Aluminum complexes of the redox-active [ONO] pincer ligand

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Supporting Information

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Figure S1. UV-vis-NIR spectra of [ONO\textsuperscript{aq}]Al(acacPh\textsubscript{2})Cl (2) and [ONO\textsuperscript{aq}]Al(acacPh\textsubscript{2})(py) (4) in C\textsubscript{6}H\textsubscript{6} at 298 K.

Supplemental \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR Spectra of Diamagnetic Compounds
NMR spectra were collected with Bruker Avance 500 MHz spectrometers (\textsuperscript{1}H 500 MHz, \textsuperscript{13}C 128 MHz) in either C\textsubscript{6}D\textsubscript{6} or CD\textsubscript{3}CN solvents that were degassed by several freeze-pump-thaw cycles, dried with sodium benzophenone ketyl radical or CaH\textsubscript{2}, respectively, and vacuum-distilled before use. \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectra were referenced to the residual \textsuperscript{1}H and \textsuperscript{13}C impurities in the solvent (7.15 and 128.02 for C\textsubscript{6}D\textsubscript{6}; 1.94 and 1.24 for CD\textsubscript{3}CN, respectively). NMR spectra were measured at 298 K and chemical shifts are reported by using the standard \(\delta\) notation in parts per million.
[ONHO$^{cat}$]HAICl(OEt$_2$) (1a): $^1$H NMR (C$_6$D$_6$):
[ONHO\textsuperscript{cat}]\textit{AlBr(THF)} (1b): \textit{^1H} NMR (C\textsubscript{6}D\textsubscript{6}): 

\textbf{C\textsubscript{6}D\textsubscript{6}}

\textit{^13C} {\textit{^1H}} NMR (C\textsubscript{6}D\textsubscript{6}): 

\textbf{C\textsubscript{6}D\textsubscript{6}}
[ONO\textsuperscript{6}]Al(acacPh\textsubscript{2})Cl (2): \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}): 

\[ \text{13C}\{\text{1H}\} \text{ NMR (C\textsubscript{6}D\textsubscript{6}):} \]
[ONO⁹]Al(quinO)Cl (3): ¹H NMR (C₆D₆):

¹³C{¹H} NMR (C₆D₆):
**Crystallographic Refinement Details**

* [ONHO*-*]AlBr(THF) (1b):* A hemisphere of data was collected on a colorless plate of approximate dimensions 0.57 × 0.17 × 0.10 mm using a 25 sec/frame scan time. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P2₁/n that was later determined to be correct.

* [ONO*]Al(acacPh₂)Cl (2):* A hemisphere of data was collected on a black prism of dimensions 0.38 × 0.20 × 0.19 mm using a 45 sec/frame scan time. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P2₁/n that was later determined to be correct.

* [ONO]Al(o-O₂C₆H₆Cl₄)(py) (6):* A hemisphere of diffraction data was collected on a black block of dimensions 0.20 × 0.12 × 0.10 mm using a 60 sec/frame scan time. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P2₁/c that was later determined to be correct. There was a pocket of disordered solvent that was positioned across an inversion center. Although diethyl-ether molecules could be seen in this disorder, modeling them using standard modeling procedures was not very stable. Additionally, the largest Q-peak was directly on the inversion center too far from another atom to be included in reasonable disorder modeling. Thus, the program SQUEEZE¹ by Spek et. a. in the PLATON² software suite was used to calculate the electron count in this solvent pocket at 69 electrons. This corresponds roughly to 1.5 diethyl-ether molecules, resulting in a total of 3 disordered ether molecules per unit cell, consistent with the disorder observed in the structure during initial refinement.

* [ONO]Al(o-O₂C₁₆H₈)(py) (8):* A hemisphere of diffraction data was collected on a black plate of dimensions 0.27 × 0.18 × 0.06 mm using a 35 sec/frame scan time. The diffraction
symmetry was 2/m and the systematic absences were consistent with the monoclinic space group \( P2_1/c \) that was later determined to be correct. One of the two THF molecules was disordered over two positions with a freely-refined occupancy of 65:35, and was modeled using standard distance restraints.

References