Two novel tripodal ligands, (BIMPNMes,Ad,Me)\(^-\) and (MIMPNMes,Ad,Me)\(^2-\), combining two types of donor atoms, namely, NHC and phenolate donors, were synthesized to complete the series of N-anchored ligands, ranging from chelating species with tris(carbene) to tris(phenolate) chelating arms. The complete ligand series offers a convenient way of tuning the electronic and steric environment around the metal center, thus, allowing for control of the complex’s reactivity. This series of divalent complexes of Mn, Fe, and Co was synthesized and characterized by \(^1\)H NMR, IR, and UV/vis spectroscopy as well as by single-crystal X-ray diffraction studies. Variable-temperature SQUID magnetization measurements in the range from 2 to 300 K confirmed high-spin ground states for all divalent complexes and revealed a trend of increasing zero-field splitting \(|D|\) from Mn(II), to Fe(II), to Co(II) complexes. Zero-field \(^{57}\)Fe Mössbauer spectroscopy of the Fe(II) complexes 3, 4, 8, and 11 shows isomer shifts \(\delta\) that increase gradually as carbenes are substituted for phenolates in the series of ligands. From the single-crystal structure determinations of the complexes, the different steric demand of the ligands is evident. Particularly, the molecular structure of 1 in which a pyridine molecule is situated next to the Mn–Cl bond and those of azide complexes 2, 4, and 6 demonstrate the flexibility of these mixed-ligand derivatives, which, in contrast to the corresponding symmetrical TIMENR ligands, allow for side access of, e.g., organic substrates, to the reactive metal center.