which isomer is present, however, the following results suggest that the *meso* rotamer is formed preferentially. The reaction of **3c** with two equiv. of $PhCH_2MgCl$ yields the *meso* dibenzyl complex (**5c**) in quantitative yield by proton NMR spectroscopy [eq. (1)].

The ^{1}H NMR spectrum of **5c** shows a single AB quartet for the ligand methylene protons (CH_2N),



one *tert*-butyl resonance, and two benzyl resonances ($ZrCH_2Ph$); all in accordance with the presence of the *meso* isomer. Compound **5c** can also be prepared from $Zr(CH_2Ph)_4$ [26] and ligand **1c**. As noted above, a sbp geometry in compound **5c** would reduce the steric interactions between the benzyl groups and the *tert*-butyl groups. The monoalkyl derivatives [2,6-$(RNCH_2)_2NC_5H_3$]ZrClR′ and (R = 2-^{t}BuC$_6$H$_4$; R′ = CH_2CMe_2Ph, CH_2SiMe_3), prepared from compound **3c** and the corresponding alkylating reagent, also display resonances associated with only the *meso* isomer [27].

As expected, the proton NMR spectrum of compound **3d** displays resonances for two rotamers in a ratio of about 1 : 1.15. It would appear that no change in the isomeric ratio, within limits of detection, takes place during the metathesis reaction with $ClSiMe_3$. Furthermore, no change in this ratio is observed upon heating to 80°C.

The dichloride complexes **3a–c** react with 2 equiv. of methyl Grignard to afford the dimethyl derivatives (**4a–c**) in 67–85% yield as white crystalline solids (Scheme 1). The spectroscopic data for the Zr–Me groups is consistent with other related dimethyl species [17]. The proton NMR spectrum of the 2-phenylaryl substituted complex **4a** displays resonances for a single C_{2v}-symmetric species down to −80°C.

The 2-isopropylaryl substituted complex **4b** exhibits fluxional behavior. A stacked plot of a portion of the ^{1}H NMR spectrum of complex **4b** at several temperatures is shown in Fig. 3. The spectrum at 23°C displays a singlet at 4.84 ppm for the ligand methylene protons (CH_2N), a septet at 3.57 ppm for the isopropyl methine ($CHMe_2$), a doublet at 1.31 ppm for the chemically equivalent isopropyl methyl groups ($CHMe_2$), and a singlet for the $Zr–Me_2$ groups at 0.46 ppm. The low temperature limiting spectrum (−60°C) shows an AB quartet for the ligand methylene protons, a broad resonance for the isopropyl methine, a broad pattern for the isopropyl methyl groups, and three broad zirconium methyl resonances in a ratio of 1 : 1.3 : 1. We assign these resonances to a *meso/rac* mixture in a ratio of 1.5 : 1. The above resonances coalesce at −20°C yielding a barrier to rotation of the aryl groups of $\Delta G‡ = 12.0$ (5) kcal mol^{-1}.

The reaction of **3c** with bulky alkylating reagents affords exclusively *meso* type complexes (*vide supra*). Interestingly, the reaction of **3c** with two equiv. of methyl Grignard yields a mixture of rotameric isomers

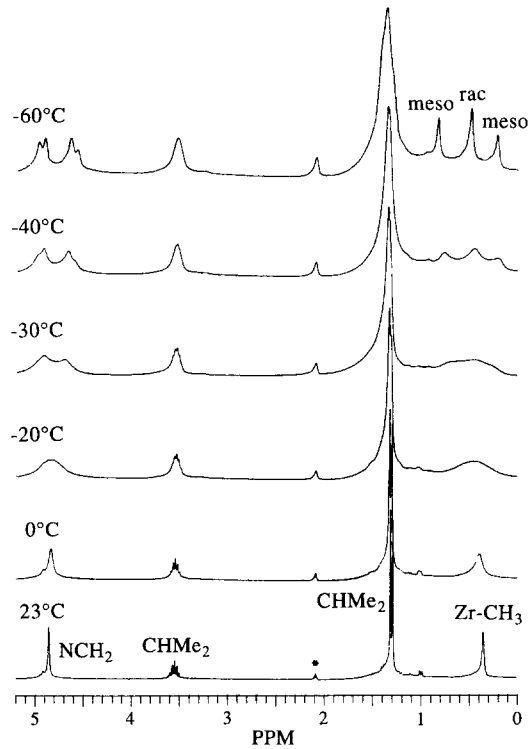


Fig. 3. Variable temperature ^{1}H NMR spectra of **4b** in d_8-toluene (* denotes solvent).

in a ratio of about 3 : 1 (*meso/rac*). The temperature invariant (−80°C to +80°C) ^{1}H NMR spectrum of **4c** shows two slightly off-centred AB quartets for the ligand methylene protons, two *tert*-butyl resonances, and three Zr–*Me* singlets (ratio, 1.5 : 1 : 1.5). Interestingly, the 2-*tert*-butyl substituted ligand appears to isomerize readily under metathetical type conditions, yet is stable to such processes under thermal conditions. We are currently examining the details of the transformation. Consistent with the lack of rotation in the 2,6-disubstituted aryl complexes [17,26], the dimethyl compound **4d** shows the same *meso/rac* ratio (1 : 1.14) as does the dichloride precursor **3d**.

EXPERIMENTAL

General details

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk Techniques or in an Innovative Technology Inc. glovebox. Solvents were distilled from sodium/benzophenone ketyl (THF, hexanes, diethylether) or molten sodium (toluene). 2-Isopropylaniline, 2-*tert*-butylaniline, 2-phenylaniline, and 2-isopropyl-6-methylaniline were purchased from Aldrich and distilled under reduced pressure before use. MeMgCl and $ZrCl_4$ were purchased from Aldrich and used as received. 2,6-

Bis(bromomethyl)pyridine was prepared using previously reported synthesis [18]. Unless otherwise specified, proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in C_6D_6 at approximately 23°C on a Varian 300-XL spectrometer. The proton chemical shifts were references to internal C_6D_5H ($\delta = 7.15$ ppm) and the carbon resonances to C_6D_6 ($\delta = 128.0$ ppm). Some resonances are obscured by C_6D_6 and/or are overlapping. The elemental analysis were performed using sealed tin cups on a Fisons Instruments model 1108 elemental analyzer by Mr Peter Borda of this department. The following abbreviations for the ligands are used: 2,6-$(RHNCH_2)_2$ NC_5H_3 ($(BPhP)H_2$, R = 2-PhC_6H_4; $(BMPP)H_2$, R = 2-$^i PrC_6H_4$; $(BMBP)H_2$, R = 2-$^t BuC_6H_4$, $(MPPP)H_2$, R = 2-^{i}Pr-6-MeC_6H_3).

(BPhP)H$_2$ (**1a**). A THF (150 cm^3) solution of LiNHR (5.144 g, 29.4 mmol) was added slowly to a stirring THF (100 cm^3) solution of 2,6-bis(bromomethyl)pyridine (3.890 g, 14.7 mmol) at −78°C. The mixture was warmed to room temperature and stirred for 12 h. The solution was quenched with a saturated $NaHCO_3$ solution (100 cm^3) and extracted with dichloromethane. The solvent was removed *in vacuo* to give a yellow oil (**1a**) which was used as isolated (6.000 g, 13.6 mmol, 93%). ^{1}H NMR δ 7.50 (d, 4H, m Ar/Ph), 7.09–7.40 (m, 10H, Ar/Ph), 6.97 (t, 1H, py), 6.80 (t, 2H, Ar/Ph), 6.73 (d, 2H, Ar/Ph), 6.60 (d, 2H, Ar), 5.15 (t, 2H, N*H*), 4.08 (d, 4H, NCH_2). ^{13}C{^{1}H} δ 158.28, 145.17, 140.31, 136.79, 130.61, 129.84, 129.16, 128.17, 127.39, 119.27, 117.64, 111.26, 49.25. MS (EI) *m/z* 441.220 (M^+). Calcd for $C_{31}H_{27}N_3$: 441.220.

(BMPP)H$_2$ (**1b**). The preparation of compound **1b** is identical to **1a** except for the work up. LiNHR (5.335 g, 37.4 mmol) and 2,6-bis(bromomethyl)pyridine (5.000 g, 18.9 mmol) yield a white solid. The solid was dissolved in a minimal amount of an ether, hexanes added until the solution is cloudy, and cooled to −30°C. A white crystalline solid (**1b**) was isolated by filtration and dried under vacuum (4.500 g, 12.0 mmol, 63%). ^{1}H NMR δ 7.18 (dd, 2H, Ar), 7.11 (dd, 2H, Ar), 6.97 (m, 1H, py), 6.84 (td, 2H, Ar), 6.77 (d, 2H, py), 6.62 (dd, 2H, Ar), 4.77 (br s, 2H, N*H*), 4.29 (s, 4H, NCH_2), 2.87 (sept, 4H, C*H*Me$_2$), 1.23 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} δ 158.68, 144.98, 136.94, 132.43, 127.21, 125.31, 119.77, 118.09, 111.33, 49.61, 27.70, 22.49. MS (EI) *m/z* 373.252 (M^+). Calcd for $C_{25}H_{31}N_3$: 373.252.

(BMBP)H$_2$ (**1c**). The preparation of compound **1c** is identical to **1b**. LiNHR (5.865 g, 37.8 mmol) and 2,6-bis(bromomethyl)pyridine (5.000 g, 18.9 mmol) gave **1c** as a white crystalline solid (5.820 g, 14.4 mmol, 76%). ^{1}H NMR δ 7.35 (d, 2H, Ar), 7.16 (dd, 2H, Ar), 7.02 (td, 1H, py), 6.84 (d, 2H, Ar), 6.82 (t, 2H, py), 6.628 (d, 2H, Ar), 4.24 (broad s, 2H, NH), 4.32 (s, 4H, NCH_2), 1.49 (s, 18H, *t*-Bu). ^{13}C{^{1}H} δ 158.39, 146.24, 137.04, 133.55, 54.52, 55.33, 54.48, 56.22, 49.82, 34.41, 30.08. MS (EI) *m/z* 401.283 (M^+). Calcd for $C_{27}H_{35}N_3$: 401.283.

(MPPP)H$_2$ (**1d**). The preparation of compound **1d** is identical to **1b**. LiNHR (7.750 g, 49.9 mmol) and 2,6-bis(bromomethyl)pyridine (5.000 g, 18.9 mmol) gave **1d** as a white crystalline solid (4.910 g, 12.2 mmol, 65%). ^{1}H NMR δ 7.13 (d, 2H, Ar), 7.00–7.03 (m, 5H, py/Ar), 6.75 (d, 2H, py), 4.34 (s, 2H, N*H*), 4.18 (s, 4H, NCH_2), 3.45 (sept, 2H, C*H*Me$_2$), 2.31 (s, 6H, Me), 1.21 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} δ 159.01, 145.46, 141.45, 136.75, 131.21, 128.88, 124.13, 123.39, 120.29, 55.33, 27.99, 24.16, 19.03. MS (EI) *m/z* 401.283 (M^+). Calcd for $C_{27}H_{35}N_3$: 401.283.

(BPhP)Zr(NMe$_2$*)*$_2$ (**2a**). A toluene solution of $Zr(NMe_2)_4$ (3.635 g, 13.6 mmol) was added to a toluene solution (50 cm^3) of **1a** (6.000 g, 13.6 mmol) and stirred for 12 h. The solvent was removed *in vacuo* and the resulting solid extracted with hexanes (3 × 50 cm^3) and filtered through Celite. The volume of the filtrate was reduced and the solution cooled to −30°C, affording **2a** as a yellow crystalline solid (7.715 g, 12.5 mmol, 92%). ^{1}H NMR δ 7.74 (d, 2H, Ar/Ph), 7.71 (d, 2H, Ar/Ph), 7.32–7.36 (m, 4H, Ar/Ph), 6.98–7.11 (m, 8H, Ar/Ph), 6.56 (t, 1H, py), 6.00 (d, 2H, py), 4.66 (s, 4H, NCH_2), 2.94 (s, 12H, N*Me*$_2$). ^{13}C{^{1}H} δ 164.67, 153.33, 143.59, 137.46, 135.30, 131.95, 128.45, 128.32, 128.196, 127.76, 126.34, 122.55, 116.93, 63.29, 41.92.

(BMPP)Zr(NMe$_2$*)*$_2$ (**2b**). The preparation of compound **2b** is identical to **2a**. $Zr(NMe_2)_4$ (2.150 g, 8.03 mmol) and **1b** (3.000 g, 8.03 mmol) gave **2b** as a yellow crystalline solid (4.100 g, 7.44 mmol, 93%). ^{1}H NMR δ 7.41 (dd, 2H, Ar), 7.32 (dd, 2H, Ar), 7.21 (td, 2H, Ar), 1.11 (td, 2H, Ar), 8.87 (t, 1H, py), 6.42 (d, 2H, py), 4.93 (s, 4H, NCH_2), 3.53 (sept, 4H, C*H*Me$_2$), 2.76 (s, 12H, NMe$_2$), 1.29 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} δ 164.64, 152.91, 145.71, 137.59, 129.27, 126.32, 126.14, 124.04, 117.34, 67.26, 42.03, 27.29, 25.23.

(BMBP)Zr(NMe$_2$*)*$_2$ (**2c**). The preparation of compound **2c** is identical to **2a**. $Zr(NMe_2)_4$ (2.150 g, 8.04 mmol) and **1c** (3.000 g, 8.03 mmol) gave **2c** a yellow crystalline solid (3.987 g, 7.24 mmol, 90%). The following data is for both rotamers (*meso*/*rac*, 2.6 : 1). ^{1}H NMR δ 7.48 (t, Ar), 7.24 (t, Ar), 7.07 (t, Ar), 6.90 (t, py), 6.49 (d, py), 4.91 (s, *meso* NCH_2), 4.90 (AB quartet, $^2J_{HH}$ = 20.0 Hz, *rac* NCH_2), 3.01 (s, *meso* N*Me*$_2$), 2.65 (s, *rac* N*Me*$_2$), 2.42 (s, *meso* N*Me*$_2$), 1.57 (s, *rac* C*Me*$_3$), 1.51 (s, *meso* C*Me*$_3$). ^{13}C{^{1}H} δ 163.88, 163.14, 156.07, 154.46, 146.67, 137.73, 132.32, 132.12, 128.90, 127.94, 126.95, 126.76, 124.30, 123.73, 117.25, 68.40, 43.25, 42.15, 41.05, 36.56, 32.64, 32.41.

(MPPP)Zr(NMe$_2$*)*$_2$ (**2d**). The preparation of compound **2d** is identical to **2a**. $Zr(NMe_2)_4$ (2.671 g, 10.0 mmol) and **1d** (4.010 g, 10.0 mmol) gave **2d** as a yellow crystalline solid (3.090 g, 5.34 mmol, 54%). The following data is for both rotamers (*meso*/*rac*, 1 : 1.13). ^{1}H NMR δ 7.23–7.27 (m, Ar/Ph), 7.05–7.16 (m, Ar/Ph), 6.93 (t, py), 6.48 (d, py), 4.68 (AB quartet, $^2J_{HH}$ = 20.3 Hz, *rac* NCH_2), 4.65 (AB quartet, $^2J_{HH}$ = 20.3 Hz, *meso* NCH_2), 4.00 (sept, *meso* C*H*Me$_2$), 3.82 (sept, *rac* C*H*Me$_2$), 2.88 (s, *meso* N*Me*$_2$), 2.57 (s, *rac* N*Me*$_2$), 2.32 (s, *rac* Me), 2.30 (s, *meso* N*Me*$_2$), 2.19 (s, *meso* Me), 1.39 and 1.38 (d, *meso*

$CHMe_2$), 1.32 and 1.29 (d, *rac* $CHMe_2$). $^{13}C\{^1H\}$ δ 164.12, 163.81, 152.39, 152.12, 146.41, 146.38, 137.60, 137.54, 135.37, 135.10, 123.86, 123.77, 117.25, 65.06, 64.92, 42.59, 41.33, 40.08, 27.64, 26.92, 26.76, 24.28, 24.04, 19.16, 19.07.

(BPhP)ZrCl$_2$ (**3a**). Excess $ClSiMe_3$ (2 cm^3) was added dropwise to a toluene solution (50 cm^3) of compound **2a** (2.315 g, 3.74 mmol) at 23°C. The solution was stirred for 12 h during which time **3a** precipitated as a beige solid. Hexanes (100 cm^3) was added and the solution was cooled to −30°C for 12 h. The solid was isolated by filtration and dried under vacuum (2.152 g, 3.57 mmol, 96%). ^1H NMR δ 8.44 (d, 2H, Ph), 7.80–7.90 (m, 4H, Ph), 6.90–7.40 (m, 12H, Ar/Ph), 6.39 (t, 1H, py), 5.84 (d, 2H, py), 4.54 (s, 4H, NCH_2). Compound **3a** is poorly soluble in organic solvents which precludes its convenient characterization by $^{13}C\{^1H\}$ NMR.

(BMPP)ZrCl$_2$ (**3b**). The preparation of compound **3b** is identical to **3a**. Excess $ClSiMe_3$ (2 cm^3) and **2b** (1.500 g, 2.72 mmol) affords **3b** as a beige solid (1.190 g, 2.23 mmol, 82%). ^1H NMR δ 7.98 (br d, 2H, Ar), 7.29 (m, 2H, Ar), 7.15 (m, 4H, Ar), 6.89 (t, 1H, py), 6.34 (d, 2H, py), 4.73 (br s, 4H, NCH_2), 3.48 (br sept, 4H, $CHMe_2$), 1.33 (br s, 12H, $CHMe_2$). $^{13}C\{^1H\}$ (d_8-toluene, 80°C) δ 164.31, 147.20, 146.33, 138.63, 130.34, 127.41, 127.33, 126.74, 117.71, 69.32, 27.60, 25.01.

(BMBP)ZrCl$_2$ (**3c**). The preparation of compound **3c** is identical to **3a**. Excess $ClSiMe_3$ (2 cm^3) and **2c** (1.000 g, 1.73 mmol) affords **3c** as a beige solid (0.860 g, 1.54 mmol, 89%). ^1H NMR δ 7.95 (d, 2H, Ar), 7.47 (d, 2H, Ar), 7.18 (m, 4H, Ar), 6.81 (t, 1H, py), 6.34 (d, 2H, py), 4.78 (AB quartet, $^2J_{HH}$ = 20.1 Hz, 4H, NCH_2), 1.47 (s, 18H, *t*-Bu). $^{13}C\{^1H\}$ δ 162.66, 147.23, 146.05, 138.79, 131.46, 131.01, 127.46, 127.16, 117.76, 70.21, 37.09, 33.31.

(MPPP)ZrCl$_2$ (**3d**). The preparation of compound **3d** is identical to **3a**. Excess $ClSiMe_3$ (2 cm^3) and **2d** (1.700 g, 2.94 mmol) affords **3d** as a beige solid (1.327 g, 2.36 mmol, 80%). The following data is for both rotamers (*meso*/*rac*, 1:1.15). ^1H NMR (CD_2Cl_2) δ 8.04 (t, py), 7.52 (d, py), 7.09–7.25 (m, Ar), 5.06 (AB quartet $^2J_{HH}$ = 21.3 Hz, NCH_2), 5.05 (AB quartet $^2J_{HH}$ = 21.3 Hz, NCH_2), 3.56 (sept, $CHMe_2$), 3.48 (sept, $CHMe_2$), 2.35 (s, Me), 2.31 (s, Me), 1.35 (d, $CHMe_2$), 1.32 (d, $CHMe_2$), 1.18 (d, $CHMe_2$), 1.16 (d, $CHMe_2$). $^{13}C\{^1H\}$ NMR ($CDCl_2$) δ 164.16, 164.12, 147.52, 147.38, 145.22, 145.19, 141.53, 139.92, 136.18, 136.05, 129.33, 128.74, 128.70, 128.51, 127.41, 126.87, 125.59, 125.21, 124.77, 118.74, 67.20, 67.16, 28.03, 27.91, 27.73, 27.54, 23.81, 23.42, 19.50, 19.46.

(BPhP)ZrMe$_2$ (**4a**). MeMgCl (3.70 cm^3, 0.99 M, 3.67 mmol) were added to a CH_2Cl_2 (25 cm^3) solution of compound **3a** (1.000 g, 1.66 mmol) at −78°C. The mixture was stirred for 12 h and then the solvent removed *in vacuo*. The resulting solid was extracted with toluene and filtered through Celite. The solvent was removed *in vacuo* and the remaining solid dissolved in a minimum amount of CH_2Cl_2 and cooled to −30°C for 12 h. **4a** was isolated as a white crystalline solid and dried under vacuum (0.625 g, 1.11 mmol, 67%). ^1H NMR δ 8.10 (d, 2H, Ph), 7.73 (d, 4H, Ph), 7.38 (d, 2H, Ar/Ph), 7.28–7.31 (m, 2H, Ar/Ph), 7.08–7.15 (m, 6H, Ar/Ph), 6.99 (m, 2H, Ar/Ph), 6.49 (t, 1H, py), 5.93 (d, 2H, py), 4.62 (s, 4H, NCH_2), 0.73 (s, 6H, Zr-*Me*). $^{13}C\{^1H\}$ NMR δ 164.02, 148.94, 142.66, 137.59, 136.82, 133.01, 129.06, 128.68, 128.49, 128.17, 126.84, 125.21, 116.97, 64.51, 42.38 (Zr-CH_3). Anal. Calcd for $C_{33}H_{31}N_3Zr$: C, 70.67; H, 5.57; N, 7.49. Found: C, 70.60; H, 5.55; N, 7.19.

(BMPP)ZrMe$_2$ (**4b**). MeMgCl (0.78 cm^3, 3.0 M, 2.35 mmol) was added to a diethylether (23 cm^3) solution of compound **3b** (0.500 g, 0.94 mmol) at 23°C. The mixture was stirred for 12 h and then the solvent removed *in vacuo*. The resulting solid was extracted with toluene and filtered through Celite. The solvent was removed *in vacuo* and the remaining solid dissolved in a minimum amount of diethylether and cooled to −30°C for 12 h. **4b** was isolated as a white crystalline solid and dried under vacuum (0.445 g, 0.90 mmol, 85%). ^1H NMR δ 7.69 (m, 2H, Ar), 7.36 (m, 2H, Ar), 7.20 (m, 4H, Ar), 6.87 (t, 1H, py), 6.38 (d, 2H, py), 4.84 (s, 4H, NCH_2), 3.57 (sept, 4H, $CHMe_2$), 1.31 (d, 12H, $CHMe_2$), 0.46 (br s, 6H, Zr-*Me*). $^{13}C\{^1H\}$ NMR δ 164.02, 148.50, 147.54, 131.08, 129.27, 127.21, 127.67, 126.29, 117.35, 58.31, 41.23 (Zr-CH_3), 27.25, 25.39. Anal. Calcd for $C_{27}H_{35}N_3Zr$: C, 65.81; H, 7.16; N, 8.53. Found: C, 66.03; H, 7.18; N, 8.68.

(BMBP)ZrMe$_2$ (**4c**). The preparation of compound **4c** is identical to **4b**. MeMgCl (0.52 cm^3, 3.0 M, 1.55 mmol) and **3c** (0.350 g, 0.62 mmol) gave **4c** as a white crystalline solid (0.234 g, 0.45 mmol, 73%). The following data is for both rotamers (*meso*/*rac*, 3:1). ^1H NMR δ 7.78 (d, Ar), 7.54 (d, Ar), 7.20 (m, Ar), 6.87 (t, py), 6.43 (d, py), 4.91 (AB quartet, $^2J_{HH}$ = 20.7 Hz, *meso* NCH_2), 4.83 (AB quartet, $^2H_{HH}$ = 20.7 Hz, *rac* NCH_2), 1.55 (s, *rac t*-Bu), 1.49 (s, *meso t*-Bu), 0.82 (s, *meso* Zr-Me), 0.62 (s, *rac* Zr-Me), 0.26 (s, *meso* Zr-Me). $^{13}C\{^1H\}$ NMR δ 163.66, 163.21, 149.43, 147.18, 137.90, 133.98, 132.75, 130.93, 127.06, 126.92, 126.02, 125.88, 117.47, 70.03, 69.71, 45.71 (Zr-CH_3), 44.73 (Zr-CH_3), 39.57, 37.18, 33.34. Anal. Calcd for $C_{29}H_{39}N_3Zr$: C, 66.87; H, 7.55; N, 8.07. Found: C, 66.64; H, 7.77; N, 7.91.

(MPPP)ZrMe$_2$ (**4d**). The preparation of compound **4d** is identical to **4b**. MeMgCl (0.75 cm^3, 3.0 M, 2.23 mmol) and **3d** (0.500 g, 0.89 mmol) gave **4d** as a white crystalline solid (0.316 g, 0.61 mmol, 69%). The following data is for both rotamers (*meso*/*rac*, 1:1.4). ^1H NMR δ 7.00–7.23 (m, Ar), 6.91 (t, py), 6.45 (d, py), 4.75 (AB quartets $^2J_{HH}$ = 20.8 Hz, NCH_2), 4.74 (AB quartets $^2J_{HH}$ = 20.8 Hz, NCH_2), 3.90 (sept, $CHMe_2$), 2.38 (s, Me), 2.11 (s, Me), 1.45 (d, $CHMe_2$), 1.43 (d, $CHMe_2$), 1.25 (d, $CHMe_2$), 1.23 (d, $CHMe_2$), 0.45 (s, *meso* Zr-*Me*), 0.39 (s, *rac* Zr-*Me*), 0.32 (s, *meso* Zr-*Me*). $^{13}C\{^1H\}$ NMR δ 164.23, 164.17, 147.78, 147.75, 147.28, 137.79, 136.43, 129.28, 128.67, 128.51, 125.97, 125.64, 124.54, 117.42, 65.96, 44.35, 43.71,

42.67, 28.63, 28.51, 27.71, 23.75, 23.63, 21.40, 19.09. Anal. Calcd for $C_{29}H_{29}N_3Zr$: C, 66.87; H, 7.55; N, 8.07. Found: C, 66.79; H, 7.51; N, 8.24.

(BMBP)Zr(CH$_2$Ph)$_2$ (**5c**). $PhCH_2MgCl$ (2.50 cm^3, 0.89 M, 2.22 mmol) was added to a diethylether (25 cm^3) solution of compound **3c** (0.500 g, 0.89 mmol) at −30°C. The mixture was stirred for 12 h and then the solvent removed *in vacuo*. The resulting solid was extracted with toluene and filtered through Celite. The solvent was removed *in vacuo* and the remaining solid dissolved in a minimum amount of diethylether and cooled to −30°C for 12 h. **5c** was isolated as a bright yellow crystalline solid and dried under vacuum (0.438 g, 0.65 mmol, 73%). ^{1}H NMR δ 7.50 (m, 1H, Ar), 7.42 (m, 1H, Ar), 7.18 (m, 4H, Ar and Ph), 7.04 (m, 2H, Ar and Ph), 6.81 (t, 2H, Ar and Ph), 6.73 (t, 1H, py), 6.35 (d, 2H, py), 5.71 (m, 2H, Ph), 4.66 (AB quartet, $^2J_{HH}$ = 20.5 Hz, 4H, NHH_2), 2.34 (s, 2H, CH_2Ph), 1.80 (s, 2H, CH_2Ph), 1.46 (s, 18H, CMe_3). $^{13}C\{^1H\}$ δ 161.91, 149.65, 148.98, 146.61, 137.36, 137.07, 132.96, 131.10, 130.31, 130.12, 127.36, 126.56, 126.32, 124.95, 124.14, 119.58, 117.07, 69.41, 65.16, 56.69, 37.17, 33.47. Anal. Calcd for $C_{41}H_{47}N_3Zr$: C, 73.17; H, 7.04; N, 6.24. Found: C, 73.10; H, 7.15; N, 6.39.

CONCLUSIONS

A series of ortho-substituted aryl diamide complexes of zirconium have been prepared in high yield. Depending on the size of the ortho substituent on the aryl group, rotameric isomers, derived from restricted rotation about the N—C_{ipso} bond, can be observed spectroscopically and the barriers to isomerization measured. In the case of the 2-phenylaryl moiety, rapid isomerization is observed at all temperatures regardless of the substituents bound to zirconium in the equatorial plane. The 2-isopropylaryl substituted complexes exhibit fluxional behavior with the low temperature limiting ^{1}H NMR spectra showing resonances for species consistent with *meso* and *rac* rotamers. In contrast, the 2-*tert*-butylaryl derivatives are 'locked' as five coordinate species but can isomerize during metathesis reactions at the metal center. The 2-isopropyl-6-methyl complexes are also locked, however, the rotameric ratios remain the same in all derivatives of this ligand system. We are currently studying the α-olefin polymerization chemistry of these and other complexes.

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REFERENCES

1. Bochmann, M. J., *Chem. Soc., Dalton Trans.*, 1996, 255.
2. Brintzinger, H. H., Fischer, D., Mülhaupt, R., Rieger, B. and Waymouth, R. M., *Angew. Chem., Int. Ed. Engl.*, 1995, **34,** 1143.
3. Mohring, P. C., Coville, N. J. *J. Organomet. Chem.*, 1994, **479,** 1.
4. Kaminsky, W., Kulper, K., Brintzinger, H. H. and Wild, F. R. W. P., *Angew. Chem., Int. Ed. Engl.*, 1985, **24,** 507.
5. Ewan, J. A., Jones, R. L., Razavi, J. A., *J. Am. Chem. Soc.*, 1988, **110,** 6255.
6. Coates, G. W., Waymouth, R. M., *Science*, 1995, **267,** 21.
7. Tinkler, S., Deeth, R. J., Duncalf, D. J. and McCamley, A., *J. Chem. Soc., Chem. Commun.*, 1996, 2623.
8. Aoyagi, K., Gantzel, P. K., Kalai, K. and Tilley, T. D., *Organometallics*, 1996, **15,** 923.
9. Warren, T. H., Schrock, R. R. and Davis, W. M., *Organometallics*, 1996, **15,** 562.
10. Horton, A. D., de With, J., van der Linden, A. J., van de Weg, H., *Organometallics*, 1996, **15,** 2672.
11. Cloke, F. G. N., Geldbach, T. J., Hitchcock, P. B., and Love, J. B., *J. Organomet. Chem.*, 1996, **506,** 343.
12. Clark, H. C. S., Cloke, F. G. N., Hitchcock, P. B., Love, J. B. and Wainwright, A. P., *J. Organomet. Chem.*, 1995, **501,** 333.
13. Herrmann, W. A., Denk, M., Albach, R. W., Behm, H. and Herdtweck, E., *Chem. Ber.*, 1991, **124,** 683.
14. Scollard, J. D., McConville, D. H., Payne, N. C and Vittal, J. J., *Macromolecules*, 1996, **29,** 5241.
15. Scollard, J. D. and McConville, D. H., *J. Am. Chem. Soc.*, 1996, **118,** 10008.
16. Guérin, F., McConville, D. H. and Vittal, J. J., *Organometallics*, 1996, **15,** 5586.
17. Haeg, M. E., Whitlock, B. J. and Whitlock Jr., H. W., *J. Am. Chem. Soc.*, 1989, **111,** 692.
18. Scollard, J. D., McConville, D. H. and Vittal, J. J., *Organometallics*, 1995, **14,** 5478.
19. Lappert, M. F., Power, P. P., Sanger, A. R. and Srivastava, R. C., *Metal Metalloid Amides*; Ellis Horwood: Chichester (1980).
20. Bradley, D. C. and Thomas, I. M., *Proc. Chem. Soc., London*, 1959, 225.
21. Diamond, G. M., Rodewald, S. and Jordan, R. F., *Organometallics*, 1995, **14,** 5.
22. Calculations were performed using CAChe Scientific software by Tektronix.
23. Lambert, J. B., Shurvell, H. F., Lightner, D. and Cooks, R. G., *Introduction to Organic Spectroscopy*; Macmillan Publishing Company: New York, 1987, 68.
24. Diamond, G. M., Jordan, R. F. and Petersen, J. L., *Organometallics*, 1996, **15,** 4045.
25. Guérin, F., McConville, D. H. and Payne, N. C., *Organometallics*, 1996, **15,** 5085.
26. Schrock, R. R. and Wengrovius, J. H., *J. Organomet. Chem.*, 1981, **205,** 319.
27. Guérin, F. and McConville, D. H., unpublished results.