INFRARED SPECTROELECTROCHEMICAL INVESTIGATION OF CARBON DIOXIDE REDUCTION MEDIATED BY THE ANION $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ (iPr-DAB = *N*,*N′*-DIISOPROPYL-1,4-DIAZA-1,3-BUTADIENE)

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 60th birthday.

Carbon dioxide was found to react slowly with the coordinatively unsaturated anion $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ electrogenerated in an IR OTTLE cell via bielectronic reduction of $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]$. This reaction produced free CO, CO_3^{2-}, O_2CH^- and other two unidentified carboxylato species. The overall process is not catalytic in nature since the anion cannot be recovered after the attack of CO_2 due to its conversion into a stable complex tentatively assigned as $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$. Although limited, the inherent reactivity of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ towards CO_2 demonstrated that the strong π-bonding within the (Sn)Ru(iPr-DAB) metallacycle, stabilizing the five-coordinate structure, is slightly less delocalized in comparison with the closely related, but totally inert anions $[Mn(CO)_3(\alpha\text{-diimine})]^-$ (α-diimine = bpy, iPr-DAB).

Key words: Infrared spectroelectrochemistry; CO_2 reduction; Ru carbonyls; α-Diimine complexes.

Uncatalyzed electrochemical reduction of CO_2, the potential abundant and cheap source of carbon for the C_1 chemistry, is a highly energy-demanding task owing to the substantial negative kinetic overpotential (about –2.2 V vs SCE) required for the generation of the high-energy radical intermediate $CO_2^{\bullet -}$ (ref.[1]). One solution to the problem of lowering the high energetic barrier for the electron transfer is the utilization of heterogeneous of homogeneous electrocatalysis. Concerning the latter approach, much effort has been devoted last two decades to the applicaiton of a variety of transition metal complexes as precursor of active electrocatalysts of the CO_2 reduction, producing mainly CO, formic acid, or formaldehyde[2,3]. Among them, the class of transition metal (Re, Ru, Rh, Os, Ir, Cr, Fe, Co, Ni) complexes with basic α-diimine ligands like 2,2′-bipyridine (bpy), 2,2′:6′,2″-terpyridine (tpy), or 1,10-phenanthroline (phen) has received a great deal of attention[2–10]. Up to now, the most efficient electrocatalytic systems of this class are based on the complexes $[Cr(4\text{-vinyl-tpy})_2]^3$,

$[Re(Cl)(CO)_3(N,N)]$ (N,N = bpy, 4,4′-dimethyl-bpy, 4-methyl-4′-vinyl-bpy) (refs[9–12]), $[Ru(CO)_2(bpy)_2]^{2+}$ and $[Ru(Cl)_2(CO)_2(bpy)]$ (refs[6–8]), dissolved in mixed protic/aprotic solvents or forming strongly adherent electropolymerized films on cathode surfaces. These catalytic systems have been investigated mainly by transient electrochemical techniques (in particular by cyclic voltammetry) and by preparative scale electrolysis. In the case of carbonyl complexes, whose IR $\tilde{\nu}$(CO) wavenumbers and band patterns sensitively respond to changes of their oxidation state and/or composition, also IR spectroelectrochemistry may be employed as a very useful tool for the determination of the reduction pathways of the catalyst precursors. Furthermore, IR spectra recorded in the course of the electrocatalytic process may also considerably help to assign in situ the products formed out of the reduced CO_2. Such studies have been, however, still rather scarce[11–13].

The incorporation of the above basic aromatic α-diimine ligands into the catalysts of the electrochemical CO_2 reduction like $[Re(Cl)(CO)_3(bpy)]$ has been substantiated by two simultaneously operating factors. First, the conveniently low energetic position of the π*(α-diimine) LUMO as an electron reservoir enables the electrocatalytic reduction to occur at rather positive potentials with respect to the reduction of free CO_2 (refs[9,11,12]). Secondly, the strong σ,π-donation of these α-diimines in their reduced state(s) (i.e., radical anion, dianion) largely directed toward axial co-ligands L at the six-coordinate metal center[14,15] facilitates significantly the cleavage of the metal–L bond and creation of free sites at electronically rich metal centers as the necessary prerequisite[5] for the electrophilic attack of CO_2 followed by electron transfer. To date, no attempts have been made to employ for this purpose the *N,N″*-dialkyl-1,4-diaza-1,3-butadiene (R-DAB) ligands. In comparison with 2,2′-bipyridine, the R-DAB (R = *t*-Bu, iPr) ligands possess a stronger π-acceptor capacity, as testified in the more positive reduction potentials of the complexes $[M(Br)(CO)_3(R\text{-}DAB)]$ (M = Mn (ref.[16]), Re (refs[17,18])) and $[Ru(I)(Me)(CO)_2(R\text{-}DAB)]$ (refs[19,20]) with respect to their bipyridine-derivatives[14,20,21]. On the other hand, the non-aromatic character of R-DAB is responsible for a substantial delocalization of the added electron(s) over the metal(R-DAB) chelate ring in the reduced complexes[16–18]. This feature results in the reactivity patterns comparable with those of the reduced bipyridine complexes[14–17,20,21]. The question has thus emerged whether some of the R-DAB complexes are also capable of acting as electrocatalysts of the CO_2 reduction.

In this paper we report the mechanism of CO_2 reduction mediated by the complex $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]$, as studied by in situ IR spectroelectrochemistry at an optically transparent Pt minigrid electrode. In our previous report on the electrochemistry of the complexes $[Ru(E)(R)(CO)_2(iPr\text{-}DAB)]$ (E = $SnPh_3$, $PbPh_3$; R = Cl, Me, $SnPh_3$, $GePh_3$, $PbPh_3$) (ref.[22]), the reduction path of $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]$ has been shown to involve both the five-coordinate radical $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^{\bullet}$ and the corresponding anion $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^{-}$. These species are thus closely related to the coordinatively unsaturated complexes $[Re(CO)_3(bpy)]^\bullet$ and $[Re(CO)_3(bpy)]^-$ whose simultaneous catalytic activity towards the CO_2 reduction has recently been confirmed by an IR spectroelectrochemical study[12]. Contrary to the Re–bpy complexes, the catalytic cycle of $[Ru(Cl)_2(CO)_2(bpy)]$ has recently been recognized to involve the polymeric catalyst precursor $[\{Ru(CO)_2(bpy)\}_n]$ that probably loses one CO ligand upon one-electron reduction to promote the coordination of CO_2 (ref.[7]).

The molecular structures of the parent complex and some of its reduction products are schematically depicted in Fig. 1.

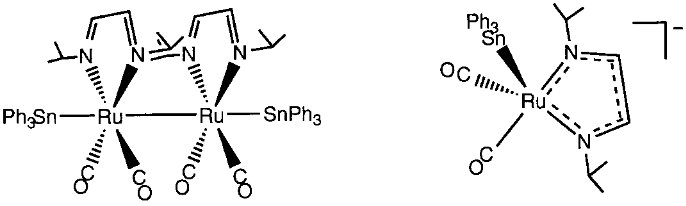
EXPERIMENTAL

Chemicals. Tetrahydrofuran, THF (Janssen), high purity grade, was distilled prior to use from Na/benzophenone under an atmosphere of dry nitrogen. Tetrabutylammonium hexafluorophosphate, Bu_4NPF_6 (Fluka) was recrystallized twice from absolute ethanol and dried in vacuo at 80 °C for 10 h. The complex $[Ru(Cl)(SnPh_3)(CO)_2$(iPr-DAB)] was synthesized according to the literature procedure[23]. All spectroelectrochemical samples were handled carefully under a nitrogen atmosphere. CO_2 was introduced into the solutions by bubbling through a S_3 frit.

(Spectro)electrochemistry. The FTIR spectrometer used was a Bio-Rad FTS 7 (a Globar source, a DTGS detector, 2 cm^{-1} spectral resolution). Spectroelectrochemical experiments were carried out in an IR OTTLE cell[24] equipped with a Pt minigrid working electrode (5 × 4 mm rectangle, 32 wires/cm) and CaF_2/NaCl windows. Cyclic voltammograms were recorded in a three-electrode gas-tight cell equipped with a Pt disk (d = 0.5 mm) working, Pt gauze auxiliary and Ag wire pseudo-reference electrodes. Potential control at the working electrode was achieved by a PA 4 (EKOM,

[Ru(Cl)(SnPh$_3$)(CO)$_2$(iPr-DAB)]

iPr-DAB



[Ru(SnPh$_3$)(CO)$_2$(iPr-DAB)]$_2$

[Ru(SnPh$_3$)(CO)$_2$(iPr-DAB)]$^-$

FIG. 1

Schematical representation of the complex $[Ru(Cl)(SnPh_3)(CO)_2$(iPr-DAB), its reduction products $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]_2$ and $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$, and the ligand iPr-DAB

Czech Republic; spectroelectrochemistry) or PAR Model 283 (cyclic voltammetry) potentiostats. The spectroelectrochemical samples were $5 \cdot 10^{-3}$ and $3 \cdot 10^{-1}$ M in [Ru((Cl)($SnPh_3$)$(CO)_2$(iPr-DAB)] and Bu_4NPF_6, respectively. All the redox potentials reported hereinafter are given against $E_{1/2}$ of the standard[25] Ferrocene/Ferrocenium (Fc/Fc$^+$) redox couple.

RESULTS AND DISCUSSION

As previously shown[22], the reduction of the complex [Ru(Cl)($SnPh_3$)$(CO)_2$(iPr-DAB)] at $E_{p,c}$ = –1.48 V in CO_2-free THF (as measured by cyclic voltammetry at ν = 100 mV/s) has to be viewed as a complex ECEC process that finally gives the dimer [Ru($SnPh_3$)$(CO)_2$(iPr-DAB)$]_2$ with an eclipsed conformation of the iPr-DAB ligands as drawn in Fig. 1. The reaction sequence can be described by Eqs (*1*)–(*4*).

$$\text{E } [\text{Ru(Cl)(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})] + \text{e} \longrightarrow [\text{Ru(Cl)(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})]^{\bullet -} \quad (1)$$

$$\text{C } [\text{Ru(Cl)(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})]^{\bullet -} \longrightarrow [\text{Ru(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})]^{\bullet} + \text{Cl}^- \quad (2)$$

$$\text{E } [\text{Ru(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})]^{\bullet} + \text{e} \longrightarrow [\text{Ru(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})]^- \quad (3)$$

$$\text{C } [\text{Ru(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})]^- + [\text{Ru(Cl)(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})] \longrightarrow$$

$$\longrightarrow [\text{Ru(SnPh}_3)(\text{CO})_2(\text{iPr–DAB})]_2 + \text{Cl}^- \quad (4)$$

The secondary chemical reaction of the radical anion [Ru(Cl)($SnPh_3$)$(CO)_2$(iPr-DAB)$]^{\bullet -}$ (see Eq. (*2*)) is a very fast process, as was also found[16] for the Br^- dissociation from the closely related complex [Mn(Br)$(CO)_3$(iPr-DAB)$]^{\bullet -}$ characterized by the first-order rate constant $k > 10^7$ s^{-1}. The resulting five-coordinate radical [Ru($SnPh_3$)$(CO)_2$(iPr-DAB)$]^{\bullet}$ is also a very short-lived species owing to its instantaneous reduction to give the anion [Ru($SnPh_3$)$(CO)_2$(iPr-DAB)$]^-$ (Eq. (*3*)). The driving force for this step is provided by the more positive value of the standard redox potential of the redox couple in Eq. (*3*) with respect to that of the redox couple in Eq. (*1*) (refs[16,22]). Consequently, the direct dimerization of [Ru($SnPh_3$)$(CO)_2$(iPr-DAB)$]^{\bullet}$ cannot compete with the second electron transfer step (Eq. (*3*)). The dimer [Ru($SnPh_3$)$(CO)_2$(iPr-DAB)$]_2$ is then only formed via the coupling reaction described by Eq. (*4*), that was independently confirmed by a chemical reaction between parent [Ru(Cl)($SnPh_3$)$(CO)_2$(iPr-DAB)] and the anion [Ru($SnPh_3$)$(CO)_2$(iPr-DAB)$]^-$ (ref.[22]). The latter secondary reaction is the rate determining step in the above ECEC mechanism. It is not complete on the time scale of 10^{-1} s (i.e., at slow cyclic voltammetric scans), where the total number of electrons transferred was determined to be n_{total} = 1.3. On the time scale of minuted n_{total} = 1, and the dimer [Ru($SnPh_3$)$(CO)_2$(iPr-DAB)$]_2$ was indeed observed as the single product during the IR spectroelectrochemical experiment at T = 293 K (ref.[22]). The subsequent reduction of the dimer at $E_{p,c}$ = –1.68 V (in THF, vs Fc/Fc^+) gives finally the anion $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ (Eq. (*5*)) (ref.[22]).

$$1/2\ [Ru(SnPh_3)(CO)_2(iPr\text{–}DAB)_2] + e \xrightarrow{\qquad} [Ru(SnPh_3)(CO)_2(iPr\text{–}DAB)]^- \qquad (5)$$

In order to examine whether some deviation from the above reduction path (Eqs (*1*)–(*5*)) arises in the presence of CO_2, the reduction of $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]$ in CO_2-saturated THF was followed in situ by IR spectroscopy. The reduction led initially to the replacement of the ν(CO) bands of the parent complex at 2 025 and 1 964 cm^{-1} by those at 1 990, 1 963 and 1 934 cm^{-1} belonging[22] to the dimer $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]_2$ (Fig. 2a). This product was further reduced to give within a few seconds the anion $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ absorbing at 1 925 and 1 857 cm^{-1} (Fig. 2a), in accordance with Eq. (*5*).

Figures 2a and 2b reveal that the appearance of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ was also accompanied by the gain of absorbance in the 1 500–1 700 cm^{-1} region. Peaks were observed at 1 606 and 1 640 cm^{-1}, that indicated[12] reduction of CO_2 followed by a formation of free CO_2H^- and CO_3^{2-} (in the form of an ion-pair[26]), respectively. The presence of CO_3^{2-} in the solution implies formation of free CO. However, this product absorbs only very weakly and its band at 2 137 cm^{-1} is hardly observable at room temperature, unless a large amount of CO_2 is converted to CO (refs[11,12]). In most of the OTTLE experiments production of CO is evidenced by bubbles developed at the working electrode[12], that also applied for this experiment. Another band present at 1 632 cm^{-1} might belong to coordinated CO_2H^-, as was found[12] for stable $[Re(CO_2H)(CO)_3(bpy)]^{\bullet -}$ (ν_{as}(COO) = 1 630 cm^{-1}). In our case, however, such stability of the related radical anionic complex $[Ru(CO_2H)(SnPh_3)(CO)_2(iPr\text{-}DAB)]^{\bullet -}$ to allow its IR spectroscopic detection is highly improbable in view of the rapid dissociation of Cl^- from the related $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]^{\bullet -}$ (see Eq. (*2*)). In favour of this assumption no ν(CO) bands attributable to the formato complex were observed (see below). The band at 1 632 cm^{-1} has therefore remained unassigned. The same applies for another band in this reagion that grew at 1 674 cm^{-1}. It has been documented[12] that this band accompanies the band of free CO_3^{2-} at 1 640 cm^{-1} but it grows independently of the latter, particularly at the beginning of the CO_2 reduction.

The generation of free CO, CO_3^{2-} and O_2CH^- clearly proves that $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ is capable of CO_2 reduction. This process is however rather sluggish, as evidenced at its beginning by the fact that the anion could be observed in high concentration. Contrary to this, the anion $[Re(CO)_3(bpy)]^-$, that reacts efficiently with CO_2, could not be detected by IR spectroscopy in the course of the electrocatalyzed CO_2 reduction[12]. The anion $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ also does not reduce CO_2 in high yield. Figure 2b has witnessed to its gradual conversion into another dicarbonyl species with ν(CO) at 1 985 and 1 918 cm^{-1}. This product closely resembles the complex $[Ru(CO)_2(iPr\text{-}DAB)]_2$ re-

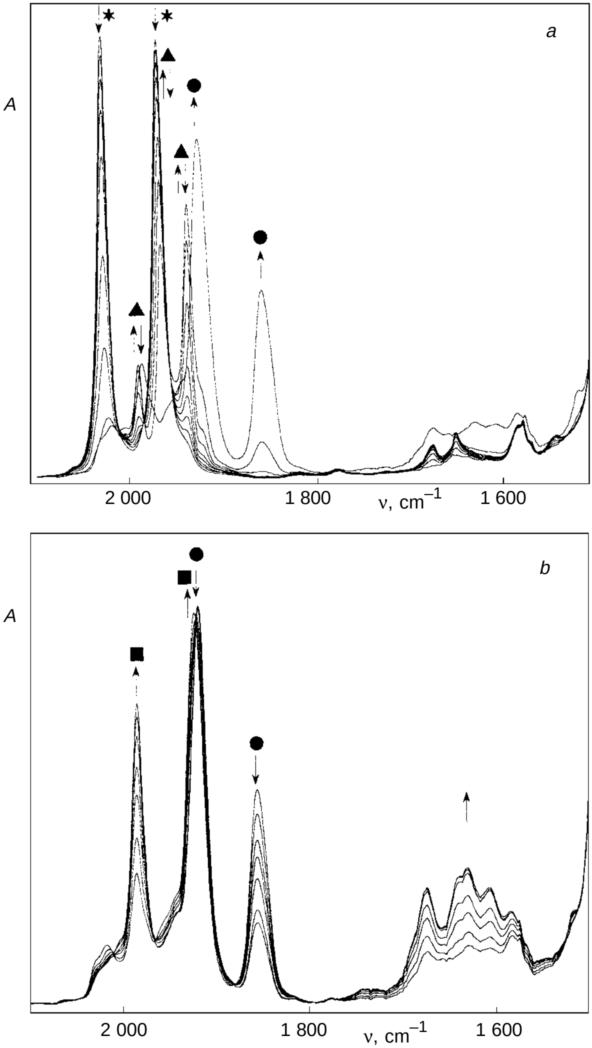


FIG. 2

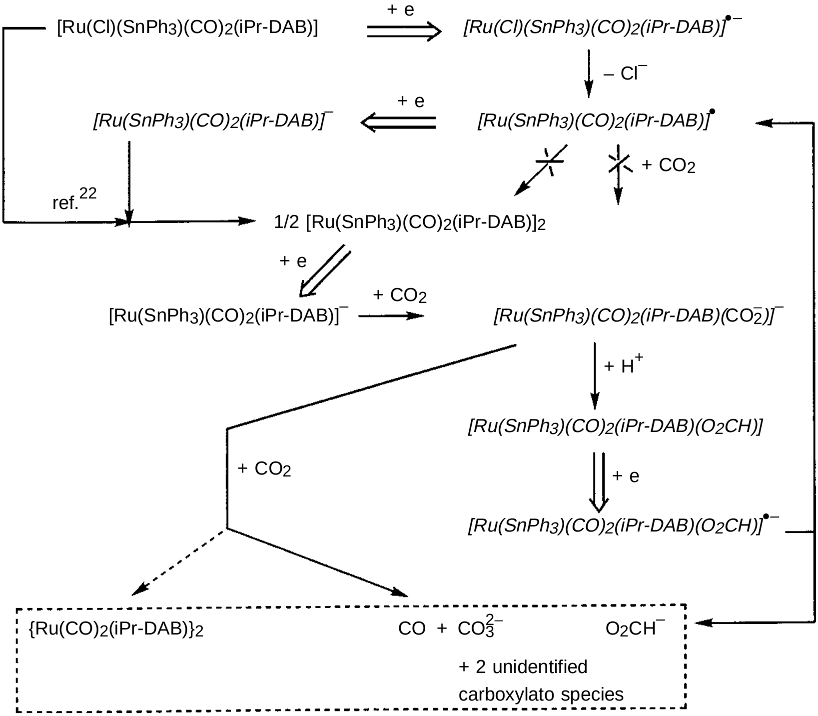
IR spectral changes following OTTLE cell reduction of [Ru(Cl)(SnPh$_3$)(CO)$_2$(iPr-DAB)] in CO$_2$ saturated THF solution (arrows indicate whether the bands decrease ↓ or increase ↑). *a* Reduction of [Ru(Cl)(SnPh$_3$)(CO)$_2$(iPr-DAB)] (✶) results in the initial production of the dimer [Ru(SnPh$_3$)(CO)$_2$(iPr-DAB)]$_2$ (▲) followed by the anion [Ru(SnPh$_3$)(CO)$_2$(iPr-DAB)]$^-$ (●). Spectral changes in the 1 500–1 700 cm^{-1} region are negligible until the reduction of the dimer is complete. *b* A slow reaction between the electrogenerated anion [Ru(SnPh$_3$)(CO)$_2$(iPr-DAB)]$^-$ (●) and CO$_2$ results in appearance of several bands in the 1 500–1 700 cm^{-1} region due to free O$_2$CH$^-$, CO$_3^{2-}$ (accompanied by free CO absorbing very weakly at 2 137 cm^{-1}, not shown) and two unassigned carboxylato products (see Results and Discussion). The CO$_2$ reduction becomes inhibited by the conversion of [Ru(SnPh$_3$)(CO)$_2$(iPr-DAB)]$^-$ into {Ru^0(CO)$_2$(iPr-DAB)]$_2$ (■)

ported by Staal et al.[27] that possesses the two $\tilde{\nu}$(CO) wavenumbers at 1 983 and 1 922 cm^{-1} (in CH_2Cl_2). The molecular structure of the latter highly symmetric dimer consists of two $Ru(CO)_2$ units joint together through two iPr-DAB ligands forming a bridge via $\sigma N,\sigma' N,\eta^2 C{=}N$-coordination. Our preliminary ^1H NMR data also indicate such coordination mode for iPr-DAB in the above product; although, they do not clearly answer the question what happened with the $SnPh_3$ ligand. The species is therefore only tentatively assigned as $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$. The proposed formulation of the metal center as Ru^0 gets support from also very similar $\tilde{\nu}$(CO) wavenumbers of the complex $[Ru^0((PPh_3)(CO)_2(iPr\text{-}DAB)]$ (1 980, 1 920 cm^{-1} in hexane)[28]. Apparently, $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ was formed at a very similar reaction rate as the above CO_2 reduction products (see Fig. 2b). We therefore propose that the reaction of CO_2 with $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ has no catalytic but stoichiometric character, resulting in net one-electron oxidation of the anion to give $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$. Here it should be remarked that without CO_2 present in the solution, $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ electrochemically generated in the OTTLE cell is inherently stable in dry deoxygenated solvents and can subsequently be reoxidized to give primarily the radical $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^{\bullet}$ that rapidly converts into the metal-metal bonded dimer[22] $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]_2$. The "chemical" oxidation of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ via the reaction with CO_2, leading to $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$, thus appeared to be more favourable pathway than the production of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]_2$. This assumption was further confirmed by slow decomposition of the anion $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$, produced independently by bielectronic reduction of $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]$ in THF with 1% Na/Hg (see Eqs (*1*)–(*3*)), that also gave no dimer $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]_2$ but $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ in high yield as an air-stable red-coloured compound soluble in common organic solvents (ν(CO) at 1 987 and 1 921 cm^{-1} in THF; 1 989.5 and 1 923 cm^{-1} in benzene). (Note that $[Ru(CO)_2(iPr\text{-}DAB)]_2$ is yellow[27].) The facile oxidation of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ might be a result of its high affinity to adventitious water in the solution (as a source of H^+) or to traces of oxygen slowly diffusing into the Schlenk tube. However, as the anion proved to be stable when generated inside the OTTLE cell without CO_2 present in the thin solution layer, its conversion to $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ in the course of the above spectroelectrochemical experiment is ascribed exclusively to the attack of CO_2.

The redox properties of $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ were characterized by cyclic voltammetry. The complex is irreversibly oxidized at $E_{p,a} = +0.225$ V and irreversibly reduced at $E_{p,c} = -2.90$ V vs Fc/Fc^+. The irreversible reduction of $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ led to partial recovery of the anion $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$, for its anodic peak was observed on the reverse voltammetric scan at $E_{p,a} = -1.15$ V (ref.[22]). Another support for this conclusion was obtained from a corresponding IR OTTLE experiment that also clearly proved the formation of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$. The big gap between the reduction potential of $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ and the oxidation potential of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ points to a substantially different bonding situation in these complexes. Further research is needed to characterize $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ in more detail.

Figure 2b shows that the conversion of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ into $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ completely inhibits further reduction of CO_2. The latter process however became considerably accelerated after the potential of the working minigrid electrode had been set at the reduction potential of $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ (see above). Neglecting the recovery of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ during the reduction of $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$, the efficient generation of CO, CO_3^{2-} and O_2CH^- observed in this case can reasonably be attributed to the reduction of free CO_2 itself since the applied reduction potential was slightly more negative than the value of the $CO_2/CO_2^{\bullet -}$ redox couple in THF (≈ –2.8 V vs Fc/Fc^+).

The events in the mechanism of the CO_2 reduction initiated by the reduction of $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]$ are summarized in Scheme 1. The key role in the mechanism is played by the five-coordinate anion $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ that



SCHEME 1

slowly coordinated CO_2, probably in the η^1-CO_2 fashion[29,30]. This step is accompanied by the transfer of the negative charge towards the CO_2 ligand, producing the transient $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)(CO_2^-)]^-$. Although not detected by IR spectroscopy, the latter species is indirectly revealed by the production of free O_2CH^-. The source of protons that attack the sufficiently basic oxygen in the η^1-CO_2^- ligands is either the adventitious water in the electrolyzed solution, or the supporting electrolyte $Bu_4N^+PF_6^-$ (via the Hofmann degradation of the quarternary ammonium salts[5]). In analogy with the complexes $[Re(L)(CO)_3(bpy)]$ ($L = Cl^-$, O_2CH^-) (ref.[12]) it is expected that the reduction potential of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)(O_2CH)]$ does not deviate significantly from parent $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]$. The former complex is therefore thought to be instantaneously reduced into $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)(O_2CH)]^{\bullet -}$. The radical anion is expected to be very unstable, similarly to $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]^{\bullet -}$ (see above). It probably readily loses O_2CH^- to give $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^{\bullet}$ at re-enters the reaction cycle. The transient species $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)(CO_2)]^-$ can also react with another CO_2 molecule to produce CO and CO_3^{2-}, as was described[11,12] for $[Re(CO)_3(bpy)(CO_2)]^-$. It is probably this reaction step that finally leads to the formation of stable $\{Ru^0(CO)_2(iPr\text{-}DAB)\}_2$ and to the total inhibition of further CO_2 reduction. As a consequence of the deactivation of $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$, the whole reduction mechanism for CO_2 thus possesses only negligible catalytic character.

Differently from the electrocatalytic mechanism of $[Re(Cl)(CO)_3(bpy)]$ in THF (ref.[12]), there is no one-electron pathway for the CO_2 reduction in this case, i.e., no reaction between CO_2 and the five-coordinate radical $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^{\bullet}$ occurs. Obviously, this can be ascribed to the instantaneous one-electron reduction of the radical leading to $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ (see Eq. (*3*)), that prevents competition of any secondary chemical reaction (dimerization, coordination of solvent molecules or CO_2).

In conclusion, this study contributes to a better understanding of the reactivity of CO_2 towards reduced transition metal complexes with basic α-diimine ligands. Eventhough $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^-$ was not found to act as an efficient catalyst of CO_2 reduction, the conclusive ability to react with CO_2 enables to distinguish this five-coordinate anion from the totally inert complexes[31] $[Mn(CO)_3(\alpha\text{-diimine})]^-$ (α-diimine = bpy, iPr-DAB). The latter anions possess a very strongly delocalized π-bonding within the $\{Mn(\alpha\text{-diimine})]^-$ metallacycle[16,17] that stabilizes their five-coordinate geometry and completely prevents coordination and subsequent reduction of CO_2. Contrary to this, the π-bonding in the anions $[Re(CO)_3(\alpha\text{-diimine})]^-$ (α-diimine = bpy, iPr-DAB) was shown to be significantly less delocalized[14,17]. The electrophilic attack of CO_2 at the Re center in $[ReCO)_3(bpy)]^-$ is therefore possible, being the initial step in the mechanism of the efficient electrocatalytic CO_2 reduction with this anion[11,12]. As previously shown[22], the reduction pathway of the investigated complex $[Ru(Cl)(SnPh_3)(CO)_2(iPr\text{-}DAB)]$ resembles more that of $[Mn(Br)(CO)_3(iPr\text{-}DAB)]$ rather than that of $[Re(Br)(CO)_3(iPr\text{-}DAB)]$.

Furthermore, both five-coordinate anions $[Mn(CO)_3(iPr\text{-}DAB)]^–$ and $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^–$ exhibit comparably strongly delocalized π-bonding over the {M(iPr-DAB)} moiety, as documented by their similar resonance Raman spectra and negligible tendency to coordinate Lewis bases[22]. However, these anions still differ in their reactivity towards CO_2. The occurence of the slow reaction of CO_2 with $[Ru(SnPh_3)(CO)_2(iPr\text{-}DAB)]^–$ may again be explained by a slightly less delocalized π-bonding as a result of a worse matching of the more diffused 4d valence orbitals on the Ru center with the frontier orbitals of iPr-DAB, involved in the σ- and π-bonding, as compared with the less expanded 3d-Mn center in the non-reactive anion $[Mn(CO)_3(iPr\text{-}DAB)]^–$.

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