

a resonance for coordinated  $\text{CH}_3\text{CN}$  which is slightly shifted from that of free  $\text{CH}_3\text{CN}$  and a py-Me resonance at  $\delta$  2.40.<sup>7</sup> The latter indicates that the py group is substantially or completely dissociated in  $\text{CD}_2\text{Cl}_2$  solution. Thermolysis of **11** in  $\text{CD}_2\text{Cl}_2$  (55 °C, sealed tube, 12 h) followed by drying under vacuum affords **13** (Scheme II).<sup>6</sup> When this reaction is monitored by  $^1\text{H}$  NMR spectroscopy, the  $\text{CH}_3\text{CN}$ -insertion product **12** is observed as a transient intermediate (Scheme II).<sup>7</sup> Cyclization via  $\text{CH}_3\text{CN}$  displacement followed by tautomerization (or vice versa) of **12** affords the thermodynamically favored conjugated metallacycle **13**. Similar 1,3-hydrogen shifts have been observed in related systems.<sup>1j,4c,8</sup> The  $^1\text{H}$  NMR spectrum of **13** exhibits singlets at  $\delta$  2.00 and 1.96 for the py-Me and  $\text{NHC}(\text{Me})=\text{groups}$ , a broadened singlet at  $\delta$  5.81 for the vinylic proton, and a broad resonance at  $\delta$  6.79 for NH. The py-Me resonance at  $\delta$  2.00 establishes that the py group in **13** is coordinated to Zr. The FTIR spectrum of **13** exhibits an NH absorbance at  $3320\text{ cm}^{-1}$ .

The high reactivity of **2** is ascribed to the extensive formation of the reactive THF-free species **3** in solution and to the relief of ring strain which accompanies substrate insertion. The selectivity for single olefin insertion leading to the formation of metallacycles **4–6** is notable as the acyclic complex  $\text{Cp}_2\text{Zr}(\text{Me})(\text{THF})^+$  (**1**) polymerizes ethylene<sup>5a</sup> and dimerizes propene<sup>9</sup> under the conditions studied here. Presumably, the lack of further olefin insertion of **4–6** is due to the size and stability of the six-membered chelate ring which disfavors olefin coordination. The high Lewis acidity of the cationic Zr(IV) center in **3** promotes coordination and activation of unsaturated substrates and is responsible for the unusually high insertion reactivity relative to that of titanacyclobutenes, 1-zirconia-3-silacyclobutanes, and related neutral group 4 metallacycles.<sup>4</sup> Additionally, the observation of **11** in the reaction of **3** with  $\text{CH}_3\text{CN}$  suggests that substrate-promoted ring opening of **3** (which is not possible for the neutral group 4 metallacycles) may precede insertion in some cases. The regiochemistry observed in these insertions is similar to that observed for reactions of  $\text{Cp}_2\text{M}(\text{benzynes})$ ,  $\text{Cp}_2\text{M}(\text{pyridyl})^+$ , and related complexes.<sup>1,3,9</sup>

We have demonstrated here that the cationic four-membered metallacycle **2**, which in solution exists predominantly in its THF-dissociated form **3**, exhibits high insertion reactivity with a variety of organic substrates. The combination of the C–H activation and insertion chemistry summarized in Schemes I and II constitutes a general approach to the zirconium-mediated functionalization of the methyl C–H bonds of 2,6-lutidine and other *o*-alkylpyridine derivatives.<sup>9,10</sup> We are currently exploring the development of catalytic<sup>3a</sup> and stereoselective<sup>5f</sup> versions of this chemistry.

**Acknowledgment.** This work was supported by DOE Grant DE-FG02-88ER13935, NSF Grant CHE8816445, and the Iowa EARDA program. NMR spectra were obtained in the University of Iowa Highfield NMR Facility. R.F.J. gratefully acknowledges a Sloan Foundation Research Fellowship (1989–1991) and Union Carbide Research Innovation Awards (1989, 1990).

(7) Key  $^1\text{H}$  NMR data for **11** ( $\text{CD}_2\text{Cl}_2$ , 300 MHz):  $\delta$  2.40 (s, 3 H, Me), 1.95 (s, 6 H, MeCN), 1.85 (s, 2 H,  $\text{CH}_2$ -py). Key FTIR data for **11** (KBr pellet):  $\nu_{\text{CN}}$  2279, 2250  $\text{cm}^{-1}$ . Key  $^1\text{H}$  NMR data for **12** (from a mixture of **11**, **12**, and **13**) ( $\text{CD}_2\text{Cl}_2$ , 300 MHz):  $\delta$  6.06 (s, 10 H, Cp), 3.58 (br s, 2 H, py- $\text{CH}_2$ ), 2.53 (s, 3 H, py-Me), 1.78 (br s, 3 H, MeCN). Key FTIR data for **12** (from a mixture of **11** and **12**) (KBr pellet):  $\nu_{\text{CN}}$  2308, 2279,  $\nu_{\text{C=N}}$  1685  $\text{cm}^{-1}$ .

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**Supplementary Material Available:** Details of experimental procedures and spectroscopic and analytical data for complexes **4–13** (7 pages). Ordering information is given on any current masthead page.

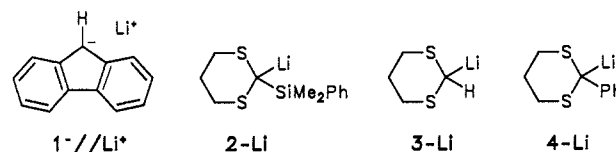
## Direct Nuclear Magnetic Resonance Spectroscopic Determination of Organolithium Ion Pair Structures in THF/HMPA Solution<sup>1</sup>

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The reactivity of organolithium reagents depends in a profound way on the fine details of association among the anionic carbon, the lithium cation, and the solvent.<sup>2</sup> We have reported that lithium cations coordinated by HMPA (hexamethylphosphoric triamide) often undergo sufficiently slow dynamic exchange on the NMR time scale at low temperatures to allow the direct observation of distinct cation–HMPA complexes.<sup>1a</sup> It is frequently possible to detect  $^2J_{\text{Li-P}}$  scalar coupling, and hence the number of HMPA molecules coordinated to  $\text{Li}^+$  can be measured.<sup>3</sup> We now report the application of this NMR procedure for the direct and unambiguous determination of important features of lithium–carbanion and other ion pair structures.



Figures 1 and 2 illustrate the contrasting behavior of a separated ion pair (SIP), fluorenyllithium ( $1^-//\text{Li}^+$ ),<sup>4</sup> and a contact ion pair (CIP), [2-(phenyldimethylsilyl)-1,3-dithian-2-yl]lithium (**2-Li**),<sup>5</sup> on treatment with HMPA. Fluorenyllithium has been exhaustively studied by a variety of techniques and is known to be a SIP in THF at low temperature,<sup>4b</sup> and largely SIP even at 25 °C.<sup>4c</sup> Indeed, the  $^7\text{Li}$  signal at  $-120\text{ °C}$  is sharp ( $\nu_{1/2} = 1.1\text{ Hz}$ ), as expected for a symmetrically coordinated ion. Addition of HMPA to fluorenyllithium in THF produced first a doublet in the  $^7\text{Li}$  spectra, then a triplet, a quartet, and finally a quintet corresponding to  $\text{Li}(\text{HMPA})_n^+$  with  $n = 1-4$  (we will abbreviate:  $\text{Li}(\text{HMPA})_n^+ = \text{Li}(\text{HMPA})_n^+$ ). The concentration of the separated  $\text{Li}(\text{HMPA})_n^+$  species throughout the HMPA titration and the  $^7\text{Li}$  and  $^{31}\text{P}$  NMR properties were virtually identical in all other SIPs we have examined.<sup>1a</sup> Thus the nature of the anion has little effect on the NMR properties or on the formation constants of the various  $\text{Li}(\text{HMPA})_n^+$  species. Fluorenyllithium differs from other SIPs in that small

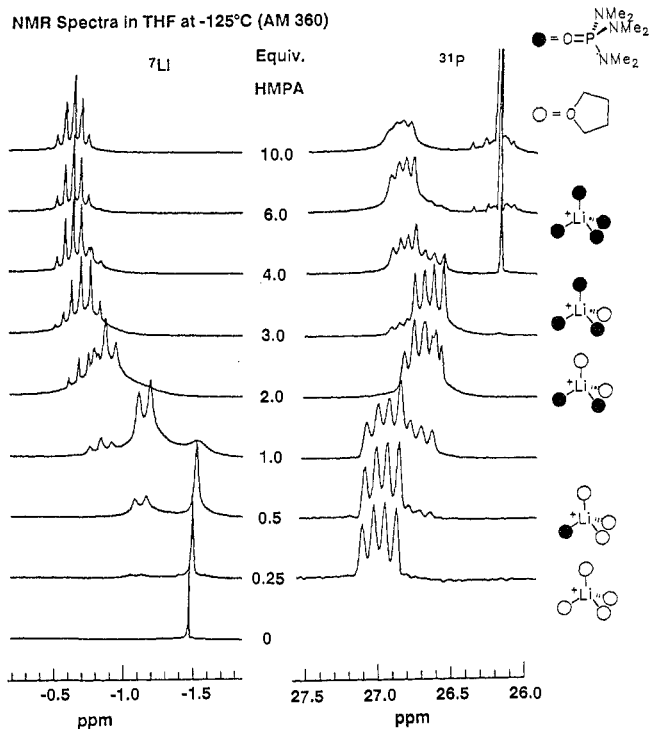
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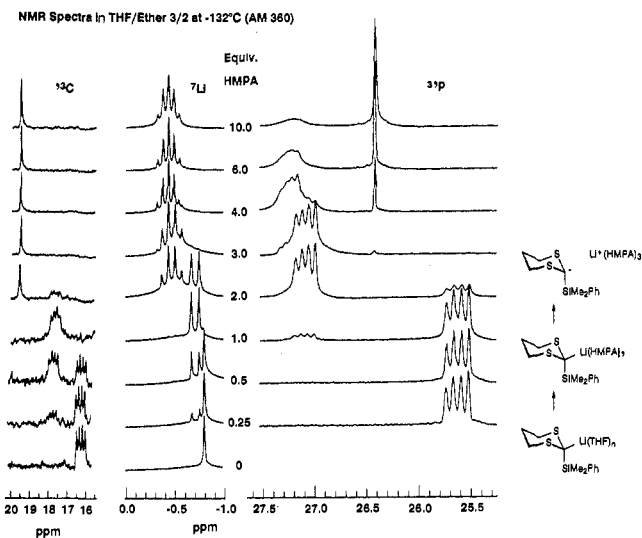
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**Figure 1.** HMPA titration of 0.16 M fluorenyllithium in 20/1 THF/hexane at  $-125^{\circ}\text{C}$ .  $^7\text{Li}$  shifts were referenced to external 0.3 M LiCl in methanol.



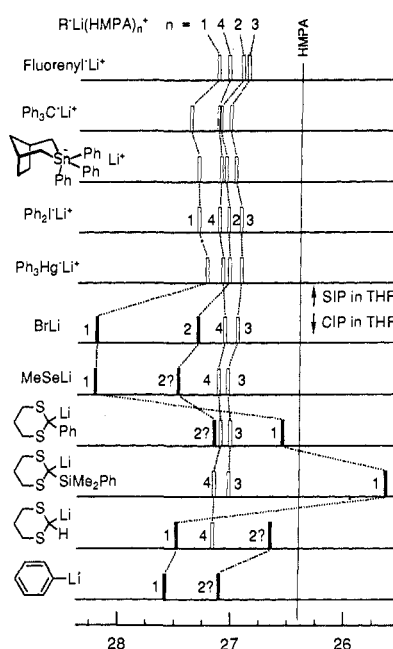
**Figure 2.** HMPA titration of 0.16 M **2-Li** in 60/40 THF/ether at  $-132^{\circ}\text{C}$ . The  $^{13}\text{C}$  signals correspond to C-2 of the dithiane.

upfield lithium and phosphorus chemical shifts were observed, caused by the nearby aromatic fluorenyl anion.<sup>4a</sup> Figure 3 illustrates the  $^{31}\text{P}$  shifts of a number of ions in graphical form.<sup>6</sup> The open bars have been identified as SIPs; the solid bars, CIPs. Note the near constancy of the former and the wide variations in the latter.

When HMPA causes the separation of a CIP, the same  $^7\text{Li}$  and  $^{31}\text{P}$  signals are again observed. This phenomenon is illustrated for the case of **2-Li** (Figure 2). This lithium reagent is probably monomeric in THF at  $-132^{\circ}\text{C}$  since the C-2 resonance ( $^{13}\text{C}$  NMR) showed coupling to only a single  $^6\text{Li}$  or  $^7\text{Li}$ ,<sup>7</sup> but it could

(6) The ate complexes were prepared by reaction of PhLi with the appropriate metalloids; the organolithium reagents, by metalation with *n*-BuLi or PhLi.

(7) For **2-Li**:  $J_{\text{LiC}} = 14.6$  Hz. For **2-LiH**:  $J_{\text{LiC}} = 13.8$  Hz,  $J_{\text{LiP}} = 10.9$  Hz. The Li-C coupling coalesces at a lower temperature than does the Li-P coupling. All couplings are reported for  $^7\text{Li}$ .



**Figure 3.**  $^{31}\text{P}$  chemical shifts of  $\text{RLi}(\text{HMPA})_n$  species in 20/1 THF/hexane at  $-120^{\circ}\text{C}$ . Open bars are SIPs; solid, CIPs.

also be dimerized through the sulfur (like 2-methyl-2-lithio-1,3-dithiane-TMEDA<sup>5b</sup>). Addition of small increments of HMPA produced a new species, which showed a striking upfield shift in the  $^{31}\text{P}$  NMR spectrum with well-resolved  $^{31}\text{P}$ - $^7\text{Li}$  coupling, a doublet in the  $^7\text{Li}$  spectrum, and detectable  $^7\text{Li}$ - $^{13}\text{C}$  and  $^6\text{Li}$ - $^{13}\text{C}$  coupling in the  $^{13}\text{C}$  NMR spectrum. This is therefore a CIP, probably monomeric,<sup>8</sup> with one HMPA coordinated to lithium. Further addition of HMPA produced, *without any other detectable intermediate species*, the characteristic  $^7\text{Li}$  and  $^{31}\text{P}$  signals of SIP **2**<sup>-</sup>//LiH<sub>3</sub><sup>+</sup> and finally **2**<sup>-</sup>//LiH<sub>4</sub><sup>+</sup>. The identification of these species as separated ions was supported by the  $^{13}\text{C}$  signal of C-2, which showed Li-C coupling for **2**-Li and **2**-LiH<sub>1</sub>, but a narrow line for **2**<sup>-</sup>//LiH<sub>3</sub><sup>+</sup> and **2**<sup>-</sup>//LiH<sub>4</sub><sup>+</sup>.

Apparently, **2**-LiH<sub>2</sub> is thermodynamically unstable and disproportionates to **2**<sup>-</sup>//LiH<sub>3</sub><sup>+</sup> and **2**-LiH<sub>1</sub>. Compound **2-Li** is, in this context, similar to several other contact ion pairs which form separated ions with HMPA and which either form little or no R-LiH<sub>2</sub> (LiBr, LiSeMe, [1-phenyl-1-(phenylsulfonyl)ethyl]lithium), or "skip" over R-LiH<sub>3</sub>, going from contact R-Li<sub>1</sub> or R-LiH<sub>2</sub> to R<sup>-</sup>//LiH<sub>4</sub><sup>+</sup> (**3**-Li, LiSMe). Such behavior can be understood on the basis that anionic ligands reduce the electrophilicity of lithium more effectively than do neutral ligands like THF or HMPA. In fact, the observation of R-LiH<sub>1</sub> and SIP R<sup>-</sup>//LiH<sub>3</sub><sup>+</sup> together in substantial concentrations when 2 equiv of HMPA have been added demonstrates that R-LiH<sub>1</sub> is *not* a separated ion, since if it were the two ions would comproportionate to form R<sup>-</sup>//LiH<sub>2</sub><sup>+</sup>.

Localized carbanions such as phenyllithium,<sup>1b</sup> 2-furyllithium, or lithium phenylacetylide complex HMPA relatively weakly (e.g., PhLi formed Ph-LiH<sub>1</sub> and small amounts of what is probably Ph-LiH<sub>2</sub> even when excess HMPA was present). For such reagents free HMPA appeared when as little as 1 equiv of HMPA had been added, and no indication of significant formation of separated (or triple<sup>9</sup>) ions could be found. Also, they typically show  $J_{\text{LiP}}$  which is poorly resolved (or unresolved) due to faster dynamic exchange (shorter  $T_2$ ) and more effective quadrupolar relaxation of  $^7\text{Li}$  (shorter  $T_1$ ).<sup>10,11</sup> The former problem can sometimes be

(8) A dimeric species should behave differently: 0.5 equiv of HMPA should produce (**2-Li**)<sub>2</sub>H<sub>1</sub>; 1 equiv, a second species, (**2-Li**)<sub>2</sub>H<sub>2</sub>.

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(11) It is reasonable that localized carbanions would produce greater electric field gradients at the lithium cation than neutral solvent molecules or delocalized anions and, hence, more effective quadrupolar relaxation.

solved by running the experiment at lower temperature in mixed solvents;<sup>12</sup> the latter, by using <sup>6</sup>Li.<sup>13</sup> In contrast, the separated ions had detectable amounts of free HMPA only when >3 equiv of HMPA had been added and always showed well-resolved Li and P multiplets below -110 °C even with <sup>7</sup>Li.

In summary, the relative concentrations of R-Li<sub>n</sub><sup>+</sup> species during an HMPA titration provides reliable information on the CIP/SIP dichotomy which complements and supports assignments made on the basis of chemical shifts and other arguments. The formation of contact HMPA-coordinated lithium species during the early steps of an HMPA titration reliably identifies the ion pair structure as CIP in the absence of HMPA (i.e., in pure THF), since HMPA is unlikely to cause the conversion of a SIP to a CIP. We are now in an excellent position to study the effect of ion pair structure on reactivity.<sup>2b</sup>

**Acknowledgment.** We thank the National Science Foundation for support of this research.

(12) We have found that we can routinely work with supercooled THF solutions at -116 to -125 °C with 0.16 M RLi and 0.04-1.6 M HMPA for Li and P NMR. The longer acquisition times of <sup>13</sup>C NMR can result in freezing of the solvent. In this situation and to work at still lower temperatures (to -135 °C), 60/40 THF/ether or THF/dimethyl ether mixtures can be used.

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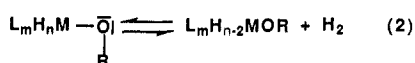
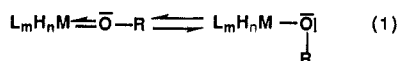
### Alkoxide $\pi$ -Donation to Iridium(III)

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The overwhelming majority of transition-metal polyhydride compounds L<sub>m</sub>MH<sub>n</sub> (L = PR<sub>3</sub>,  $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)<sup>1</sup> are coordinatively saturated. As a result of the absence of empty metal d orbitals, such transition-metal polyhydrides are relatively unreactive toward nucleophiles, especially toward conventional unsaturated hydrocarbons.<sup>2,3</sup> Transition-metal polyhydrides do react readily with electrophiles,<sup>4</sup> and the case of H<sup>+</sup> as electrophile has led to H<sub>2</sub> complexes which can be useful precursors, via H<sub>2</sub> dissociation, to unsaturated metal complexes that catalyze hydrogenation under very mild conditions.<sup>5-7</sup> We explore here an alternative approach to reactive polyhydride compounds: the incorporation of  $\pi$ -donor coligands into a polyhydride environment in order to make unsaturated polyhydrides available either through nondissociative valence isomerization (eq 1) or via facilitation of H<sub>2</sub> loss (eq 2) with concomitant creation of unsaturation.



The recent work of Goldman and Halpern<sup>8</sup> supports this proposal, since they have shown IrH<sub>2</sub>(OR)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> (R = CH<sub>2</sub>CF<sub>3</sub>) to be reactive for coupling of aldehydes and dehydrogenation of secondary alcohols to ketones. This molecule is much more re-

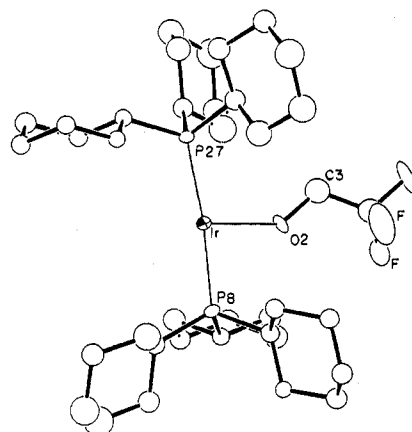


Figure 1. ORTEP drawing of the non-hydrogen atoms of IrH<sub>2</sub>(OCH<sub>2</sub>CF<sub>3</sub>)(PCy<sub>3</sub>)<sub>2</sub>, showing selected atom labeling.

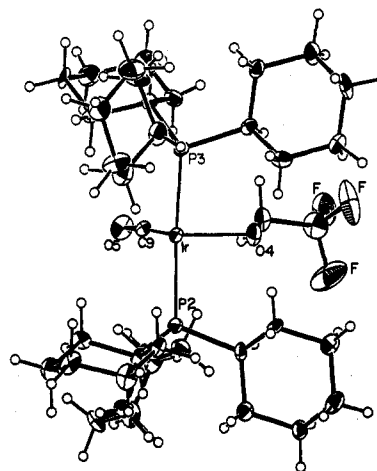


Figure 2. ORTEP drawing of IrH<sub>2</sub>(OCH<sub>2</sub>CF<sub>3</sub>)(CO)(PCy<sub>3</sub>)<sub>2</sub>, showing selected atom labeling. Hydride hydrogens were not located.

active than IrH<sub>3</sub>P<sub>3</sub> species. Those workers established that IrH<sub>2</sub>(OR)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> is a monomer with equivalent phosphorus nuclei and apparently equivalent hydride ligands. We have determined the structure of the related IrH<sub>2</sub>(OR)(PCy<sub>3</sub>)<sub>2</sub>, Figure 1.<sup>9</sup> Since the hydrides were not evident in the X-ray data, this discussion will be limited to the Ir(OCH<sub>2</sub>CF<sub>3</sub>)(PCy<sub>3</sub>)<sub>2</sub> portion of the molecule. The IrP<sub>2</sub>O substructure is planar to within 0.01 Å, and the O-C line makes an angle of only 9.9° with the IrP<sub>2</sub>O plane. There is no evidence for agostic interactions with hydrogens of the alkoxy or the cyclohexyl groups. The Ir-O-C angle, 138.0 (11)°, is enlarged over the tetrahedral angle,<sup>10</sup> and the Ir-O bond length is 2.032 (10) Å. Without a reference value for an Ir-O single bond, the significance of this bond length is uncertain. However, we present the following evidence concerning the nature of the Ir-OR bond in IrH<sub>2</sub>(OR)(PCy<sub>3</sub>)<sub>2</sub>:

1. The structure of IrH<sub>2</sub>(OR)CO(PCy<sub>3</sub>)<sub>2</sub> (Figure 2)<sup>11</sup> provides an opportunity to compare an Ir-OR bond length which is unequivocally a single bond, and in a ligand environment most relevant to that in IrH<sub>2</sub>(OR)(PCy<sub>3</sub>)<sub>2</sub>. The Ir-O distance of 2.169 (7) Å and the Ir-O-C angle of 118.4 (7)° are sufficiently longer and smaller, respectively, than in IrH<sub>2</sub>(OR)(PCy<sub>3</sub>)<sub>2</sub> to support the conclusion that there is O→Ir  $\pi$ -donation in IrH<sub>2</sub>(OR)(PCy<sub>3</sub>)<sub>2</sub>.<sup>12</sup>

(9) Crystal data (-170 °C): *a* = 21.884 (6) Å, *b* = 33.299 (9) Å, *c* = 10.816 (3) Å with *Z* = 8 in space group *Pbca*. With 2315 reflections with *F* > 3 $\sigma$ (*F*), *R*(*F*) = 0.0441 and *R*<sub>w</sub>(*F*) = 0.0433.

(10) For aryloxides (as distinct from alkoxides), M-O-C angles may not be indicative of O→M  $\pi$ -donation. See: Coffindaffer, T. W.; Steffy, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E. *J. Am. Chem. Soc.* 1989, 111, 4742. Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* 1983, 22, 2906.

(11) Crystallographic data (-154 °C): *a* = 17.919 (6) Å, *b* = 10.909 (3) Å, *c* = 22.304 (7) Å,  $\beta$  = 114.56 (2)°, *Z* = 4 in space group *P2<sub>1</sub>/c*. With 4187 reflections with *F* > 3 $\sigma$ (*F*), *R*(*F*) = 0.0516 and *R*<sub>w</sub>(*F*) = 0.0471.

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