Rhenium(I) di- and tri-carbonyl compounds of polypyridyl-like ligands: electrochemical reactions of *fac*-[Re(CO)$_3$(dpk)Cl] (dpk = di-2-pyridyl ketone) with electrophiles and Group I and II metal ions

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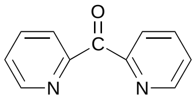
In contrast to the facile formation of *fac*-[Re(CO)$_3$(dpk)Cl] **1** from the reaction between [Re(CO)$_5$Cl] and dpk [(C$_5$H$_4$N)$_2$C(O)], in refluxing toluene, [Re(CO)$_5$Cl] was recovered unchanged when di-2-pyridylamine, dpa [(C$_5$H$_4$N)$_2$NH], was allowed to react with [Re(CO)$_5$Cl] under a variety of conditions. However, a mixture of [Re(CO)$_5$Cl] and PPh$_3$ in refluxing toluene followed by a CH$_2$Cl$_2$ solution of dpa gave *cis*-[Re(CO)$_2$(PPh$_3$)(dpa)Cl]. The intermediate involved appears to be a general synthon for the binding of the Re^{I}(CO)$_2$(PPh$_3$)Cl chromophore to a variety of bi- and mono-dentate nitrogen-donor ligands and has been utilized to isolate *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl]. Nucleophilic addition of water at the carbonylic carbon atom of co-ordinated dpk in **1** and *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] resulted in the hydration of the keto group and formation of *fac*-[Re(CO)$_3$-{(C$_5$H$_4$N)$_2$C(O)(OH)}] and *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}]. The compounds isolated exhibit rich electrochemical and photochemical properties and the potential application of *fac*-[Re(CO)$_3$(dpk)Cl] as an electrochemical sensor for electrophiles and Group I and II metal ions is demonstrated.

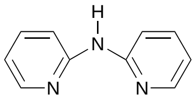
Metal compounds containing polypyridyl-like ligands of the type (C$_5$H$_4$N)$_2$X (X = π-donor or -acceptor ligand) are of current interest for their rich physicochemical properties, diverse reactivity patterns, and potential applications in many important chemical processes.[1–10] Our interest in the chemistry of polypyridyl-like compounds such as di-2-pyridyl ketone (dpk) and di-2-pyridylamine (dpa) was aroused because of their ability to undergo a variety of interesting reactions upon binding to transition metals and we were intrigued to explore how variations in the backbone of these ligands affect their reactivity and the physicochemical properties of their compounds compared to those containing 2,2′-bipyridine (bipy).

Di-2-pyridyl ketone has been reported to form stable compounds with a variety of metal ions in a bidentate N,N- or a tridentate N,O,N-co-ordination mode.[9–18] In the former mode the back π bonding is enhanced as a result of delocalization of electrons through the pyridine rings and the oxygen atom of the keto group. Such delocalization of electron density provides a span of charged species from a single neutral precursor and a low-energy M→L charge-transfer pathway which are important in electro- and photo-catalysis.[9] The three-co-ordination mode results from a nucleophilic attack at the carbonyl moiety and leads to the loss of π-accepting ability of the ligand and an increase in electron density around the metal centre.[2–5] A variety of transition-metal compounds containing di-2-pyridylamine has been reported and the acidity of the amine group has been utilized to graft some of these compounds into solid supports.[1,19,20]

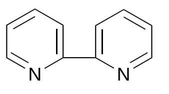
Although rhenium compounds containing polypyridyl ligands have been extensively studied and their potential applications as catalysts, sensors, sensitizers for energy and electron transfer and photo probes for DNA have been demonstrated, rhenium compounds containing polypyridyl-like ligands are scarce.[21–34] Only two reports have appeared on the synthesis of high-valent rhenium(V) compounds containing a tridentate N,O,N-donor ligand (C$_5$H$_4$N)$_2$C(O)(OR) (R = H or alkyl) which resulted from nucleophilic addition of water or alcohol at the ketonic carbon atom of di-2-pyridyl ketone during these reactions.[17,18] We recently described the electrochemical reactions of CO$_2$ with the first rhenium(I)-tricarbonyl compound containing di-2-pyridyl ketone *fac*-[Re(CO)$_3$(dpk)Cl].[35] These reactions are solvent dependent, controlled by the rate of diffusion of electroactive species from the electrode surface. Fast diffusion due to solvent or scan-rate variations inhibits the carboxylation of the carbonylic carbon atom of the radical anion *fac*-[Re{(C$_5$H$_4$N)$_2$C(O)$^{\bullet -}$}(CO)$_3$Cl] leading to the generation of co-ordinatively unsaturated *fac*-[Re{(C$_5$H$_4$N)$_2${C(O)$^{\bullet -}$}(CO)$_3$] which binds CO$_2$ to form *fac*-[Re{(C$_5$H$_4$N)$_2$C(O)$^{\bullet -}$}(CO)$_3$-(CO$_2$)]. Slow diffusion facilitates the carboxylation of the carbonylic carbon atom of *fac*-[Re{(C$_5$H$_4$N)$_2$C(O)}(CO)$_3$Cl] to form *fac*-[Re{(C$_5$H$_4$N)$_2$C(O$^-$)(CO$_2^{\bullet}$)}(CO)$_3$] which undergoes a second electron transfer followed by chemical steps leading to the formation of *fac*-[Re{(C$_5$H$_4$N)$_2$C(O)(CO$_2$H)}(CO)$_3$]. Here, we report the isolation and physicochemical properties of the first series of tri- and di-carbonyl compounds of Re^{I} that contain di-2-pyridyl ketone and di-2-pyridylamine along with the electrochemical reactions of *fac*-[Re(CO)$_3$(dpk)Cl] with methyl chloroformate and Group I and II metal ions.



dpk



dpa



bipy

Experimental

Reagents and reaction procedures

Solvents were reagent grade and thoroughly deoxygenated prior to use. All other reagents were obtained from commercial sources and used without further purification. The compound *fac*-[Re(CO)$_3$(dpk)Cl] **1** was prepared as described previously.[35] All reactions were performed under a nitrogen atmosphere using standard vacuum-line techniques.

Preparations

(*a*) *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] 2. A quantity of *fac*-[Re(CO)$_3$(dpk)Cl] (200 mg, 0.42 mmol) was suspended in ethanol (50 cm^3), water (0.5 cm^3) was added and the mixture was refluxed for 24 h. It was then allowed to cool to room temperature. An off-yellow solid was filtered off, washed with hexane, diethyl ether and dried; yield 180 mg, 0.38 mmol (90%) (Found: C, 35.8; H, 1.9; N, 5.9. $C_{14}H_9N_2O_5Re$ requires C, 35.65; H, 1.95; N, 6.05%). IR (KBr): ν(C≡O) 2019, 1927, 1866, ν(py) 1608, ν(C–O) 1240, ν(OH) ≈ 3050 cm^{-1}. ^1H NMR $[(CD_3)_2SO]$: δ 8.82 (d), 8.08 (t), 7.70 (s) and 7.40 (t).

When a quantity of *fac*-$[Re(CO)_3(dpk)Cl]$ was allowed to reflux in absolute ethanol or ethanol solution containing a few drops of concentrated hydrochloric acid for an extended period no colour change was observed and *fac*-$[Re(CO)_3(dpk)Cl]$ was recovered unchanged. The identity of the product was confirmed from its electrochemical and spectroscopic properties. The IR spectrum (KBr pellet) of the orange-yellow solid showed the stretching mode of the ketonic group ν(C=O) at 1680 cm^{-1}.

(*b*) *cis*-$[Re(CO)_2(PPh_3)(dpk)Cl]$ 3. A mixture of $[Re(CO)_5Cl]$ (150 mg, 0.42 mmol), PPh_3 (250 mg, 0.95 mmol) and toluene (80 cm^3) was refluxed for 24 h. To the hot orange solution a quantity of dpk (220 mg, 1.21 mmol) dissolved in CH_2Cl_2 (5 cm^3) was added. The reaction mixture changed to brown instantly and was refluxed for 72 h. It was then reduced in volume to ≈10 cm^3 and pentane added. A red-brown solid was isolated, chromatographed on an alumina column (CH_2Cl_2 as eluent) and recrystallized from CH_2Cl_2–diethyl ether. A red-brown solid was filtered off, washed with hexane, diethyl ether and dried; yield 160 mg, 0.22 mmol (52%) (Found: C, 50.8; H, 3.25; N, 3.75. $C_{31}H_{23}ClN_2O_3PRe$ requires C, 51.4; H, 3.2; N, 3.85%). IR (KBr): ν(C≡O) 1931, 1852, ν(C=O) 1692, ν(Ph) 1633, ν(py) 1610 cm^{-1}. ^1H NMR $[(CD_3)_2SO]$: δ 9.18 (d), 8.22 (d), 8.07 (t), 7.50–7.25 (m) and 7.02 (t).

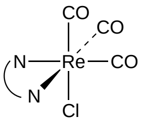
(*c*) *cis*-$[Re(CO)_2(PPh_3)\{(C_5H_4N)_2C(O)(OH)\}]$ 4. A quantity of *cis*-$[Re(CO)_2(PPh_3)(dpk)Cl]$ (50 mg, 0.07 mmol) was suspended in ethanol (35 cm^3) and water (0.5 cm^3) was added. The purple mixture slowly changed to yellow and was refluxed for 5 h. The resulting bright yellow solution was reduced in volume to ≈10 cm^3 and a microcrystalline yellow solid was filtered off, washed with hexane, diethyl ether and dried; yield 20 mg, 0.03 mmol (43%) (Found: C, 52.45; H, 3.8; N, 3.65. $C_{31}H_{24}N_2O_4PRe$ requires C, 52.75; H, 3.45; N, 3.95%). IR (KBr): ν(C≡O) 1911, 1828, ν(Ph) 1637, ν(py) 1619, ν(C–O) 1234 cm^{-1}.

(*d*) *cis*-$[Re(CO)_2(PPh_3)(dpa)Cl]$ 5. A mixture of $[Re(CO)_5Cl]$ (200 mg, 0.58 mmol), PPh_3 (360 mg, 1.40 mmol) and toluene (80 cm^3) was refluxed for 24 h. To the hot orange reaction mixture was added dpa (225 mg, 1.0 mmol) dissolved in CH_2Cl_2 (10 cm^3) and the mixture was allowed to reflux for 20 h. The resulting reaction mixture was cooled to room temperature and the solution reduced in volume to ≈20 cm^3. A bright yellow solid was filtered off, washed with hexane, diethyl ether and dried; yield 240 mg (86%) (Found: C, 50.65; H, 3.45; N, 5.9. $C_{30}H_{24}ClN_3O_3Re$ requires C, 50.65; H, 3.4; N, 5.9%). IR (KBr): ν(C≡O) 1900, 1820, ν(Ph) 1625, ν(py) 1580, ν(NH) 3358 cm^{-1}. ^1H NMR $[(CD_3)_2SO]$: δ 9.9 (s), 8.51 (d), 7.67 (t), 7.12 (m), 7.06 (t) and 6.72 (d).

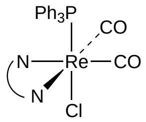
Electrochemical reactions

(*a*) Methyl chloroformate with *fac*-$[Re(CO)_3(dpk)Cl]$. The electrochemical responses in the presence/absence of methyl chloroformate or CO_2 were measured for 1–10 mmol dm^{-3} MeCN or dimethylformamide (dmf) solutions of *fac*-$[Re(CO)_3(dpk)Cl]$ in the presence of 0.1 mol dm^{-3} $NBu^n_4PF_6$.

(*b*) Group I and II metal ions with *fac*-$[Re(CO)_3(dpk)Cl]$. The electrochemical responses in the absence and presence of stoichiometric amounts of the metal ions were measured for 1–10 mmol dm^{-3} MeCN or dmf solutions of *fac*-$[Re(CO)_3(dpk)Cl]$ in the presence of 0.1 mol dm^{-3} $NBu^n_4PF_6$.



fac-$[Re(CO)_3(L–L)Cl]$



cis-$[Re(CO)_2(PPh_3)(L–L)Cl]$

Physical measurements

Electronic absorption spectra were recorded on an HP-8452A spectrophotometer. Solution ^1H NMR spectra were recorded on a Bruker ACE 200-MHz Fourier-transform spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. Electrochemical measurements were made in solutions of acetonitrile or dimethylformamide with 0.1 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. A glassy carbon disc (0.07 cm^2) was used as a working electrode. All potentials were referenced to the saturated sodium chloride calomel electrode (SSCE) at room temperature and are uncorrected for junction potentials. The reversible one-electron couple of ferrocene was employed as an internal standard to determine the number of electrons and reversibility of the electrochemical waves. Voltammetric experiments were performed with the use of a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat and model 276 interface in conjunction with a 286 personal computer. Data were acquired with the use of the EG&G PARC HEADSTART program and manipulated using the Microsoft EXCEL program. A PAR 179 digital coulometer was used in conjunction with a PAR 173 galvanostat/potentiostat for coulometry experiments. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 1600 Series FT-IR spectrometer, emission spectra on an SLM Aminco Booman Series 2, luminescence spectrometer.

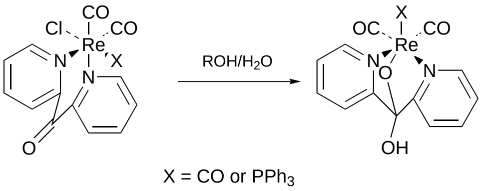
Elemental microanalyses were performed by MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, UK.

Results and Discussion

Preparation of *cis*-$[Re(CO)_2(PPh_3)(L–L)Cl]$ (L–L = dpk or dpa)

When dpa was allowed to react with $[Re(CO)_5Cl]$ in high-boiling solvents or in the solid state as a melt it was recovered unchanged. These reactions are in contrast to the facile reaction observed between $[Re(CO)_5Cl]$ and dpk in refluxing toluene to form *fac*-$[Re(CO)_3(dpk)Cl]$.[35] The failure to incorporate dpa into rhenium(I) carbonyl moieties directly from $[Re(CO)_5Cl]$ prompted us to search for alternative precursors. The PPh_3 ligands in *trans*-$[Re(CO)_3(PPh_3)_2Cl]$ are substitution labile and the compound has been used as a precursor for the synthesis of a variety of rhenium(I) carbonyl compounds.[36] When a mixture of $[Re(CO)_5Cl]$ and ≈2 equivalents of PPh_3 was refluxed in toluene for 24 h an orange solution developed. This was allowed to cool to room temperature, changing to yellow, and on refluxing again it became orange again. The addition of a stoichiometric amount of dpa dissolved in CH_2Cl_2 to the hot orange mixture led to the quantitative formation of bright yellow *cis*-$[Re(CO)_2(PPh_3)(dpa)Cl]$. Following an identical procedure *cis*-$[Re(CO)_2(PPh_3)(dpk)Cl]$ was isolated in good yield when dpk was used in place of dpa.

However, when 2,2′-bipyridine was used in place of dpa a mixture of *fac*-$[Re(CO)_3(bipy)Cl]$, *cis*-$[Re(CO)_2(PPh_3)(bipy)Cl]$ and other products was obtained. The identity of this mixture, and the solution chemistry of *cis*-$[Re(CO)_2(PPh_3)(bipy)Cl]$, are currently under investigation.[37] The isolation of the rhenium(I) dicarbonyl compounds marks the first instance of a series of dicarbonylchlororhenium(I) compounds containing a bidentate nitrogen ligand and are rare examples of rhenium(I) dicarbonyl compounds containing bidentate nitrogen ligands. The known rhenium(I) dicarbonyl salts containing polypyridyl ligands are those reported by Casper *et al.*[38] *trans*,



Scheme 1 X = CO or PPh$_3$

cis-[Re(CO)$_2$(PMe$_2$Ph)$_2$(bipy)]PF$_6$, *trans,cis*-[Re(CO)$_2$(PPh$_3$)$_2$(bipy)]PF$_6$ and *cis*-[Re(CO)$_2$(bipy)$_2$]PF$_6$. These salts were prepared from the reaction between *fac*-[Re$^{\text{I}}$(CO)$_3$(bipy)Z]^n (Z = monodentate ligand; $n = 0$ or $+1$) with an excess of Z in refluxing ethylene glycol or from direct carbonylation of *trans,cis*-[Re(PMe$_2$Ph)$_2$(bipy)Cl$_2$]PF$_6$ using formic acid.

The intermediate involved in the synthesis of the *cis*-dicarbonylchlororhenium(I) compounds appears to be a versatile synthon for the binding of the Re$^{\text{I}}$(CO)$_2$(PPh$_3$)Cl moiety to a variety of bi- and mono-dentate ligands.[37] Its identity and reactions with nucleobases and other nitrogen-donor ligands are currently under investigation.

Nucleophilic addition of water at the ketonic carbon atom of co-ordinated di-2-pyridyl ketone in *fac*-[Re(CO)$_3$(dpk)Cl] and *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl]

When a sample of *fac*-[Re(CO)$_3$(dpk)Cl] or *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] was suspended in an alcoholic solvent containing a trace amount of water *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] or *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] was isolated (Scheme 1). In the presence of a trace amount of concentrated HCl the starting material was recovered unchanged. This marks the first instance where a pair of rhenium compounds containing non-hydrated N,N-bidentate di-2-pyridyl ketone and hydrated N,O,N-tridentate hydroxydi-2-pyridylmethoxide were isolated. The hydration of co-ordinated di-2-pyridyl ketone has been observed in a variety of molecular systems and provides an interesting pathway for attaching these systems to insoluble supports.[2–7] High-valent rhenium(V)– and technetium(V)–oxo compounds containing hydrated di-2-pyridyl ketone have recently been reported and there has been no evidence for the isolation of such compounds containing co-ordinated di-2-pyridyl ketone in the bidentate mode.[17,18]

Spectroscopic properties. The CO stretching frequencies of the compounds are given in Table 1 and Fig. 1 shows the infrared spectra of *fac*-[Re(CO)$_3$(dpk)Cl], *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] and *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl]. Three strong bands appeared in the ν(C≡O) stretching region of the tricarbonyl compounds similar to those reported for the carbonyl stretching modes of *fac*-[Re(CO)$_3$(bipy)Cl] and other *fac*-tricarbonylhalogenorhenium(I) compounds containing α-diimine ligands and confirm the assigned *fac* geometry.[24–26] In the spectra of the dicarbonyl compounds two strong bands appeared in the ν(C≡O) stretching region due to the symmetrical and antisymmetrical stretching vibrations of the two mutually *cis* CO ligands. These bands are similar to those reported for other *cis*-dicarbonylrhenium(I) compounds and consistent with the assigned *cis* geometry.[36–40] For example, the IR spectrum of [Re(CO)$_2${MeC(CH$_2$PPh$_2$)$_3$}]$^+$ shows two strong bands in the ν(C≡O) stretching region at 1948 and 1887 cm^{-1}.[36]

The N,N-co-ordinated dpk complexes, *fac*-[Re(CO)$_3$(dpk)Cl] and *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl], have their ketonic ν(C=O) stretching band and the combined ν(C=C) and ν(C=N) stretching modes of the pyridine rings shifted to higher energy (≈10–20 cm^{-1}) compared to free dpk. This is consistent with the decrease in electron density in the rings and in accord with results reported for a variety of transition-metal compounds containing dpk in a bidentate N,N-co-ordination mode.[11,12,16]

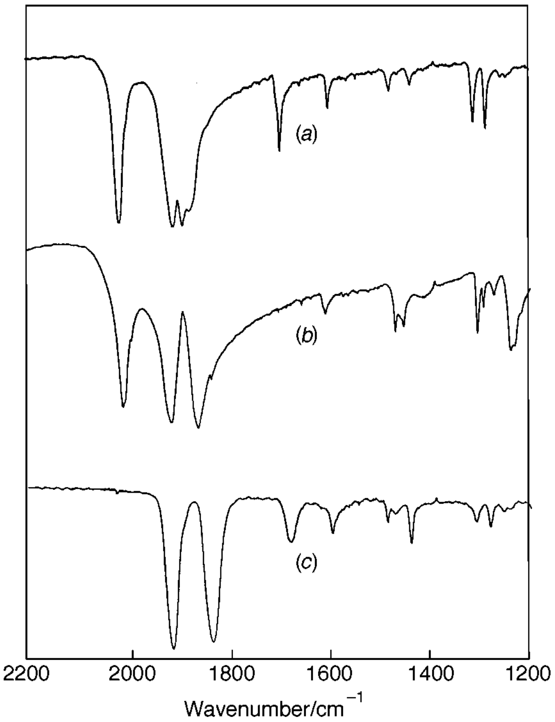


Fig. 1 Infrared spectra of (*a*) *fac*-[Re(CO)$_3$(dpk)Cl], (*b*) *cis*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] and (*c*) *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] in KBr pellets

Table 1 Infrared (KBr) CO stretching bands (cm^{-1})

Compound	ν(C≡O)
fac-[Re(CO)$_3$(dpk)Cl]^a	2020, 1913, 1893
fac-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}]^b	2019, 1927, 1866
cis-[Re(CO)$_2$(PPh$_3$)(dpk)Cl]^c	1930, 1852
cis-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}]^d	1911, 1828
cis-[Re(CO)$_2$(PPh$_3$)(dpa)Cl]	1900, 1820
fac-[Re(CO)$_3$(bipy)Cl][33]	2019, 1917, 1895
cis-[Re(CO)$_2$(PPh$_3$)(bipy)Cl][37]	1925, 1845
trans,cis-[Re(bipy)(PMe$_2$Ph)$_2$(CO)$_2$]PF$_6$[38]	1961, 1890
trans,cis-[Re(bipy)(PPh$_3$)$_2$(CO)$_2$]PF$_6$[38]	1966, 1894
trans,cis-[Re(bipy)$_2$(CO)$_2$]PF$_6$[38]	1922, 1853

^{a} ν(C=O) 1698 cm^{-1}. ^{b} ν(C–O) 1235 cm^{-1}. ^{c} ν(C=O) 1692 cm^{-1}. ^{d} ν(C–O) 1234 cm^{-1}.

For *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] and *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] in which the ketone group underwent nucleophilic addition by water the ketonic ν(CO) in the range 1690–1660 cm^{-1} disappeared, and the pyridine vibrations appeared at higher energy compared to those of the unhydrated precursors. Bands appeared at ≈1235 and ≈3400 cm^{-1} assigned to ν(C–O) and ν(OH) stretching modes, respectively. These results are consistent with those reported for a variety of transition-metal compounds in which the ketone group suffered hydrolysis.[13,15–18] In the spectrum of *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] a band appeared at 1637 cm^{-1} assigned to the ν(C=C) stretching vibrations of the phenyl group and confirms the presence of co-ordinated PPh$_3$.

In the IR spectrum of *cis*-[Re(CO)$_2$(PPh$_3$)(dpa)Cl] a sharp band appeared at 3330 cm^{-1} assigned to the ν(NH) stretching mode consistent with the presence of the NH group and the absence of hydrogen bonding. The ν(C≡O) stretching modes appeared at lower wavenumbers compared to those of *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] consistent with the stronger π-donor ability of dpa compared to dpk. The combined ν(C=C) and ν(C=N) pyridine vibrations appeared at higher wavenumbers than those observed for free dpa.

In the ^{1}H NMR spectra of these compounds a series of resonances were observed consistent with the presence of the

Table 2 Electronic absorption spectral data and electrochemical properties

Compound	Electronic absorption spectra,[a] λ/nm (ε/dm^3 mol^{-1} cm^{-1})	CV wave potentials,[b] *E*/V *vs.* SSCE
1 *fac*-[Re(CO)$_3$(dpk)Cl]	388 (3082), 284 (13 418), 232 (11 393)	−0.82, −1.32, −1.47
2 *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}]	380 (sh) (600), 310 (1900), 266 (3100), 240 (3240), 221 (sh) (5360), 200 (13 100)[c]	+1.3, −1.98 ($E_{p,c}$), −2.20 ($E_{p,c}$)
3 *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl]	472 (3556), 328 (5418), 270 (13 268), 234 (23 678)	+1.03, −0.99, −1.67 ($E_{p,c}$)
4 *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}]	410 (sh) (450), 356 (5980), 270 (9758), 252 (11 650), 230 (sh) (24 674)	+0.75, −2.17 ($E_{p,c}$)
5 *cis*-[Re(CO)$_2$(PPh$_3$)(dpa)Cl]	502 (4190), 356 (5100), 292 (7590), 232 (10 466)[d]	+1.65 ($E_{p,a}$), +0.88, −2.18 ($E_{p,c}$)
6 *fac*-[Re(CO)$_3$(bipy)Cl]	386 (4356), 294 (18 598), 242 (19 057)	−1.35, −1.71[29,e]

[a] Recorded on MeCN solutions. [b] Half-wave potentials (unless otherwise stated) recorded in 0.1 mol dm^{-3} NBu$^n_4$PF$_6$–dmf using a glassy carbon disc electrode (0.07 cm^2) at ν = 400 mV s^{-1}. [c] Recorded in CH$_2$Cl$_2$ solution. [d] Incompletely soluble. [e] In 0.1 mol dm^{-3} NBu$^n_4$PF$_6$–MeCN using a platinum-disc electrode at ν = 100 mV s^{-1}.

Table 3 Solvent dependence of the MLCT absorption maxima of *fac*-[Re(CO)$_3$(dpk)Cl] **1**, *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] **3** and *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] **4** at 298 K

	E_{MLCT}/kJ mol^{-1}			
Solvent	**1**	**3**	**4**	(π*)[42,43]
Triethylamine	300.61	251.35	318.20	0.14
Diethyl ether	305.21	253.48	323.36	0.27
Tetrahydrofuran	311.57	255.65	325.12	0.58
Dimethylformamide	319.90	261.12	332.34	0.88
Dimethyl sulfoxide	321.62	262.37	334.20	1.0
Carbon tetrachloride	291.81	246.18	326.00	0.29
Chloroform	302.13	250.03	329.60	0.58
Chlorobenzene	305.21	253.48	330.51	0.71
Methylene chloride	308.36	254.56	333.27	0.83
Mesitylene	302.13	252.41	323.36	0.41
Toluene	302.13	252.41	323.36	0.54
Benzene	302.13	252.41	326.90	0.59
Anisole	308.36	254.45	328.69	0.73
Pyridine	311.57	256.75	330.51	0.87

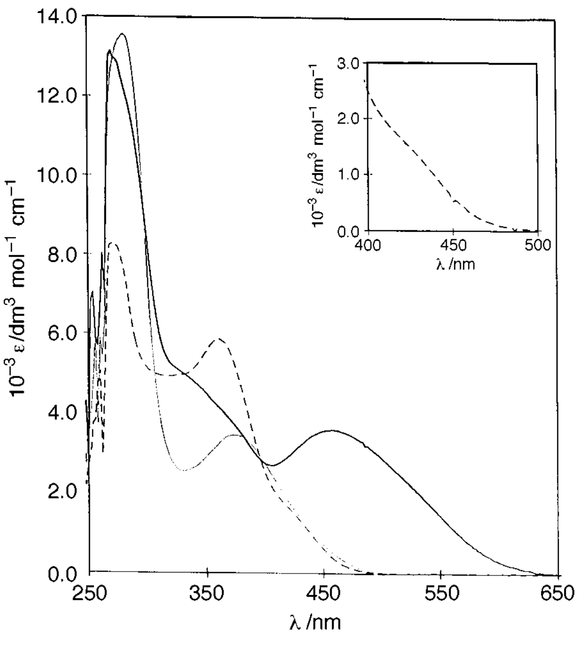


Fig. 2 Electronic absorption spectra of *fac*-[Re(CO)$_3$(dpk)Cl] (······), *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] (——) and *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] (------) in MeCN

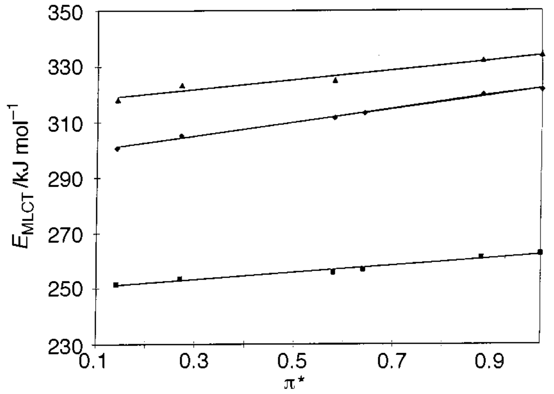


Fig. 3 Energies of MLCT absorption (E_{MLCT}) of (◆) *fac*-[Re(CO)$_3$(dpk)Cl], (▲) *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] and (■) *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] plotted against Taft's π* solvent values in non-chlorinated aliphatic solvents

ligands. Four sets of ring resonances appeared in the spectrum of each molecule pointing to the presence of a mirror plane of symmetry consistent with the assigned geometry.

The electronic absorption spectral properties of the compounds are summarized in Table 2 and Fig. 2 shows the spectra of *fac*-[Re(CO)$_3$(dpk)Cl], *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] and *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] measured in dmf. A low-energy absorption band assigned to a d_π(Re) $\longrightarrow$ π*(N–N) metal-to-ligand charge transfer (MLCT) transition and intense high-energy bands originating from ligand-to-metal charge-transfer (LMCT) transitions appeared in the spectra of these compounds. These features are similar to those reported for *fac*-[Re(CO)$_3$(bipy)Cl] and other rhenium(I)–diimine complexes of the type *fac*-[Re(CO)$_3$(L–L)Cl] (L–L = α-diimine ligand).[24–28] The dicarbonyl compounds have their d_π(Re) $\longrightarrow$ π* (MLCT) transitions red shifted compared to the tricarbonyl compounds due to the substitution of a CO ligand with PPh$_3$ which elevates the energy of the d orbitals and subsequently increases the π-back-bonding capacity of the co-ordinating diimines. This effect has been observed previously for a variety of low-valent metal carbonyl compounds containing α-diimine ligands.[28] The lowest absorption bands in these complexes exhibit a marked solvatochromic behaviour, a characteristic property of MLCT transitions.[41,42] The solvent dependence of the MLCT absorption maxima, E_{MLCT}, is given in Table 3 and plots of Taft's solvent-polarity scale,[42,43] π*, *vs.* E_{MLCT} for *fac*-[Re(CO)$_3$(dpk)Cl], *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] and *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] in non-chlorinated aliphatic solvents are shown in Fig. 3. Straight lines were obtained with slopes of 24.30, 17.30 and 12.70 for *fac*-[Re(CO)$_3$(dpk)Cl], *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}Cl] and *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl], respectively. The higher the value of the slope the higher is the sensitivity of the MLCT transition to solvent variation and points to a large increase in charge-transfer character of the transition in accord with the increase in energy gap between the highest occupied molecular orbital (HOMO, d_π orbital) and the lowest unoccupied molecular orbital (LUMO, π* orbital). The red shift observed in the spectra of these compounds in going from *fac*-[Re(CO)$_3$(dpk)Cl] to *cis*-[Re(CO)$_2$(PPh$_3$){(C$_5$H$_4$N)$_2$C(O)(OH)}] to *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] is consistent with the decrease in the HOMO − LUMO energy gap and the sensitivity of these transitions to solvent variations. The hydration of the keto group and the co-ordination of the oxo-anion increases the electron density at both centres and elevates the

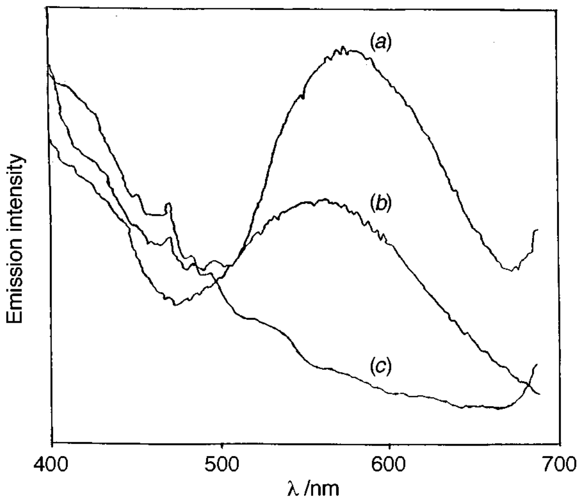
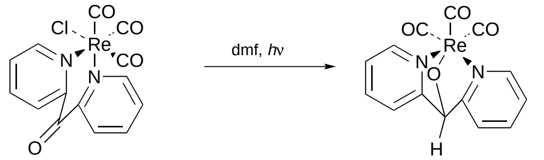


Fig. 4 Emission spectra of (*a*) *fac*-[Re(CO)$_3$(dpk)Cl] in the solid state, (*b*) *cis*-[Re(CO)$_2$(PPh$_3$)(dpa)Cl] in deoxygenated dmf solution at room temperature and (*c*) *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] in the solid state



Scheme 2

energy of both the π* and d$_π$ orbital. The energy gap in the hydrated compounds is larger than in the non-hydrated compounds consistent with the blue shift observed in their electronic absorption spectra and higher solvent sensitivity. Owing to the low solubility of *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] in a variety of solvents we were not able to compare the sensitivity of its MLCT transition to solvent variations.

Excitation of a deoxygenated sample of *cis*-[Re(CO)$_2$(PPh$_3$)(dpa)Cl] in dmf at room temperature resulted in a yellow emission at 560 nm [Fig. 4(*b*)]. Under the same conditions no emission was observed for *fac*-[Re(CO)$_3$(dpk)Cl]; however, excitation of a solid sample of it at room temperature gave a broad emission at 570 nm [Fig. 4(*a*)]. The luminescence maxima for these compounds occur in the same range as observed for other *fac*-[Re^I(CO)$_3$(α-diimine)] systems and possibly derived from the ^{3}MLCT state.[44] When a solid sample of *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] was excited at 350 nm no emission was observed [Fig. 4(*c*)]. The quenching of the excited state of *fac*-[Re(CO)$_3$(dpk)Cl] in dmf points to a low-lying metal-to-ketone charge-transfer excited state that reduces the keto group to hydrol. The photoreduction of dpk to hydrol in non-aqueous media[45] and the photosensitization of dpk to hydrol by the excited state of [Ru(bipy)$_3$]$^{2+}$ have been reported[46] and *fac*-[Re(CO)$_3$(dpk)Cl] because of its high extent of delocalization of electrons/charge and the presence of a low-lying MLCT transition is unexceptional in this regard. This is in accord with the lack of emission in the hydrated complex, *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] and consistent with the photoreduction of ketones to alcohols by the excited state of *fac*-[Re(CO)$_3$L$_2$X] (X = Cl or I, L = 4-benzoylpyridine or 4-acetylpyridine).[47] The reduction of the keto group changes the hybridization of the carbonic carbon atom from sp^2 to sp^3, and places the oxo-anion at right angles to the N$_2$Re plane in close proximity to the octahedral co-ordination site. This arrangement leads to a steric congestion or a strain around the metal and the co-ordination of the oxo-anion (Scheme 2), and is analogous to the addition of nucleophiles at the ketonic carbon atom of co-ordinated dpk which changes its co-ordination mode from bi- to tri-dentate (Scheme 1).

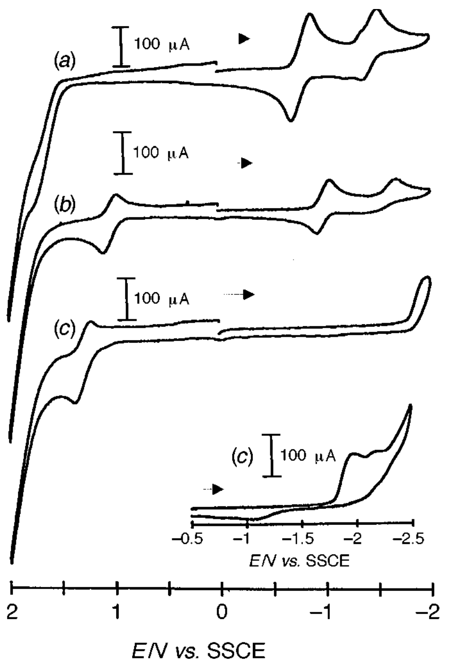


Fig. 5 Cyclic voltammograms of (*a*) *fac*-[Re(CO)$_3$(dpk)Cl], (*b*) *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] and (*c*) *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] in dmf solutions (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) at a glassy carbon working electrode (0.07 cm^2) and a scan rate of 400 mV s^{-1} *vs.* SSCE

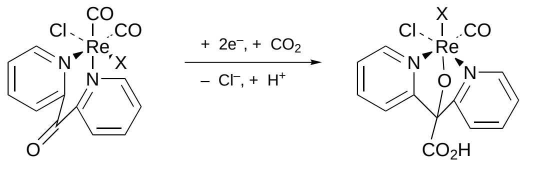
Electrochemical properties. The electrochemical properties of these compounds were investigated using voltammetric (cyclic and square-wave) techniques and the results are summarized in Table 2. Fig. 5 shows cyclic voltammograms of *fac*-[Re(CO)$_3$(dpk)Cl], *fac*-[Re(CO)$_3${(C$_5$H$_4$N)$_2$C(O)(OH)}] and *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl]. These results reveal the presence of three waves/peaks assigned to Re$^{II/I}$, diimine/diimine$^{•-}$ and Re$^{I/0}$ consistent with those reported for a variety of tricarbonylhalogenorhenium(I) compounds containing polypyridyl or α-diimine ligands.[29,33]

The hydrated compounds have their potentials shifted negatively compared to the non-hydrated precursors consistent with the decrease in electron-withdrawing ability of the hydrated ligands and the increase in electron density around the metal as a result of substitution of the chloride anion with the strong σ-donor alkoxy group. The shift is most pronounced for the first reduction wave which for the hydrated compounds occurs ≈1.20 V to more negative potentials as compared to the non-hydrated compounds.

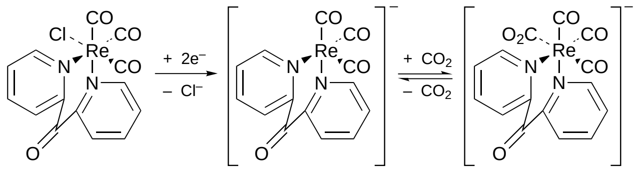
In the voltammograms of *cis*-[Re(CO)$_2$(PPh$_3$)(L–L)Cl] (L–L = dpk or bipy) the oxidation wave assigned to the Re$^{I/II}$ couple is significantly negatively shifted and the reduction waves are slightly negatively shifted compared to those of the tricarbonyl compounds. This is consistent with the increase in electron density around the metal and the elevation of the energy of the d orbitals when a CO is substituted with the better σ donor PPh$_3$ and in accord with the red shift observed in the electronic absorption spectra of the dicarbonyl compared to the tricarbonyl compounds.

A comparison of the voltammetric data for *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl], *cis*-[Re(CO)$_2$(PPh$_3$)(bipy)Cl] and *cis*-[Re(CO)$_2$(PPh$_3$)(dpa)Cl] reveals that a decrease in the electron-withdrawing ability of the diimine ligands causes the reduction potentials to shift to more negative values. The shift is pronounced for the first reduction wave where the dpa complex has potentials 0.92 and 1.19 V more negative than those of the compounds containing bipy and dpk, respectively. The energy of the π* orbital increases in the order dpk > bipy ≫ dpa.

Electrochemical reactions of *fac*-[Re(CO)$_3$(dpk)Cl] with CO$_2$. The electrochemical reactions of CO$_2$ with *fac*-[Re(CO)$_3$-



Scheme 3



Scheme 4

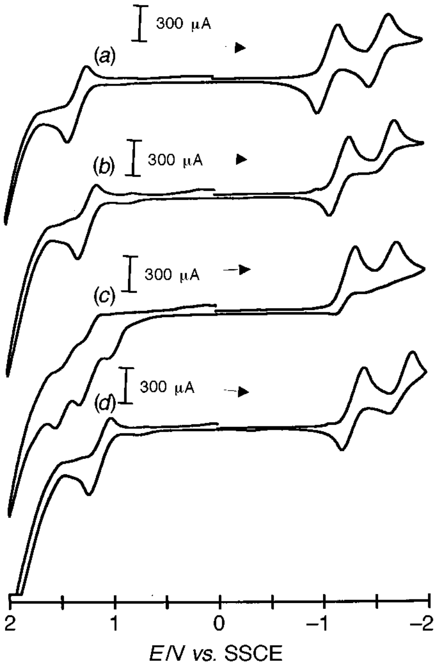
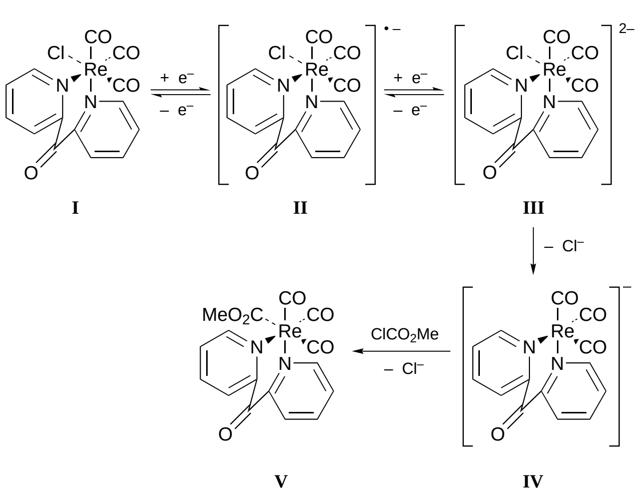


Fig. 6 Cyclic voltammograms of *fac*-[Re(CO)$_3$(dpk)Cl] (0.01 mol dm^{-3}) in MeCN (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) at a glassy carbon working electrode (0.07 cm^2) at a scan rate of 400 mV s^{-1} *vs.* SSCE: (*a*) under a nitrogen atmosphere, (*b*) in the presence of ClCO$_2$Me (0.01 mol dm^{-3}), (*c*) as in (*b*) but saturated with CO$_2$ and (*d*) as in (*c*) after removal of CO$_2$ by purging with N$_2$

(dpk)Cl] were published elsewhere.[35] These reactions are solvent dependent and controlled by the rate of diffusion of the electroactive species from the electrode surface. In dmf at scan rates <800 mV s^{-1} and in MeCN at scan rates <80 mV s^{-1} a stoichiometric carboxylation of the carbonylic carbon atom followed by rapid chemical steps leading to displacement of the chloride anion and attack of the oxo-anion at the metal (Scheme 3). In MeCN, at scan rates >80 mV s^{-1}, and in dmf at scan rates >800 mV s^{-1} the reaction of CO$_2$ with the electrochemically generated radical anion is slow and a second electron transfer leads to the formation of a co-ordinatively unsaturated intermediate that binds to CO$_2$ (Scheme 4).

Electrochemical reactions of *fac*-[Re(CO)$_3$(dpk)Cl] with methyl chloroformate. The reductive carboxylation of unsaturated organic compounds such as ketones, nitro compounds, *n*-heterocycles and phthalazine with methyl chloroformate have been described and the electrophilic character of methyl formate cation was demonstrated.[49] Cyclic voltammograms of *fac*-[Re(CO)$_3$(dpk)Cl] in the absence/presence of ClCO$_2$Me and CO$_2$ in MeCN are shown in Fig. 6. In the presence of ClCO$_2$Me electrochemical signatures [Fig. 6(*b*)] similar to those we observed for the electrochemical reactions between CO$_2$ and *fac*-[Re(CO)$_3$(dpk)Cl] were noted although subtle differences are apparent. In a reductive scan the first wave maintained its reversibility and the second wave lost its reversibility signalling an electrochemical reaction following the second electron transfer. When the electrochemical cell was saturated with CO$_2$ the first and second reductive waves lost their reversibility [Fig. 6(*c*)] signalling electrochemical reaction(s) at both sites. When the electrochemical cell was purged with nitrogen the resulting solution [Fig. 6(*d*)] showed an electrochemical behaviour similar to that observed before treatment with CO$_2$. These results suggest that CO$_2$ is more reactive than ClCO$_2$Me and can be confirmed by calculating the rate constants for the reaction of CO$_2$ and ClCO$_2$Me with the electrochemically generated species at the first and second electron transfer. The rate constant for the reaction of ClCO$_2$Me with the electrochemically generated radical anion can be estimated from the standard reduction potentials of first reduction wave ($E°_1$) and ClCO$_2$Me–ClCO$_2$Me$^{•-}$ ($E°_2$) from $RT \ln K = -nF(E°_1 - E°_2)$ where $K = k_1/k_{-1}$ and k_{-1} is taken as the diffusion limit, $k_{\text{diff}} = 5 \times 10^9$ dm^3 mol^{-1} s^{-1}, to estimate an upper value for k_1.[35] The potential for the ClCO$_2$Me–ClCO$_2$Me$^{•-}$ couple was estimated to be <-2.60 V *vs.* SSCE.[48] Thus, $\ln K < -nF/RT\ (-0.9 + 2.6)$ and $k_1 < 9.00 \times 10^{-22}$ dm^3 mol^{-1} s^{-1}. The value for the reaction of the same radical anion with CO$_2$ was estimated to have an upper value of 5.00×10^{-13} dm^3 mol^{-1} s^{-1}.[35] These values are in accord with observed reactivity patterns and point to insignificant reaction between ClCO$_2$Me and the electrochemically generated radical anion at the first electron transfer.



Scheme 5

The quasi-reversibility of the second reduction wave hints at a slow chemical reaction following the second electron transfer. As the scan rate decreases the wave shifts to more positive potentials, signifying a decrease in electron density around the metal. The rate constants for the reaction of ClCO$_2$Me and CO$_2$ at the second electron transfer are estimated to have upper values of 2.54×10^{-11} and 1.46×10^{-4} dm^3 mol^{-1} s^{-1}, respectively.[35] The low reactivity of ClCO$_2$Me is due to its slow electrochemical dissociation to $^+$CO$_2$Me and Cl$^-$ as reflected by appearance of a pre-wave before the first reduction wave. The results of these voltammograms reveal an electrochemical pathway for the reaction between ClCO$_2$Me and *fac*-[Re(CO)$_3$(dpk)Cl] as shown in Scheme 5. This mechanism is similar to that we reported for the electrochemical reaction of *fac*-[Re(CO)$_3$(dpk)Cl] with CO$_2$ in MeCN,[35] and is consistent with the positive shift noted for the second reduction wave as the scan rate decreases, absence of any reactivity upon the first electron transfer and the appearance of a chloride–chlorine oxidation wave.

The electrochemical responses (cyclic voltammograms) of *fac*-[Re(CO)$_3$(dpk)Cl] in the presence of ClCO$_2$Me in dmf are shown in Fig. 7. In these voltammograms a pre-wave appeared before the first reduction wave and as the concentration of

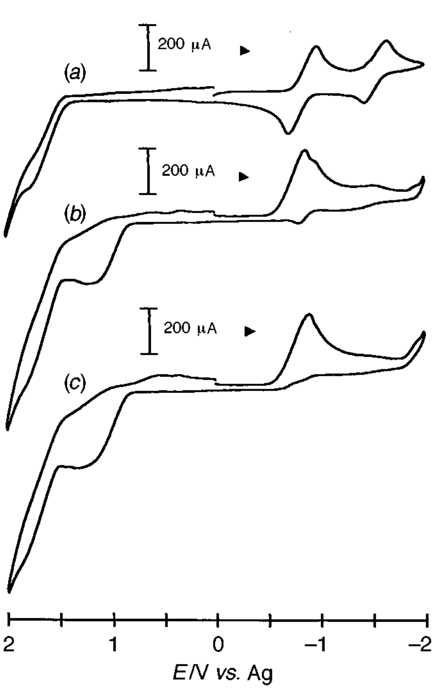
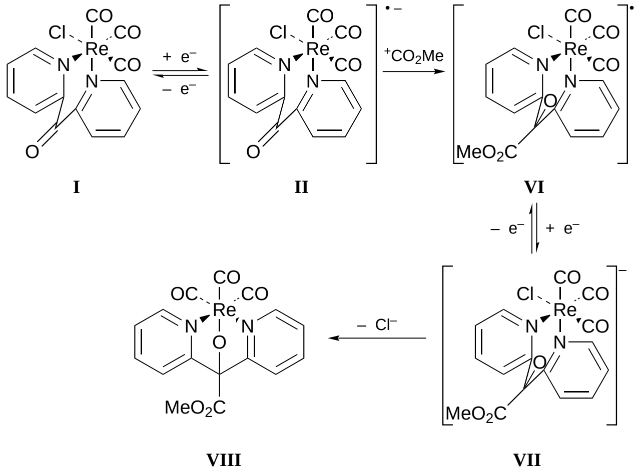


Fig. 7 Cyclic voltammograms of *fac*-[Re(CO)$_3$(dpk)Cl] (0.01 mol dm^{-3}) in dmf (0.1 mol dm^{-3} NBu$^n_4$PF$_6$). Other details as in Fig. 6: (*a*) under a nitrogen atmosphere; (*b*) in the presence of ClCO$_2$Me (0.01 mol dm^{-3}) and (*c*) in the presence of ClCO$_2$Me (0.02 mol dm^{-3})



Scheme 6

ClCO$_2$Me increases the first wave merges with the pre-wave, becomes irreversible and the second reduction wave disappears. An electrochemically generated oxidation wave due to 2Cl$^-$–Cl$_2$ oxidation appeared only on a reductive scan. With the exception of the pre-wave, these results are similar to those we reported for the electrochemical reactions of CO$_2$ with *fac*-[Re(CO)$_3$(dpk)Cl] in dmf and point to the formylation of a carbonylic carbon atom and the attack of the oxo-anion at the metal as shown in Scheme 6. The pre-wave in these voltammograms is associated with the adsorption and dissociation of ClCO$_2$Me at the electrode surface.

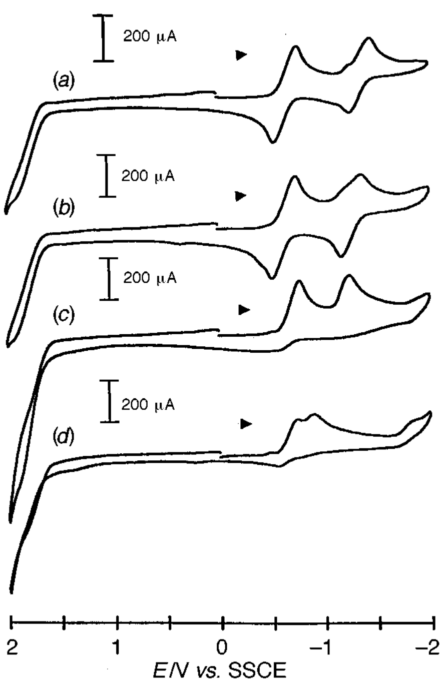


Fig. 8 Cyclic voltammograms of *fac*-[Re(CO)$_3$(dpk)Cl] (0.008 mol dm^{-3}) in dmf solutions (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) in the presence of 0.01 mol dm^{-3} KPF$_6$ (*a*), NaBF$_4$ (*b*) and Mg(ClO$_4$)$_2$ (*c*) at a glassy carbon working electrode (0.07 cm^2) at a scan rate of 400 mV s^{-1} *vs.* Ag

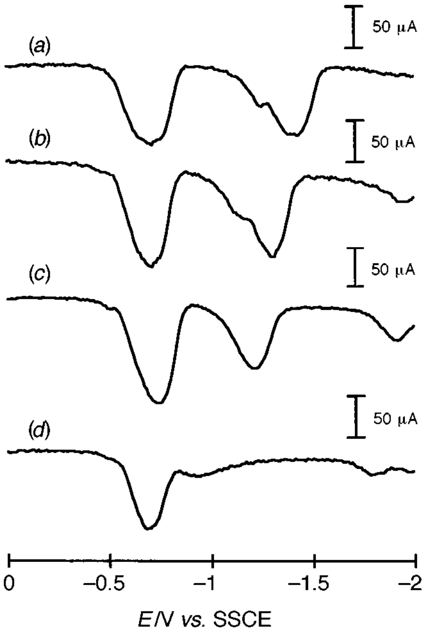


Fig. 9 Square-wave voltammograms of *fac*-[Re(CO)$_3$(dpk)Cl] (0.008 mol dm^{-3}) in dmf solutions (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) in the presence of 0.01 mol dm^{-3} KPF$_6$ (*a*), NaBF$_4$ (*b*) and Mg(ClO$_4$)$_2$ (*c*) at a glassy carbon working electrode (0.07 cm^2), a scan increment of 10 mV and a frequency of 60 Hz *vs.* Ag

Electrochemical recognition of Group I and II metal ions by *fac*-[Re(CO)$_3$(dpk)Cl]. Cyclic voltammograms of *fac*-[Re(CO)$_3$(dpk)Cl] in dmf in the presence of NaBF$_4$, KPF$_6$ and Mg(ClO$_4$)$_2$ are shown in Fig. 8 and Fig. 9 shows square-wave voltammograms measured for the same solutions. These voltammograms reveal that *fac*-[Re(CO)$_3$(dpk)Cl] electrochemically senses Group I and II metal ions in solution. Although subtle differences in their responses were noted, the general trend is that metal ions are sensed at the first and second reduction waves and the latter is more sensitive. The first reduction wave shows a slight increase in reductive current and the second shifts to more positive potentials consistent with the decrease in electron density around the metal. The magnitude of the shift depends on polarizing power of the cation, the cation with largest charge to radius ratio, Mg^{2+} > Na$^+$ > K$^+$, causing the most significant perturbation. The potassium cation due to its lower charge density slightly interacts with the metal-based couple as noted by the slight positive shift and the reversibility of this couple. These electrochemical responses are similar to those observed for a variety of transition-metal and organic redox-active macrocyclic receptor molecules in the presence of Group

I and II metal ions.[49–51] Owing to the convenient synthesis of *fac*-[Re(CO)$_3$(dpk)Cl] the current system may find a wide range of applications in a variety of voltammetric and amperometric molecular sensing devices.

Conclusion

The first series of rhenium(I) di- and tri-carbonyl compounds containing polypyridyl-like ligands has been isolated. These compounds exhibit rich physicochemical properties, and the potential application of the di-2-pyridyl ketone complexes as electrochemical sensors for electrophiles and Group I and II metal ions in solutions has been demonstrated.

Acknowledgements

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