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Effect of Substituents Mimicking Anchoring of Rhenium Carbonyl Bipyridine Molecular Catalysts for CO₂ Electroreduction

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The electrochemical reduction of CO₂ is a domain of intense activity with the aim to use CO₂ as a source of carbon for fuels or, more broadly, for commodity molecules. Efforts are thus made to develop selective catalysts for CO₂ electroreduction. In that endeavor, the advantage of molecular catalysts is that their structure and properties can be precisely controlled. Molecular compounds are usually studied as homogeneous catalysts to evaluate their figure of merits.¹ However, moving forward to applications, it is often better to design systems in which molecular catalyst are heterogenized on the electrode (or photoelectrode) surface.² Different strategies have been developed to immobilize molecular catalysts on conductive surfaces, including the direct chemical bonding which the advantage is the linkage robustness. Among the variety of molecular linking groups phosphonate and carboxylate chemical functions can be used. When the catalyst is a transition metal complex, one of these anchoring groups has to be connected to the complex through the ligands and an important question is thus raised on its influence on the redox properties and on the catalytic properties of the complex. Although the role of substituents present on ligands of molecular catalysts has been studied in many cases,³ the question of the effect of anchoring groups has not been specifically reported. Herein we will illustrate this issue through the detailed investigation of rhenium tricarbonyl bipyridine (bpy) complexes. We show that the presence of methoxycarbonyl groups on the bpy, used as a mimic for covalent attachment of the Re complex on a substrate, dramatically decrease the activity of the complex toward CO₂ electroreduction. A detailed study combining cyclic voltammetry and spectroscopies reveals the underlying reasons for such a drastic effect. Then, we show that using different mimicking anchoring groups, such as diethylmethylphosphonate ester groups not conjugated with the bpy ligand, allows preserving the catalytic activity toward CO₂ electroreduction.

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