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Research paper

Computational study of the electrochemical reduction of $W(CO)_4$(2,2′-dipyridylamine)

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The paper is dedicated to the 70th birthday of Prof. Carlo Mealli.

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ABSTRACT

Quantum mechanical calculations on $W(CO)_4$(4,6-diphenyl-2,2′-bipyridine) (**1**) and on $W(CO)_4$(2,2′-dipyridylamine) (**2**) were performed with the aim to shed light on the nature of the electrochemical behaviour previously observed under Ar. DFT confirmed the stability of **1** after 1e reduction, showing agreement between IR-SEC (spectroelectrochemical) data and computed IR frequencies. It has been found that the nature of the electrochemical irreversible behaviour of **2** after 1e reduction is due to a geometry rearrangement in which a single pyridine ring is rotated. In long time scale of the IR-SEC a proton loss accounts for the observed IR spectra. Under CO_2 a mechanism of conversion to CO and carbonate ions are herein proposed, and the corresponding transition states individuated.

1. Introduction

Nowadays, there is the need of a radical breakthrough in energy supply technologies to cope with the depletion of fossil energy resources and to reduce global warming [1–5]. Several sustainable approaches have been pursued during last decades, and sunlight conversion plays the main role. One of the most interesting strategies is mimicking the natural photosynthesis process with the aim of converting carbon dioxide and water into chemical fuels and oxygen by using sunlight, thus adopting the carbon-cycle as energy vector for solar energy conversion. Potentially, any CO_2 reduction product precursor to fuels, like methanol, methane, CO, formic acid, etc., could be used in already known technologies, spanning from thermal engines to fuel cells. However, direct artificial photosynthesis of organic molecules is still far away from providing large-scale real-world solutions. Therefore, solar energy production by the well-established photovoltaic technology has been proposed to be employed in the electrochemical conversion of chemical feedstocks (like CO_2) in fuels by solar energy [2].

The electrochemical reduction of CO_2 to fuels and/or fuel precursors still requires low-cost, efficient and selective catalysts for a sustainable energy economy. In this context, homogeneous electrocatalysis is a suitable method to achieve the goal [6–8]. We recently explored the electrocatalytic properties of group 7 metals toward CO_2 reduction [9–11]. Much fewer systems based on lower-cost group 6 metals are known [12–17], and the understanding of their CO_2 reduction mechanism is still very limited. $M(CO)_4$(diimine) complexes (M = Mo, W) usually undergo a first reversible 1e reduction followed by a second 1e chemically irreversible reduction, after which CO loss is observed. The resulting pentacoordinated species is supposed to be the active redox catalyst in CO_2 reduction. These observations have been recently reported by us also for the complex $W(CO)_4$(4,6-diphenyl-2,2′-bipyridine) (**1**) [13]. On the other hand, we show that the analogue complex $W(CO)_4$(dpa) (dpa = 2,2′-dipyridylamine) (**2**) undergoes an unusual electrochemical behaviour, namely a single 1e irreversible reduction at rather negative potentials without CO loss. In this case a sustained catalytic activity has been observed under CO_2 atmosphere with a fivefold increase of the TON values for the conversion of CO_2 into CO. We thought that the dpa ligand could play a non-innocent role in the electrochemical reduction of CO_2 by $W(CO)_4$(dpa). Indeed bpy and dpa only apparently are similar, providing completely different features to the complexes that they form [18]. The aim of this paper is to shed light by computational methods on the mechanism observed during the electrochemical reduction of **2**.

2. Experimental

Gaussian 09 Rev. D.01 was employed for all calculations [19]. Geometry optimizations were performed with the B3LYP

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functional including the conductor-like polarizable continuum model method (CPCM) [20] with acetonitrile as solvent. The LanL2DZ [21] basis sets were used for W, and 6–31G(d,p) for the other atoms. Unrestricted open-shell calculations were performed on the radical anions. The nature of all optimized structures was verified by using harmonic vibrational frequency calculations. No imaginary frequencies were found, thus indicating we had located the minima on the potential-energy surfaces. To compensate the neglecting of anharmonicity effects of the theoretical calculations, scale factor of 0.968 was applied to the computed quantum chemical harmonic vibrational frequencies [22]. In the manuscript we thoroughly reported the Gibbs free energies (ΔG).

3. Results and discussion

Calculations on $W(CO)_4$(4,6-diphenyl-2,2′-bipyridine) (**1**) and on its corresponding radical anion $\mathbf{1}^-$ show that the optimized structures have almost the same geometry, in agreement with the reversibility of the first 1e reduction process observed during CV. Furthermore, the computed and experimental IR frequencies reasonably agree (Table 1) and the M-CO bonds lengths of **1** and $\mathbf{1}^-$ are essentially equivalent.

Geometry optimization of $W(CO)_4$(dpa) (**2**) shows that dpa coordinates W with py rings bent by 28.6° with respect to the plane that include W and the two equatorial COs. These W-CO bonds are shorter (1.973 Å) in comparison with the two axial COs (~2.046 Å). Concurrently, the two py rings of dpa are tilted by 43.4° one respect the other (Fig. 1). This seems to suggest a low electron delocalization over the dpa ligand. Single crystal structure determinations show that for all the three complexes $M(CO)_4$(dpa) (M = Cr, Mo, W) the equatorial M-CO bonds are shorter than axial ones [23], albeit in the solid state the crystal packing alter bond lengths and IR stretching frequencies. Interestingly, in the solid state intermolecular N-H···O=C hydrogen bonding is present that may alter the M-CO bond lengths.

On the other hand, previous calculations of the radical anion show that electron spin density is equally distributed on the ligand, increasing the bending of dpa respect the equatorial plane from 28.6° to 31.3° and decreasing the tilting of the two py rings from 43.4° to 20.4°, with also a concomitant slightly strengthening of the W-CO bonds [13]. While these observations agree with the fact that no CO evolution is detected during the exhaustive electrolysis, they do not account for the chemical irreversible processes following the reduction of **2**. Furthermore, the DFT calculated IR stretching frequencies ν_{CO} of $\mathbf{2}^-$ (1924, 1838, 1825 and 1788 cm^{-1}) do not fit at all with the values observed in IR-SEC experiments (1996, 1868, 1843 and 1795 cm^{-1}) after 1e exhaustive electrolysis of **2** (Table 1). Several hypothesis ranging from Hofman degradation [24], metal hydrides formation [10,11], and hydrogen abstraction from acetonitrile [10,11,25,26] could be formulated if rather negative potentials are applied.

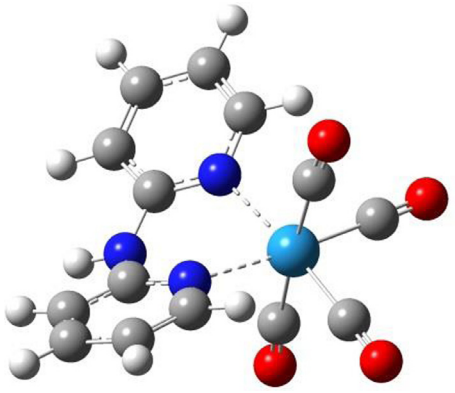

Fig. 1. Optimized geometry of **2**.

Intrigued by the structural modification displayed by the radical anion $\mathbf{2}^-$, we decided to start from the DFT optimized structure of $\mathbf{2}^-$ and to search for a transition state, $^{TS}\mathbf{2}^-$, in which one of the two py rings could rotate and point away from the metal. Fig. 2 shows the optimized structure of $^{TS}\mathbf{2}^-$, which is 28.8 kJ/mol higher in energy than $\mathbf{2}^-$ and has only one imaginary frequency at 47i cm^{-1}. This vibrational mode is associated with the reaction coordinate that involves rotation of the non-coordinated py-NH moiety.

Following this rotation by the intrinsic reaction coordinate method (IRC), as implemented in Gaussian 09, the subsequent fully geometry optimization resulted into a structure, $\mathbf{3}^-$, which is 10.1 kJ/mol lower in energy than $\mathbf{2}^-$ (Fig. 3).

The form $\mathbf{3}^-$ displays an almost planar dpa ligand, with the NH group involved in an agostic W-H interaction (2.635 Å). Moreover, the hydrogen atom is close (2.252 Å) to an equatorial CO. As a matter of fact, in $\mathbf{3}^-$ there is a vacant coordination position on W, free of steric hindrance. In MeCN solution and under inert atmosphere, this position is very probably occupied by a solvent molecule. This structure, however, does not account yet for the IR-SEC data, since the experimental ν_{CO} values are significantly higher than the computed ones (1916, 1809, 1800 and 1754 cm^{-1}), suggesting that $\mathbf{3}^-$ still possess too high metal-centred electron density. A way to lower this character is by filling the vacant coordination site. This could be accomplished by the NH moiety either by a simple long-range interaction or by a net hydrogen transfer from NH to W (thus giving an hydride specie). By considering that COs are very likely fluxional, the $W(CO)_4$ fragment could be rearranged as in $\mathbf{4}^-$ (Fig. 4, right). The energy barrier that accounts for the transformation of $\mathbf{3}^-$ into $\mathbf{4}^-$ via $^{TS}\mathbf{3}^-$ (Fig. 4 left) is 24.9 kJ/mol.

$\mathbf{4}^-$ is 5.3 kJ/mol lower in energy than $\mathbf{2}^-$ and 4.8 kJ/mol higher than $\mathbf{3}^-$. The agostic W-H interaction in $\mathbf{4}^-$ displays almost the same W-H distance (2.631 Å) of $\mathbf{3}^-$, but the vacant coordination site of W is now in front of the H atom. This structure has still a high metal-centred electron density (see Table 1), and cannot

Table 1
Experimental [13] and computed IR frequencies for the complexes under study.

Compound	Experimental IR-SEC (cm^{-1})	Computed IR (cm^{-1})	N-H (Å)
1	2006, 1885, 1826	2006, 1883, 1873, 1830	
$\mathbf{1}^-$	1985, 1854, 1796	1989, 1854, 1846, 1802	
2	2010, 1885, 1865, 1818	2010, 1874, 1872, 1824	1.012
$\mathbf{2}^-$		1924, 1838, 1825, 1788	1.011
$\mathbf{3}^-$		1916, 1809, 1800, 1754	1.023
$\mathbf{4}^-$		1917, 1810, 1796, 1773	1.022
$\mathbf{5}^-$		2009, 1888, 1879, 1795	2.675[a]
$\mathbf{6}^-$	1996, 1868, 1843, 1795	1997, 1855, 1853, 1805	
$\mathbf{7}^-$		1998, 1855, 1852, 1800	

[a] The W-H bond length in the hydride $\mathbf{5}^-$ is 1.770 Å.

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