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A New Twist on Pincer Ligands and Complexes

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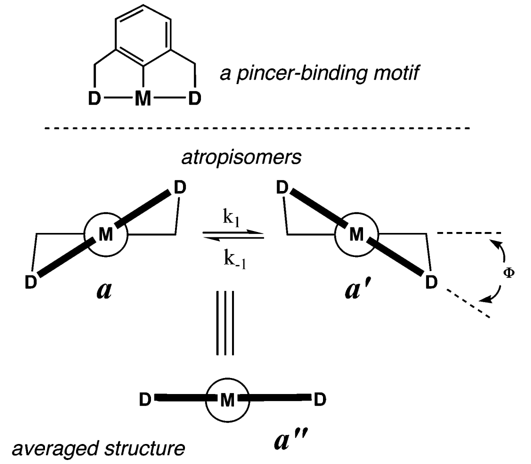
Summary: A new class of palladium pincer complexes bearing m-terphenyl scaffolds have been synthesized and structurally characterized. As a result of integrating phenyl rings into the chelating arms of m-xylyl type pincer ligands, highly twisted and rigid structures have been achieved.

Pincer ligands[1,2] are an exciting class of ligands that are receiving increasing attention for applications ranging from catalysis and sensors to materials science.[3] The name bestowed upon these ligands[3f] reflects their tenacious and terdentate binding nature. If one considers the most well-known pincer ligand platform, the *m*-xylyl framework $[2,6\text{-}(ECH_2)_2C_6H_3]^-$ (an ECE pincer, E = donor atoms or groups such as NR_2, PR_2, OR, etc.; Scheme 1, top), one can envision how the presence of a formal negative charge and two exemplary five-membered chelate rings can impart great stability to such complexes. More recently, related pincer ligands have been constructed featuring N-heterocyclic carbenes as C-donors (ECE and CEC types) that vastly increase the diversity of this ligand class. Many of these systems are also designed such that the central, "anchoring" donor atom is often part of a planar group (such as a phenyl, pyridine, or N-heterocyclic carbene group). It has been recognized that if this ring is not in the plane containing the metal and the two outer donor atoms, then a twisted conformation is realized. The C_2-symmetric and, hence, chiral nature of these complexes offers the potential of resolution and use in performing catalytic enantioselective transformations. Interconversion between these two atropisomers (Scheme 1, **a** and **a′**), however, prevents isolation of individual enantiomers, resulting in an "averaged" planar structure (Scheme 1, **a″**). Highly twisted structures have been produced,[4] and configurational stability for a twisted 2,6-lutidinyl−bis(carbene) complex was maintained up to 80 °C.[4f] It should be mentioned that chiral pincer ligands have been reported that include modifications to the methylene carbons or the use of stereogenic centers at the donor atoms of this versatile motif.[5] In this report we demonstrate not only the attainment of the highest twist angles to date but also systems having a very high degree of nonfluxionality and versatility.

Scheme 1. Typical "Pincer" Binding and Atropisomers



Our strategy was inspired by our past success in employing *m*-terphenyls to stabilize various materials having low-coordinate phosphorus atoms.[6] Specifically, we sought to reposition phosphorus atoms on a terphenyl framework, leading to a new class of pincer ligands (Scheme 2). Our initial efforts, however, were somewhat disappointing in that ligands of the form $[2,6\text{-}(2\text{-}R_2PCH_2C_6H_4)_2C_6H_4]$ did not undergo cyclometalation and pincer complex formation upon reaction with Pd(II) salts (unlike the case for $[(2,6\text{-}(R_2PCH_2)_2C_6H_4]$ ligands) but, instead, yielded complexes bearing trans-spanning diphosphines (Scheme 2, left).[7] Using a common workaround, installation of a more reactive halogen atom in place of a hydrogen atom at the critical

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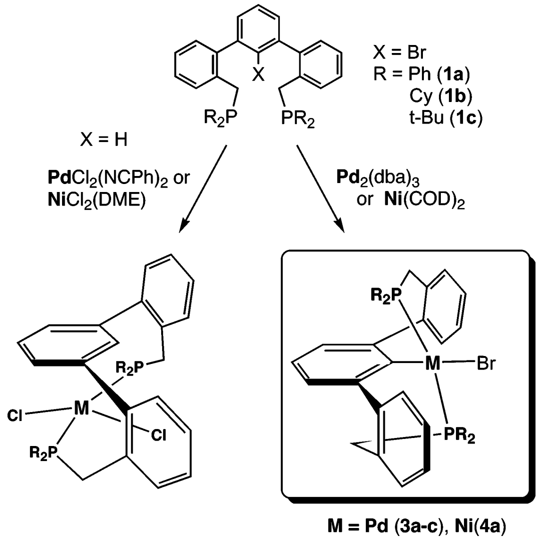
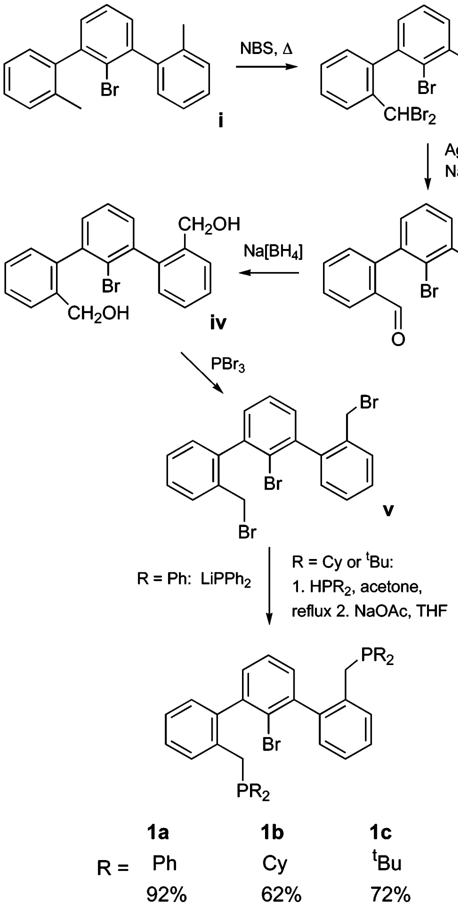
10.1021/om060256z CCC: $33.50

Scheme 2. Relationship between Previous Trans-Spanning (Left) and New Pincer Complexes (Right)



Scheme 3. Pincer Ligand Synthesis



C-1 position of the central ring afforded ligand precursors that readily reacted with low-valent complexes to provide the new C_2-symmetric pincer complexes **3** and **4** (Scheme 2, right).

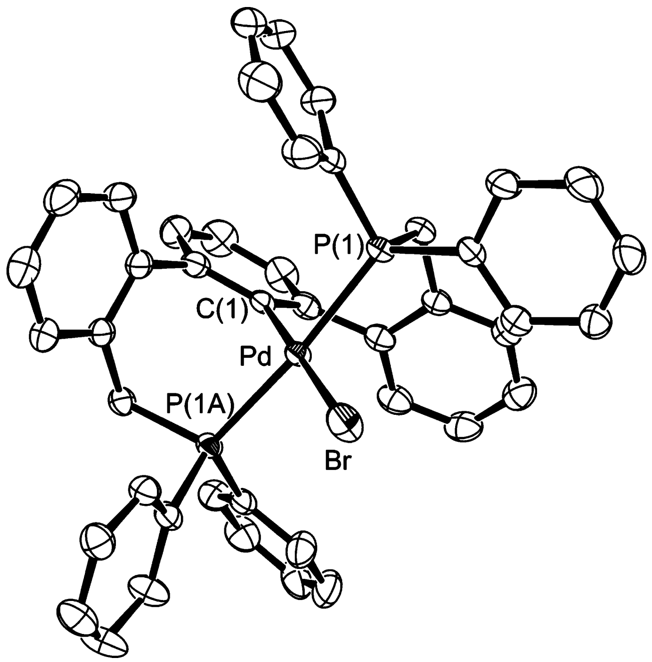


Figure 1. ORTEP drawing (30% probability ellipsoids) of the molecular structure of **3a**. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (deg): Pd−P(1), 2.3071(7); Pd−P(1A), 2.3071(7); Pd−C(1), 2.067(4); Pd−Br, 2.5024(5); P(1)−Pd−P(1A), 169.48(4); C(1)−Pd−Br, 180.0.

The synthesis of the ligand precursors [2,6-(2-$R_2PCH_2C_6H_4)_2$-C_6H_3Br] (**1a**−**c**) is outlined in Scheme 3. It was discovered that the shorter synthesis used to prepare the nonhalogenated analogues [2,6-(2-$R_2PCH_2C_6H_4)_2C_6H_4$] had to be modified. Specifically, the key intermediate [2,6-(2-$BrCH_2C_6H_4)_2C_6H_3$-Br] (**v**) could not be cleanly prepared by direct bis-monobromination of the tolyl groups of **i**, due to the formation of mixtures of mono-, bis-, tri-, and tetrahalogenated products that were difficult to separate.[8] Instead, synthesis of the readily purified **ii** allowed facile synthesis of **iii** and **iv**, which could then be used to access **v** from **i** in 56% overall yield. From precursor **v** the three new diphosphines **1a**−**c** were isolated in good yields. Each material is readily characterized by standard ^{1}H and ^{31}P NMR spectroscopy.[9] Notably, the diphosphine **1a** shows two ^{31}P NMR signals in its spectrum, consistent with the presence of two isomers (syn and anti) in about a 50:50 ratio. ^{31}P NMR spectra of diphosphines **1b**,**c** indicate a much smaller amount (ca. 10% or less) of a second isomer. The increased steric bulk of the benzyl groups in **1b**,**c** presumably disfavors the syn isomers, as the precursors **i**−**v** all show syn and anti isomers in about a 50:50 ratio (by ^{1}H NMR spectroscopy). Nevertheless, diphosphines **1a**−**c** react with $Pd_2(dba)_3$ to quantitatively yield pincer complexes **3a**−**c** (Scheme 2, right), as indicated by new signals ca. 25−35 ppm downfield from signals for the corresponding free ligands in the ^{31}P NMR spectra. Likewise, reaction of **1a** with $Ni(COD)_2$ yields the analogous nickel pincer complex **4a**. While reaction of **1a** with $Pd_2(dba)_3$ is rapid and complete in 1 h at room temperature to yield **3a**, reaction of the more hindered **1c** with $Pd_2(dba)_3$ requires 12 h or more for completion. These new pincer complexes are robust, display great air stability, and can be purified by flash column chromatography on silica gel under ambient conditions. Full characterization of **3a**−**c** and **4a** was possible by a combination of both 1-D and 2-D (HCOSY, HMQC and HMBC) NMR spectroscopy.[10]

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[9] Selected data for **1a**−**c** are as follows. **1a**: ^{31}P NMR ($CDCl_3$, 162 MHz) δ −10.3, −10.2 (~1:1). **1b**: ^{31}P NMR ($CDCl_3$, 162 MHz) δ 1.3. **1c**: ^{31}P NMR ($CDCl_3$, 162 MHz) δ 30.4, 32.4 (~10:1).

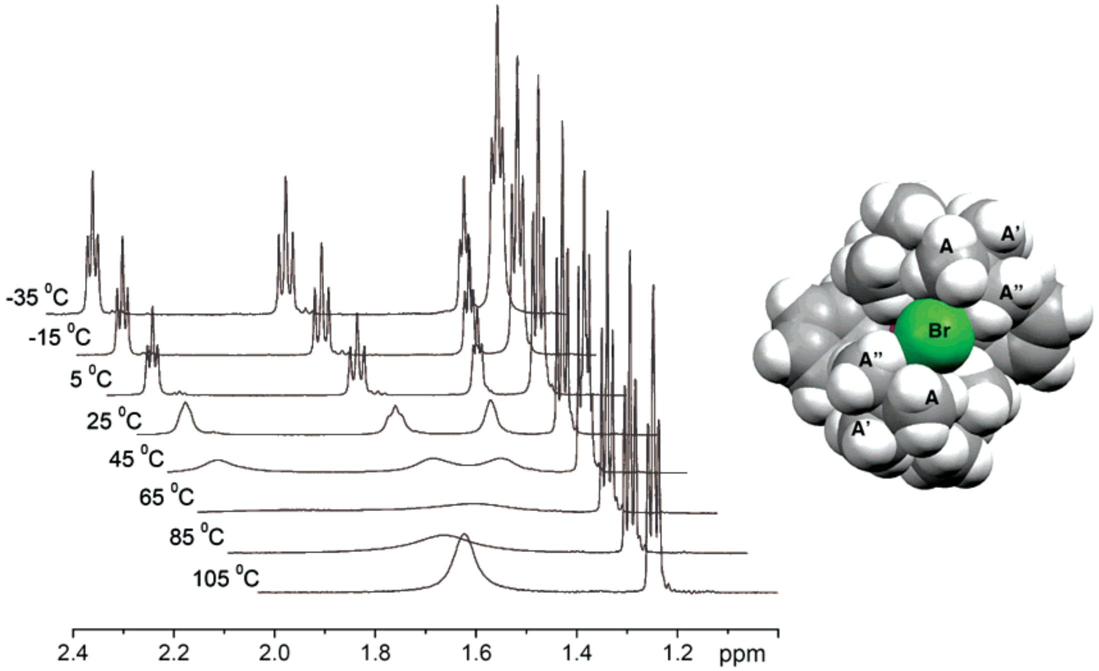

Figure 2. Temperature-dependent ^{1}H NMR spectra (toluene-d_8, 600 MHz) and a calculated (SPARTAN PM3) space-filling molecular model of **3c** (as viewed down the Br−Pd bond).

Complex **3a** was further characterized by single-crystal X-ray diffraction analysis (Figure 1).[11a] The crystal structure of **3a** reveals a four-coordinate planar palladium(II) center, as well as a crystallographically imposed C_2 axis passing through the bromine, palladium, and C(1) atoms. Although individual molecules of **3a** are chiral, the crystal is comprised of both enantiomers, which are related by a crystallographic inversion center. The bond lengths of Pd−P and Pd−C are in reasonable agreement with published values for PCP pincer complexes.[12,13] In comparison to the known closely related PCP pincer complex $[(C_6H_3(CH_2PPh_2)_2)PdBr)]$ (**5a**),[13] having P−Pd−C bond angles of 80.6 and 81.8°, complex **3a** has C(1)−Pd−P bond angles of 84.74°. These values are actually closer to those of the nonpincer analogue *trans*-$[(PPh_3)_2Pd(C_6H_5)Br]$[14] (86.3 and 88.8°), which does not possess any ring constraints. The most striking difference between the *solid-state* structures of **3a** and **5a** lies in the distortion of P atoms away from the plane containing the anchor atom C(1), its ring, and the Pd and Br atoms. One can assign the "twist" angle Φ (see Scheme 1), defined as the angle between the plane of the anchoring ring and square plane containing the metal and its four directly attached atoms, to assess this effect for comparative purposes. A Φ value of 76.0° for **3a** greatly surpasses the $\Phi = 18.4°$ found for **5a**.[13] The twist angle for **3a** is also 34° greater than that found for CEC pincer complexes (C = N-heterocyclic carbene) having the largest Φ values reported to date (up to 41.8°).[4]

The structural rigidity of this pincer platform is maintained up to 130 °C, as shown by variable-temperature ^{1}H NMR studies of **3a** in $CDCl_2CDCl_2$ (see the Supporting Information for details). Analysis of spectra for the *tert*-butyl derivative **3c** (Figure 2) revealed hindered rotation about the C(*tert*-butyl)−P bonds, as well as an equally rigid pincer backbone. At low temperature, the two types of *tert*-butyl groups are inequivalent, and remain so, up to 105 °C in toluene-d_8. One of the signals, however, is resolved into three independent methyl resonances at low temperature. This observation suggests that the *tert*-butyl

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(10) Selected data for **3a**−**c** and **4a** are as follows. **3a**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.91 (doublet of virtual triplets, $J_{HH} = 13$ Hz, 2H), 3.21 (doublet of virtual triplets, $J_{HH} = 13$ Hz; 2H), 6.38 (m, 2H), 6.65 (d, $J_{HH} = 7$ Hz, 2H), 6.73 (d, $J_{HH} = 7$ Hz, 2H), 7.02 (t, $J_{HH} = 7$ Hz, 1H), 7.10−7.15 (m, 8H), 7.20 (t, $J_{HH} = 7$ Hz, 4H), 7.28 (t, $J_{HH} = 7$ Hz, 2H), 7.45 (t, $J_{HH} = 7$ Hz, 4H), 7.57 (t, $J_{HH} = 7$ Hz, 2H), 7.58−7.61 (m, 4H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 26.3 (s). **3b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08−1.82 (m, 38 H), 1.97 (d, $J_{HH} = 12$ Hz, 2H), 2.13 (s, 2H), 2.79 (m, 2H), 2.53 (doublet of virtual triplets, $J_{HH} = 13$ Hz, 2H), 2.84 (doublet of virtual triplets, $J_{HH} = 13$ Hz, 2H), 6.75 (d, $J_{HH} = 8$ Hz, 2H), 7.04 (t, $J_{HH} = 8$ Hz, 1H), 7.22−7.25 (m, 4H), 7.27−7.31 (m, 2H), 7.34 (d, $J_{HH} = 7$ Hz, 2H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 33.7 (s). **3c**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (virtual triplet, 18H), 1.32 (broad, 6H), 1.59 (broad, 6H), 1.84 (broad, 6H), 2.69 (doublet of virtual triplets, $J_{HH} = 13$ Hz, 2H), 2.93 (doublet of virtual triplets, $J_{HH} = 13$ Hz, 2H), 6.58 (d, $J_{HH} = 8$ Hz), 6.94 (t, $J_{HH} = 8$ Hz), 7.22 (m, 2H), 7.32 (m, 4H), 7.37 (m, 2H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 55.1 (s). **4a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.71 (doublet of virtual triplets, $J_{HH} = 12$ Hz, 2H), 3.04 (doublet of virtual triplets, $J_{HH} = 12$ Hz, 2H), 6.26 (m, 2H), 6.58 (d, $J_{HH} = 7$ Hz, 2H), 6.68 (d, $J_{HH} = 7$ Hz, 2H), 6.94 (t, $J_{HH} = 7$ Hz, 1H), 7.07−7.18 (m, 12H), 7.25 (t, $J_{HH} = 7$ Hz, 2H), 7.46 (t, $J_{HH} = 7$ Hz, 4H), 7.57−7.65 (m, 6H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 27.0 (s).

(11) (a) Crystallographic data for **3a**: yellow blocks, crystal dimensions $0.45 \times 0.30 \times 0.29$ mm^3, space group $C2/c$, $a = 16.1720(7)$ Å, $b = 14.2258(7)$ Å, $c = 16.1442(8)$ Å, $\beta = 104.3920(10)°$, $V = 3597.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.499$ g cm^{-3}, μ(Mo Kα) = 1.746 mm^{-1}, data measured on a Bruker SMART 1000 CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å) at 300(1) K, structure solved by direct methods, 9361 reflections collected, 3160 unique reflections ($R_{int} = 0.0266$), data/restraints/parameters 316/0/219, final R indices ($I > 2\sigma(I)$) R1 = 0.030 and wR2 = 0.083, R indices (all data) R1 = 0.038 and wR2 = 0.086, largest difference peak and hole +0.384 and −1.277 e Å^{-3}. (b) Crystallographic data for **7a**: pale brown block, crystal dimensions $0.12 \times 0.20 \times 0.26$ mm^3, space group $Pbcn$, $a = 14.9444(2)$ Å, $b = 11.6289(2)$ Å, $c = 19.7745(3)$ Å, $V = 3436.55(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.577$ g cm^{-3}, μ(Mo Kα) = 1.833 mm^{-1}, data measured on a Bruker Kappa APEX II CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å) at 100(2) K, structure solved by direct methods, 11 657 reflections collected, 6006 unique reflections ($R_{int} = 0.0306$), data/restraints/parameters 6006/0/235, final R indices ($I > 2\sigma(I)$) R1 = 0.036 and wR2 = 0.077, R indices (all data) R1 = 0.068 and wR2 = 0.089, largest difference peak and hole +0.679 and −0.727 e Å^{-3}. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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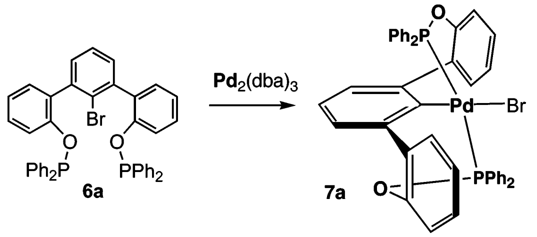
Scheme 4. Synthesis of Diphosphinite Complex 7a



groups most proximal to the bromine atom face steric clashes with the bromine atom and cause rotation about the C−CMe$_3$ bond, thus resulting in three inequivalent methyl groups (portrayed as A, A′, and A″ in Figure 2, right). If the atropisomerization process depicted in Scheme 1 were occurring, the two types of *tert*-butyl groups would undergo exchange and lead to NMR broadening. In contrast, the pincer PCP complexes $[(C_6H_3(CH_2P^tBu_2)_2)PdCl)]$[1] and $[(C_6H_3(CH_2P^tBu_2)_2)Pd(THF\text{-}d_8)]BF_4$[15] only show a single ^{1}H NMR resonance for their freely rotating and equivalent *tert*-butyl groups.

This new type of pincer architecture is expected to be very general and adaptable for a broad variety of donor atoms and for many transition metals. For example, starting with 2,6-(2-HOC$_6$H$_4$)$_2$C$_6$H$_3$Br, the new diphosphinite ligand **6a** can be prepared. This material reacts with Pd$_2$(dba)$_3$ to yield the analogous pincer complex **7a** (Scheme 4). The overall structure is quite similar to that determined for **3a** ($\Phi = 73.8°$, $d_{\text{Pd}-\text{P}} = 2.2824(5)$ Å, $d_{\text{Pd}-\text{C1}} = 2.063(3)$ Å).[11b] The other intermediates described in Scheme 3 lend themselves naturally for easy access to other types of high-twist-angle pincer ligands and complexes.[16] These pincer ligands can be contrasted to the related binding mode of the 2,6-(2-MeOC$_6$H$_4$)$_2$C$_6$H$_3$ terphenyl (Danip) developed for use in stabilizing lanthanide complexes. While twist angles of up to 41° have been characterized, the rigidity of these systems is unknown.[17]

In summary, we have prepared new pincer ligands constructed using *m*-terphenyl scaffolds and showed their efficacy in yielding novel palladium and nickel pincer complexes. A structural analysis of **3a** shows that despite a chelate ring size larger than that of earlier conventional pincer complexes (compare 7 to 5), the new pincer complexes better match the metrical parameters found for related unconstrained nonchelate structures. In addition, these systems have the greatest twist angles determined to date for pincer complexes and also display a very high degree of nonfluxionality (up to 130 °C). These air- and heat-stable materials thus hold much potential for resolution and use in catalysis. Efforts are now ongoing to resolving the enantiomers of **3a**−**c** and to examine their catalytic behavior relative to that of conventional pincer complexes.

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Supporting Information Available: Text and figures giving experimental procedures, NMR spectra, and analysis results and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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