Title:	Ligand-Based Redox: Catalytic Applications and Mechanistic Aspects
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Abstract:	For the last few decades, coordination chemists have seen many ligands whose role pervades far beyond being a supporting ancillary. The ambiguity in their electronic structure description and challenges to the precise determination of a metal's oxidation state, when such ligands are coordinated with a metal, have sparked intense debate. Owing to this issue, these ligands have been examined with multiple spectroscopic techniques aided by high-level theoretical calculations. Typically, difficulty in accurate electronic structure determination stems from significant metal–ligand covalency and hence strong electronic coupling between a metal and a ligand. Such properties of a molecule lay the ideal groundwork for developing catalysts that can be built on the mutual cooperation of both ligand and associated metal in an active manner. In the last several years the momentum has shifted to the application of such redox-active backbones in catalysis. Redox-active ligands have had a tremendous and continually growing impact on catalysis research. They can behave as a redox reservoir, or they impact the process by changing the basicity of the metal by effective substrate activation. Their utility spans over a number of areas including small molecule activation, homogeneous catalysis, carbon dioxide reduction, and hydrogen evolution reactions. Herein we briefly review the progress of ligand-based redox reactions over the last decade and highlight recent applications in catalysis research. Some of the chosen examples fascinatingly demonstrate the prowess of redox-active ligands in driving the chemistry in a preponderant manner. Some of the challenges and future aspects are also discussed.
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