A series of Werner complexes featuring the tridentate ligand smif, that is, 1,3-di-(2-pyridyl)-2-azaallyl, have been prepared. Syntheses of (smif)(2)M (1-M; M = Cr, Fe) were accomplished via treatment of M(NSiMe3)(2)(THF)(n) (M = Cr, n = 2; Fe, n = 1) with 2 equiv of (smif)H (1,3-di-(2-pyridyl)-2-azapropene); ortho-methylated ((o)Mesmif)(2)Fe (2-Fe) and ((o)Me(2)smif)(2)Fe (3-Fe) were similarly prepared. Metatheses of MX2 variants with 2 equiv of Li(smif) or Na(smif) generated 1-M (M = Cr, Mn, Fe, Co, Ni, Ru). Metathesis of VCl3(THF)(3) with 2 Li(smif) and ICi3(THF)3 in the presence of NaBPh4 gave [(smif)(2)Ir]BPh4 (1(+)-Ir).

Electrochemical experiments led to the oxidation of 1-M (M = Cr, Mn, Co) by AgOTf to produce [(smif)(2)M]OTf (1(+)-M), and treatment of Rh-2(O2CCF3)(4) with 4 equiv Na(smif) and 2 AgOTf gave 1(+)-Rh. Characterizations by NMR, EPR, and UV-vis spectroscopies, SQUID magnetometry, X-ray crystallography, and DFT calculations are presented. Intraligand (IL) transitions derived from promotion of electrons from the unique CNCnb (nonbonding) orbitals of the smif backbone to ligand π*-type orbitals are intense (epsilon approximate to 10 000-60 000 M(-1)cm(-1)), dominate the UV-visible spectra, and give crystals a metallic-looking appearance. High energy K-edge spectroscopy was used to show that the smif in 1-Cr is redox noninnocent, and its electron configuration is best described as (smif(-))(smif(2-))Cr(III); an unusual S = 1 EPR spectrum (X-band) was obtained for 1-Cr.

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