In 2013, Zadrozny et al. [1,2] discovered zero-field slow magnetic relaxation and hysteresis for the linear iron(I) complex [Fe(C(SiMe3)3)2]−, which has one of the largest spin-reversal barriers reported for mononuclear transition-metal single-molecule magnets. Theoretical calculations suggested that the magnetic anisotropy is due to pronounced stabilization of the iron 3d2z orbital in this complex compared to the neutral iron(II) complex Fe(C(SiMe3)3)2 [3]. Experimental support for this interpretation has however remained lacking. In the present study[4], we have determined the experimental electron density from high-resolution single-crystal X-ray diffraction data in Fe(C(SiMe3)3)2− and Fe(C(SiMe3)3)2, which shows that the d2z orbital is indeed more populated in Fe(C(SiMe3)3)2− than in Fe(C(SiMe3)3)2. This can be interpreted as arising from a greater stabilization of the d2z orbital in Fe(C(SiMe3)3)2− than in Fe(C(SiMe3)3)2, thus providing unprecedented experimental evidence for the origin of magnetic anisotropy in [Fe(C(SiMe3)3)2]− and the corresponding slow magnetic relaxation.