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Preliminary communication

Redox properties of the carbyne, aminocarbyne and η^2-vinyl complexes *trans*-$[ReCl(LH)(dppe)_2][BF_4]$ (LH = CCH_2Bu^t, CCH_2Ph, CNH_2 or η^2-$C(CH_2Ph)CH_2$) and of their parent vinylidene, isocyanide and allene compounds

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Abstract

The redox properties of the carbyne-, aminocarbyne- and η^2-vinyl-(metallacyclopropene) complexes *trans*-$[ReCl(LH)(dppe)_2][BF_4]$ (**1**; LH = CCH_2R (R = Bu^t or Ph), CNH_2 and η^2-$C(CH_2Ph)CH_2$; dppe = $Ph_2PCH_2CH_2PPh_2$), as well as of their parent vinylidene, isocyanide and allene complexes, *trans*-$[ReClL(dppe)_2]$ (**2**; L = C=CHR, CNH or η^2-$CH_2{=}C{=}CHPh$), have been studied by cyclic voltammetry and controlled potential electrolysis in aprotic media. The results are interpreted in terms of anodically- or cathodically-induced β-dehydrogenation processes of complexes (**1**), to give the corresponding compounds (**2**) (in the oxidized or the neutral form), as well as of a reversible dissociation of the former into the latter, in a basic solvent. The electrochemical P_L ligand parameter has been estimated for all these ligands.

The extensive chemistry of carbene and carbyne complexes [1] has involved very few studies of redox properties [2–9], in spite of the promising redox-induced chemistry of their multiple metal–carbon bonded ligands. Only a small number of examples are known, involving either cathodically-induced reactions of these ligands (such as, conformation changes [7] or protonation [8]) or anodic processes with coupled chemical reactions (e.g., vinylidene insertion into a metal–nitrogen bond [9]).

We outline below the results of an explanation of the redox behaviour of some rhenium complexes with a variety of multiple metal–carbon bonded ligands and attempt to obtain information about the net electron-acceptor/donor properties of the latter and on their activation by electron transfer.

In continuation of our interest in the activation of unsaturated carbon species by electron-rich metal sites, we have obtained series of isocyanide and alkyne-derived complexes of the type *trans*-[ReClL(dppe)$_2$] (**2**: L = CNR (R = H [10], alkyl or aryl [11]), =C=CHR (vinylidene, R = alkyl or aryl) [12] or η^2-CH$_2$$\doteq$C=CHPh (phenylallene) [13]). In these complexes, the organic ligand is activated towards β-protonation to give the corresponding aminocarbyne- [10,14], carbyne- [15] or η^2-vinyl-(metallacyclopropene) [16] species *trans*-[ReCl(LH)(dppe)$_2$]$^+$ (**1**: LH = CNHR, ≡CCH$_2$R or –CH$_2$C(CH$_2$Ph)= (denoted as η^2-C(CH$_2$Ph)CH$_2$), respectively). The redox properties of the isocyanide complexes **2** (R = alkyl or aryl) have already been described [11] and now we report a preliminary electrochemical study (by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), at a Pt electrode, in 0.2 *M* [Bu$_4$N][BF$_4$]/THF (NCMe or CH$_2$Cl$_2$)) of the other types of complexes in which the organic ligand contains at least one labile hydrogen atom in the β-position (relative to the metal).

All the neutral complexes **2** undergo, in CV, a single-electron reversible oxidation (${}^{\rm I}E_{1/2}^{\rm ox} = -0.26$ (L = CCHBu^t), -0.16 (L = CCHPh), -0.03 (L = η^2-CH$_2$$\doteq$C=CHPh) or $+0.36$ V (L = CNH) vs. SCE), which is followed by an irreversible anodic process, at a higher potential (${}^{\rm II}E_{\rm p}^{\rm ox}$ ca. 1.0 V (L = CCHBu^t, CCHPh or η^2-CH$_2$$\doteq$C=CHPh) or 1.74 V (detected in NCMe, for L = CNH)]. The low ${}^{\rm I}E_{1/2}^{\rm ox}$ values observed for these complexes are in agreement with the known [11] high electron-richness of the {ReCl(dppe)$_2$} centre.

As expected, the cationic complexes **1** exhibit anodic processes at considerably higher potentials. In fact, the carbyne complexes **1** (LH = CCH$_2$Ph or CCH$_2$Bu^t), in NCMe, show a reversible one-electron oxidation in CV at $E_{1/2}^{\rm ox} = 1.60$ or 1.56 V vs. SCE, respectively, whereas irreversible anodic processes are observed for the aminocarbyne or the η^2-vinyl compounds **1** (LH = CNH$_2$ or η^2-C(CH$_2$Ph)CH$_2$,. at $E_{\rm p/2}^{\rm ox} = 0.90$ or 1.34 V, respectively.

In terms of their net electron π-acceptor/σ-donor character, the organic LH and L ligands (the estimated values for the $P_{\rm L}$ ligand parameter of which are given in parentheses) * can be ordered in the following way: CCH$_2$Ph ($P_{\rm L} = 0.27$ V) $\gtrsim$ CCH$_2$Bu^t (0.26 V) > η^2-C(CH$_2$Ph)CH$_2$ (0.22 V) > CNH$_2$ (0.09 V) > CNH (-0.09 V) > η^2-CH$_2$$\doteq$C=CHPh ($-0.21$ V) > C=CHPh (-0.25 V) > C=CHBu^t (-0.28 V). The carbyne ligands are the best net π-electron acceptors, being (together with the η^2-vinyl and the aminocarbyne) even stronger than carbonyl ($P_{\rm L} = 0$); however, they are not as strong as acceptors as NO$^+$ ($P_{\rm L} = 1.40$ [17]). In contrast, the vinylidenes (followed by phenylallene) are the poorest net electron acceptor ligands; nevertheless, at the strong π-electron releasing (ReCl(dppe)$_2$) site they appear to behave as much better acceptors than the related ligating carbenes CXY (X = OR, SR or NRR′; Y = alkyl, aryl, etc.) **, at the much weaker π-donor (Cr(CO)$_5$) centre. As

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* The oxidation potential of the first anodic wave for complexes **1** and **2** allowed us to evaluate the net electron π-acceptor/σ-donor character of ligands LH and L, as measured by the $P_{\rm L}$ ligand parameter, which was estimated by applying eq. 1 [17] (or the analogous one where $E_{p/2}^{\rm ox}$ replaces $E_{1/2}^{\rm ox}$ for the irreversible processes) and the known [11] value of the electron-richness ($E_{\rm s}$ 0.68 V) taking account of polarisability ($\beta = 3.4$) of the binding metal site {M$_{\rm s}$} = {ReCl(dppe)$_2$}.

$$E_{1/2}^{\rm ox}[{\rm M_sL}] = E_{\rm s} + \beta \cdot P_{\rm L} \qquad (1)$$

** By considering eq. 2 [17] (which defines $P_{\rm L}$) and taking data from the literature [2], one can estimate $P_{\rm L}$ values for =CXY carbenes at the (Cr(CO)$_5$) site ($P_{\rm L}$(CXY) -0.60 to ca. -0.8 V) which are much more negative than those obtained for vinylidenes at the Re$^{\rm I}$ centre.

$$P_{\rm L} = E_{1/2}^{\rm ox}[{\rm Cr(CO)_5L}] - E_{1/2}^{\rm ox}[{\rm Cr(CO)_6}] \qquad (2)$$

expected, the isocyanide CNH is a slightly weaker net electron donor than CNMe, which, at the same Re centre, is known [11,18] to have P_L −0.17 V.

In solution (mainly in THF, which is considerably basic) complexes **1** undergo a little dissociation (with proton loss) to the corresponding neutral compounds **2**, which are fully generated on addition of NEt_3 (for **1**, LH = CNH_2 or η^2-$C(CH_2Ph)CH_2$) or potassium tri(sec-butyl) borohydride, $KB[CH(Me)Et]_3H$, (for **1**, LH = η^2-$C(CH_2Ph)CH_2$ or CCH_2R). Complexes **2** are also formed upon cathodic reduction of solutions of complexes **1** (e.g., at ca. −0.7 V for **1** (LH = CNH_2) with liberation of H_2, which was detected by gas-liquid chromatography).

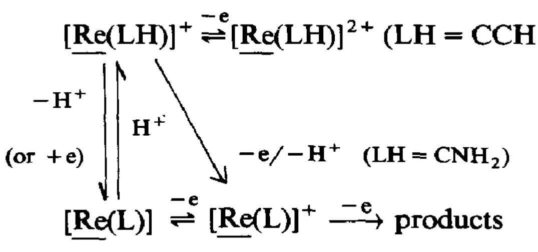
Moreover, as a result of the single-electron anodic oxidation of the aminocarbyne complex **1** (LH = CNH_2), proton loss occurs to give the isocyanide compound **2** (L = CNH) in the oxidized (+1) form. Such a type of anodic process, involving the expected enhancement of acid strength leading to β-proton elimination, conceivably may also occur with the η^2-vinyl complex **1** (LH = η^2-$C(CH_2Ph)CH_2$), but this could not be confirmed in view of its higher anodic potential relative to that of the irreversible oxidation process of the presumable oxidized allene product. A possibly related chemical reaction is known for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNHMe)]^+$ which, on treatment with Ag^+ gives $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]^+$, although the authors [19] suggest the involvement of the liberated H^+ as an oxidant.

The results obtained in the present study (except the anodic behaviour of the η^2-vinyl complex) are summarized in Scheme 1 where $\underline{Re}$ represents the $(ReCl(dppe)_2)$ site.

The anodically- or cathodically-induced formation of complexes **2** (in the oxidized or the neutral form, respectively) from the corresponding compounds **1** was recognized by CV, which allowed detection of the characteristic redox waves of the products **2** in the subsequent sweeps. The results were confirmed by CPE, followed in some cases by isolation of the products; the course of the electrolyses was monitored by CV. The reversibility of the chemical **1**-**2** conversion (deprotonation-protonation reactions) was also demonstrated by CV experiments.

Within the three types of multiple metal–carbon bonded species in complexes **1**, the carbyne ligands CCH_2R appear to be not only the strongest π-electron acceptors but also the most stable towards redox induced β-deprotonation. In contrast, the aminocarbyne ligand CNH_2 seems to behave as the weakest π-acceptor, and to exhibit the strongest protic acid character.

Although ligand deprotonation resulting from anodic oxidation [20] and H_2 evolution from cathodic reduction of a coordination compound [21] are known reactions in electrochemistry of organometallic compounds, to our knowledge the



Scheme 1. Redox processes and interconversion of complexes **1** (LH = CCH_2R, CNH_2 or η^2-$C(CH_2Ph)CH_2$) and **2** (L = CCHR, CNH or η^2-$CH_2{=}C{=}CHPh$). ($\underline{Re}$ stands for $(ReCl(dppe)_2)$). The anodic process for **1** (Lh = η^2-$C(CH_2Ph)CH_2$) is not included.

present study provides the first examples of such types of reactions for carbyne, aminocarbyne or η^2-vinyl complexes.

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