The synthetic chem. of substituted 4,4'-azobis(phenylcyanamide) ligands was investigated, and the complexes \([\text{Ru(tpy)(bpy)}_2(\mu-L)]\text{PF}_6^2\), where \(L = 2,2':5,5'-\text{tetramethyl-4,4'-azobis(phenylcyanamide)}\) (Me\(_4\)adpc\(_2\)), \(2,2':\text{dimethyl-4,4'-azobis(phenylcyanamide)}\) (Me\(_2\)adpc\(_2\)), unsubstituted (adpc\(_2\)), \(3,3'-\text{dichloro-4,4'-azobis(phenylcyanamide)}\) (Cl\(_2\)adpc\(_2\)), and \(2,2':5,5'-\text{tetrachloro-4,4'-azobis(phenylcyanamide)}\) (Cl\(_4\)adpc\(_2\)), were prepd. and characterized by cyclic voltammetry and visible-near-IR (NIR) and IR spectroelectrochem. The room temp. ESR spectrum of \([\text{Ru(tpy)(bpy)}_2(\mu-\text{Me}_4\text{adpc})]^{3+}\) showed an org. radical signal and is consistent with an oxidn.-state description \([\text{Ru}^{II}, \text{Me}_4\text{adpc}^{1-}, \text{Ru}^{III}]^{3+}\), while that of \([\text{Ru(tpy)(bpy)}_2(\mu-\text{Cl}_2\text{adpc})]^{3+}\) at 10 K showed a low-symmetry Ru\(^{III}\) signal, which is consistent with the description \([\text{Ru}^{II}, \text{Cl}_2\text{adpc}^{2-}, \text{Ru}^{II}]^{3+}\). IR spectroelectrochem. data suggest that \([\text{Ru(tpy)(bpy)}_2(\mu-\text{adpc})]^{3+}\) is delocalized and \([\text{Ru(tpy)(bpy)}_2(\mu-\text{Cl}_4\text{adpc})]^{3+}\) and \([\text{Ru(tpy)(bpy)}_2(\mu-\text{Cl}_2\text{adpc})]^{3+}\) are valence-trapped mixed-valence systems. A NIR absorption band that is unique to all \([\text{Ru(tpy)(bpy)}_2(\mu-L)]^{3+}\) complexes is obsd.; however, its energy and intensity vary depending on the nature of the bridging ligand and, hence, the complexes' oxidn.-state description.