Fig.5 Shift of the half-wave potential ($\Delta E_{1/2}$) vs log [caffeine] for the Cu(I)=Cu(0) reduction.

It should be kept in mind that these values of the stability constants and ligand numbers were calculated for caffeine concentrations between 10^{-2}M and 10^{-1}M. At lower caffeine concentrations in the electrolyte solutions used the variations of half-wave potentials are very small, which may probably indicate the existence of a series of complexes.

Comparing these results with those obtained in 0.25M sulphuric acid, we notice that the ligand numbers have changed from p=1 to p=2 and q=2 to q=1 and that the stability constants of the complexes formed are higher, namely, β^{2+} is about 10 times greater and β^+ is about 50 times greater.

REFERENCES

1 - J. E. Simão and H. M. Tavares, XI° Encontro da Soc. Port. de Química, Lisboa, 1988.

2 - A. M. Bond, "Modern Polarographic Methods in Analytical Chemistry", Marcel Dekker, Inc, New York, 1980, p. 250.

3 - Subrahmanya R. S., "Advances in Polarography", Pergamon Press, Oxford, 1960, p. 674.

ELECTRON-TRANSFER REACTIONS IN VINYLIDENE AND DERIVED CARBYNE COMPLEXES OF RHENIUM

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ABSTRACT

The vinylidene complexes trans-[ReCl(=C=CHR)(dppe)$_2$] (R=Bu^t, C$_6$H$_5$, C$_6$H$_4$Me-4 or CO$_2$Me; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and the derived carbyne compounds trans-[ReCl($\equiv$C-CH$_2$R)(dppe)$_2$]$^+$ undergo, by cyclic voltammetry, in tetrahydrofuran (or acetonitrile), at a Pt electrode, a single-electron reversible oxidation. The electrochemical P$_L$ ligand parameter has been estimated for these ligands.

The carbyne complexes are obtained by protonation of the homologous vinylidene species, but the latter are regenerated upon cathodic reduction of the former.

RESULTS AND DISCUSSION

Complexes with multiple metal-carbon bonds are intermediates in important organic syntheses and their reactivity has been widely studied. However, their electrochemical behaviour is nearly fully unexplored [1].

Therefore, we have initiated the electrochemical study of series of such type of complexes [1] and now we report the electron-transfer and coupled chemical reactions we have observed for the vinylidene complexes trans-[ReCl(C=CHR)(dppe)$_2$] (R=Bu^t, C$_6$H$_5$, C$_6$H$_4$Me-4 or CO$_2$Me; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and the carbyne compounds trans-[ReCl($\equiv$C-CH$_2$R)(dppe)$_2$]$^+$ which are derived from protonation of the former.

These compounds undergo, by cyclic voltammetry (in tetrahydrofuran or acetonitrile, at a Pt electrode), a single-electron reversible (or quasi-reversible) oxidation.

For the vinylidene complexes, $E^{ox}_{1/2}$ falls in the -0.26 to 0.38 V range, whereas the carbyne species are oxidized at a much higher potential ($E^{ox}_{1/2}$ = 1.56 to 1.63V vs. s.c.e.), in agreement with a stronger net electron acceptor character of the carbyne compared with the vinylidene ligands.

For these ligands, the P_L ligand parameter has been estimated from equation (2) derived from the application of equation (1) [2] to their complexes with the {ReCl(dppe)$_2$} metal centre with Known [3] values of the electron-richness (E_s=0.68 V) and polarisability (β=3.4) parameters.

$$E^{ox}_{1/2} [M_sL] = E_s + \beta.P_L \qquad (1)$$

$$E^{ox}_{1/2} [ReClL(dppe)_2] - E_s\{ReCl(dppe)_2\}$$

2

$$E^{ox}_{1/2} [M_sL] = E_s + \beta.P_L \qquad (1)$$

$$P_L = \frac{E^{ox}_{1/2} [ReClL(dppe)_2] - E_s\{ReCl(dppe)_2\}}{\beta\{ReCl(dppe)_2\}} \qquad (2)$$

By comparing the estimated values of P_L (in the ranges -0.28 to -0.01 and 0.26 to 0.28 V for the vinylidenes and carbynes, respectively), also with those known for related ligands, e.g., isocyanides [3] and CO, these C-bonded ligands may be ordered as follows, according to their net electron π-acceptor minus σ-donor character:
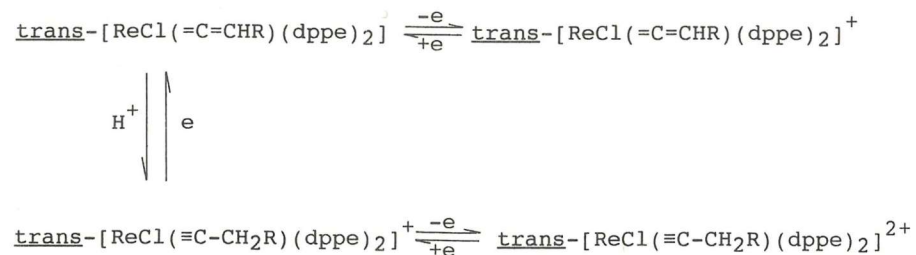
$$\equiv C-CH_2CO_2R \gtrsim \equiv C-CH_2R > CO >$$
$$= C=CHCO_2R > CNR > =C=CHR$$
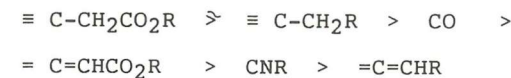
Within the vinylidene complexes, the redox potential commonly increases with the Hammett's σ or the Taft's σ^* constant of the organic group R, although for the carbyne complexes, with an sp^3 β-C-atom, $E^{ox}_{1/2}$ is almost unaffected by the substituent.

As indicated above, the carbyne complexes are formed by β-protonation of the corresponding vinylidene compounds. However, the latter can be regenerated electrochemically, by cathodic reduction of solutions of the former which leads to their deprotonation.

Moreover, as shown by cyclic voltammetry, the carbyne complexes, in a basic solvent (such as tetrahydrofuran) undergo a slight dissociation to the corresponding vinylidene species.

These reactions are summarized in Scheme 1.

$$\text{trans-}[\text{ReCl}(=\text{C}=\text{CHR})(\text{dppe})_2] \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{trans-}[\text{ReCl}(=\text{C}=\text{CHR})(\text{dppe})_2]^+$$

$$\text{trans-}[\text{ReCl}(\equiv\text{C}-\text{CH}_2\text{R})(\text{dppe})_2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{trans-}[\text{ReCl}(\equiv\text{C}-\text{CH}_2\text{R})(\text{dppe})_2]^{2+}$$

Scheme 1 - Redox behaviour and interconversion of the vinylidene complexes trans-[ReCl(=C=CHR)(dppe)2] and the derived carbyne compounds trans-[ReCl(≡C-CH2R)(dppe)2]+.

ACKNOWLEDGMENTS

REFERENCES

[1] M.A.N.D.A. Lemos and A.J.L. Pombeiro, J. Organometal. Chem., 1988, 356, C79, and references therein.

[2] J. Chatt, C.T. Kan, G.J. Leigh, C.J. Pickett and D.R. Stanley, J. Chem. Soc., Dalton Trans., 1980, 2032.

[3] A.J.L. Pombeiro, C.J. Pickett and R.L. Richards, J. Organometal. Chem., 1982, 224, 285; A.J.L. Pombeiro, Inorg. Chim. Acta, 1985, 103, 95.

REDOX PROPERTIES OF THE NITRILE COMPLEXES

trans-[ReCl(NCR)(Ph2PCH2CH2PPh2)2]
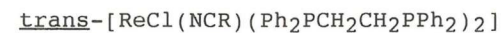
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Abstract

The nitrile complexes trans-[ReCl(NCR)(dppe)2] ($\underline{1}$;R=alkyl or aryl, dppe = Ph2PCH2CH2PPh2) undergo, in tetrahydrofuran, by cyclic voltammetry and at a Pt electrode, two successive single-electron reversible (or quasi-reversible) oxidations and, from the values of the half-wave oxidation potential ($E^{ox}_{1/2}$) of the first anodic wave, the electrochemical P_L ligand parameter was estimated for the nitrile ligands indicating that they behave as better net electron donors than isocyanides, dinitrogen or carbonyl ligands. For the aromatic nitrile complexes, $E^{ox}_{1/2}$ is shown to vary linearly with the Hammett's σ_p constant of the phenyl substituent.