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Electrochemistry of Trimetallic 'Crown-like' Iridium(I) Complexes

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The electrochemistry of trimetallic 'crown-like' iridium(I) complexes of the type $Ir_3(\mu S\text{-}{}^tBu)_3(\mu X)(CO)_6$ $[X = F_3C{-}C{\equiv}C{-}CF_3$ *(1),* $H_3COOC{-}C{\equiv}C{-}COOCH_3$ *(2)] and substituted analogues* $Ir_3(\mu S\text{-}{}^tBu)_3(\mu X)(CO)_5L$ $[X = F_3C{-}C{\equiv}C{-}CF_3$, $L = C_4F_6$ *(3),* CH_3CN *(4)] has been studied in* CH_3CN *and* CH_2Cl_2 *solvents on mercury, platinum and glassy carbon electrodes. These complexes undergo an irreversible one-electron reduction leading to the destruction of the trimetallic units. An irreversible one-electron oxidation step is also observed.*

A redox mechanism is proposed on the basis of electrochemical and IR spectroscopic results by comparison with the electrochemical behaviour of the analogous dimetallic $[Ir(\mu S\text{-}{}^tBu)(CO)_2]_2$ *(5).*

Introduction

We have previously reported [1–3] the synthesis and the characterization of unusal types of trimetallic iridium complexes $Ir_3(\mu S\text{-}{}^tBu)_3(\mu X)(CO)_4L_2$ ($X = C_4F_6$, $L = CO$ (*1*), $X = (CCOOCH_3)_2$, $L = CO$ (*2*), $X = CO$, $L = P(CH_3)_3$): in species *1* and *2*, two equivalent iridium atoms are bridged by the fluoroalkyne and were considered as being in the +II formal oxidation state, the third one remaining in the formal +I oxidation state (Fig. 1a). Further addition of C_4F_6 on (*1*) yields another trimetallic derivative $Ir_3(\mu_2S\text{-}{}^tBu)_2(\mu_3S\text{-}{}^tBu)(\mu C_4F_6)(CO)_5(\pi C_4F_6)$ (*3*) [2]: the second added C_4F_6 is then π-bonded to the iridium(I) center and the thiolato sulfur atom which was bridging the two iridium(II) atoms becomes triply bridging (Fig. 1b). The substituted complex (*3*) may undergo reversible ligand exchange: the second π-C_4F_6 can be substituted by CO or CH_3CN leading respectively to (*1*) or (*4*) [3a].

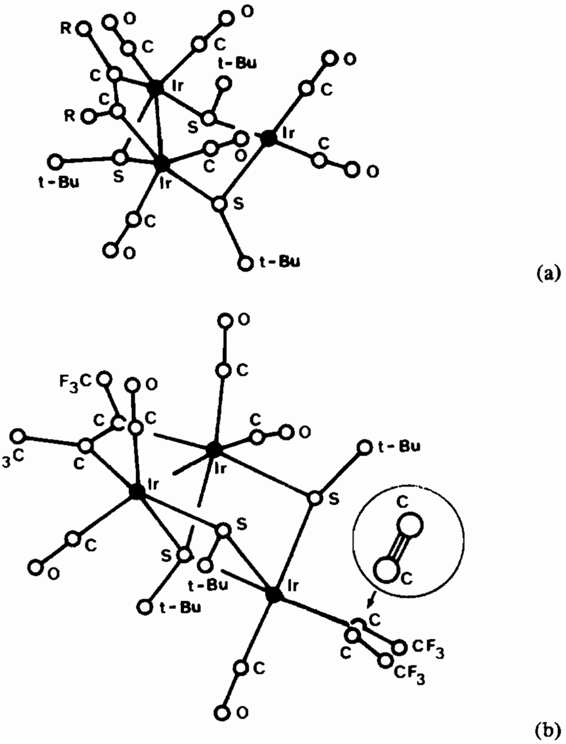

Fig. 1. Crystal structures of the studied complexes (*1*), (*2*), (*3*). a) $R = CF_3$ (*1*), $R = CCOOCH_3$ (*2*); b) (*3*).

In order to obtain additional informations on the reactivity and on the electronic structure of these new compounds, we have investigated their electrochemical properties. Previous electrochemical studies on organometallic Ir(I) complexes were only devoted to mono or dimetallic compounds [4].

Experimental

All the studied compounds have been prepared according to published methods [1, 3]. The complexes were studied by stationary voltammetry (Pt or glassy carbon electrodes, area 3.14 mm^2), cyclic

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voltammetry and coulometry (to overcome adsorption phenomena, controlled potential electrolyses were carried out on a carbon gauze). Identification of the reduction and oxidation products was attempted after exhaustive coulometry; the three-electrode cell, the electrochemical device, and the experimental procedure have been previously described [5]. Before use, the solvents CH_3CN and CH_2Cl_2, were purified by distillation. $(C_2H_5)_4NClO_4$ (TEAP) in CH_3CN and $(n\text{-}C_6H_{13})_4NClO_4$ (THAP) in CH_2Cl_2 were used as supporting electrolytes at concentration of 0.10 (TEAP) or 0.05 mol. dm^{-3} (THAP).

The solvents CH_2Cl_2 and CH_3CN were chosen in order to detect their possible interaction with the studied species and their oxidation or reduction products.

All solutions were degassed with argon for 15 min. before measurements. All potentials are measured *vs.* the saturated calomel electrode (S.C.E.). In these experimental conditions, the ferrocene/ferricinium couple exhibits a half-wave potential ($E_{1/2}$) of +0.40 V/SCE in CH_3CN and 0.1 *M*. TEAP and +0.65 V/SCE in CH_2Cl_2 and 0.05 *M* THAP. The infrared spectra were recorded in acetonitrile solution with a Perkin Elmer 225 grating apparatus. The X-band E.S.R. spectra were recorded on a Brucker ER 200-D.

Results

Electrochemical properties of the complexes (*1*) to (*5*) were studied on both platinum and glassy carbon electrodes in CH_3CN and CH_2Cl_2 solvents. Adsorption and electrode passivation were lower on glassy carbon than on platinum. Cathodic $E_{1/2}$ on a mercury dropping electrode are given for comparison.

In stationary voltammetry, all studied complexes exhibit respectively one reduction and one oxidation wave, whose limiting currents are of the same order of magnitude. Both limiting currents are proportional to the concentration of the complex in the range 10^{-3} to 10^{-4} *M*. When compared with the ferrocene oxidation wave in the same solution, the limiting current magnitudes are consistent with a one-electron exchange, in oxidation as well as in reduction (Table I). Cyclic voltammograms indicate that the two electrochemical processes are irreversible. The constant value of $ip/v^{1/2}$ (ip peak current, v potential scan rate) is consistent with the diffusion control observed in stationary voltammetry. The results obtained for the five complexes are gathered in Table I. It is informative to compare the redox characteristics of these complexes in the light of their structural similarities: (i) compounds (*1*) and (*2*), (ii) compounds (*3*) and (*4*) and (iii) compound (*5*) for comparison.

The complex (*2*) is more difficult to reduce and easier to oxidize than is (*1*). This is consistent with the relative basicity of the ligands attached to the Ir(II) centers: $(CCOOCH_3)_2$ is less electrophilic than is C_4F_6. Exhaustive electrolysis of solutions of (*1*) and (*2*) were also carried out on a carbon gauze as electrode and IR spectroscopy of the resulting solutions were recorded in the ν_{CO} region. In these experiments, only one ν_{CO} stretching band at 1960 cm^{-1} was detected after exhaustive reduction, whereas exhaustive oxidation of (*1*) and (*2*) led to a single 2070 cm^{-1} stretching band. The reduced or oxidized solutions (*ca.* 10^{-3} *M*) exhibited no visible absorption bands, nor any e.s.r. signal, even when electrolysis was carried out in the spectrometer cavity. Attempts to isolate in pure form that iridium-containing fragment failed. Nevertheless, the cyclic voltammetric peak at Ep. = 0.20 V/SCE obtained on the reverse scan (Fig. 2) of the reduction of (*1*) and (*2*) reveals that one identical electroactive fragment is generated in the electroreduction of these two complexes (*1*) and (*2*).

Complex (*3*) has a labile C_4F_6 ligand coordinated to the Ir(I) center. This lability of C_4F_6 was observable by dissolving (*3*) in CH_3CN: the reduction peak at −1.25 V/SCE gradually decreases whereas a new peak corresponding to (*4*) rises at −1.55 V/SCE (Table I). During the substitution, the generation of free C_4F_6 ligand in the solution was detected electrochemically and authentified by comparison with a sample of C_4F_6 dissolved in CH_3CN and 0.1 *M* TEAP ($E^{an}_{1/2}$ = +1.01 V/SCE). Similar substitution of the ligand C_4F_6 also occurs when CO is bubbled into a CH_2Cl_2 solution of (*3*). In this case, the complex (*3*) progressively converts into the complex (*1*). Thus, the reversible CO fixation cycle occurring without altering the trimetallic unit, can be monitored by electrochemical methods (cyclic voltammetry or stationary voltammetry). The ligand exchange is also obvious from IR data. As a consequence of the higher electrophilicity of C_4F_6 the complex (*3*) is easier to reduce and more difficult to oxidize than is the complex (*4*). After exhaustive electrolysis of (*4*), IR spectroscopy revealed after reduction one stretching band at 1960 cm^{-1}, and after oxidation, one stretching band at 2070 cm^{-1}.

These frequencies are identical to those obtained with (*1*) and (*2*) under the same experimental conditions.

The same electroactive fragment is generated by electrochemical oxidation or reduction of (*1*), (*2*) and (*4*), as already observed in cyclic voltammetry on the reverse scan (Fig. 2).

More generally comparison with the electrochemical behaviour and IR spectroscopy of (*5*), a bimetallic analogue (Table I), led us to conclude that a common fragment is indeed generated in the electro-oxidation of complexes (*1*) to (*5*). On the other hand, IR spectroscopy of the reduced solution of (*5*) shows two CO stretching bands at 2005(s) and 1925(vs), corresponding to a species which could not be

TABLE I. Spectroscopic and Electrochemical Data for the Complexes.

Studied complexes	ν_{CO} cm^{-1}/before oxidation and reduction	Electroreduction					Electrooxidation			
		$E_{1/2}$		Ep^c	n	ν_{CO} cm^{-1} ^{e} after reduction	$E_{1/2}$ ^{b}	Ep^c	n	ν_{CO} cm^{-1} after oxidation
		Hg^a	G.C.^{b}							
(*1*) $Ir_3(\mu\text{-}S^tBu)_3(\mu\text{-}C_4F_6)(CO)_6$	2089(s) 2073(vs) 2049(vs) 2038(s) 2029(m) 1983(vs)	−1.27	−1.55	−1.50	1	1960(s)	+1.50	+1.45	1	2070(s)
(*2*) $Ir_3(\mu\text{-}S^tBu)_3(\mu\text{-}CCOOCH_3)_2(CO)_6$	2085(s) 2067(vs) 2044(vs) 2034(s) 2021(m) 1977(vs)	−1.35	−1.60	−1.60	1	1960(s)	+1.30	+1.33	1	2070(s)
(*3*) $Ir_3(\mu\text{-}S^tBu)_3(\mu\text{-}C_4F_6)(CO)_5(C_4F_6)$	2096(s) 2080(vs) 2051(vs) 2036(m) 2020(s)		−1.02^d	−1.25^d	1			+1.65^d	1	
(*4*) $Ir_3(\mu\text{-}S^tBu)_3(\mu\text{-}C_4F_6)(CO)_5(CH_3CN)$	2094(s) 2078(vs) 2048(vs) 2035(m) 1991(s)	−1.70	−1.55	−1.55	1	1960(s)	+1.45	+1.47	1	2070(s)
(*5*) $[IrS^tBu(CO)_2]_2$	2061(s) 2040(vs) 1986(vs)	−1.39	−1.63	−1.58	1	2005(s) 1925(vs)	+1.65	+1.60	1	2070(s)

[a] On dropping mercury electrode in CH_3CN and 0.1 *M* TEAP: V. *vs.* SCE. [b] On rotating glassy carbon electrode (2000 r.p.m.) in CH_3CN and 0.1 *M* TEAP: V. *vs.* SCE. [c] V. *vs.* SCE scan rate 0.1 V. s^{-1} in CH_3CN and 0.1 *M* TEAP (G.C. electrode). [d] Potentials obtained immediately after dissolution of (*3*) in CH_3CN, before ligand exchange. [e] Only in CH_3CN and 0.1 *M* TEAP: no ν_{CO} are available in CH_2Cl_2 and 0.05 *M* THAP.

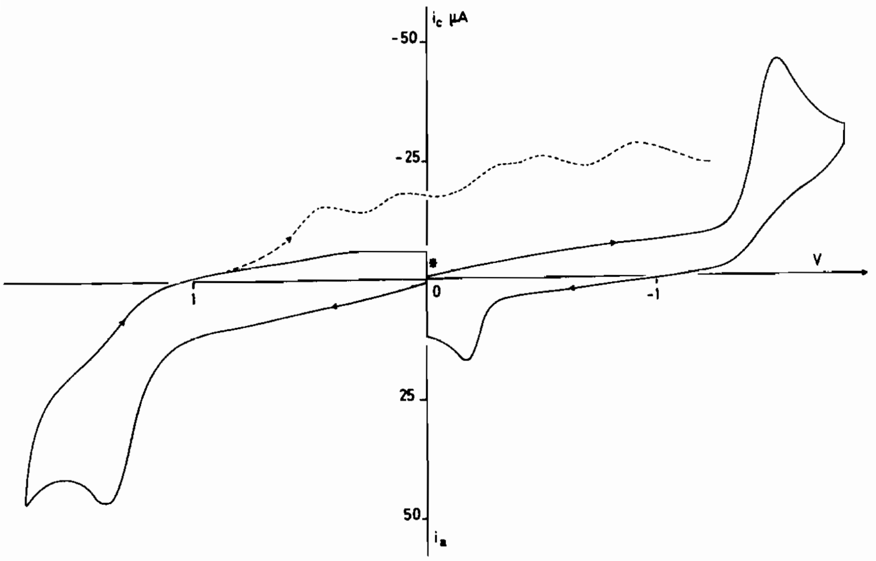

Fig. 2. Cyclic voltammetry of (*1*) at 10^{-3} Ml^{-1} medium: CH_3CN + 0.1 *M* TEAP. Electrode: glassy carbon electrode. Scan rate: 0.1 V/S. *Start of the scan. Dashed line: reverse scan at 0.5 V/S of the 0, +1.7, −1 V/SCE triangular sweep potentials.

isolated. However, on the basis of the results [6] obtained in the electroreduction of $[Rh(\mu Cl)(CO)_2]_2$ and $[Rh(\mu S^tBu)(CO)_2]_2$ and referring to the IR frequencies analogy, these species were assumed to be $[Ir(S^tBu)_2(CO)_2]^-(C_2H_5)_4N^+$.

Discussion

At first glance, complexes (*1*) and (*2*) undergo an irreversible one electron reduction according to eqn. (1):

$$Ir_3(\mu S^tBu)_3(\mu X)(CO)_6 + e \longrightarrow [Ir_3(\mu S^tBu)_3(\mu X)(CO)_6]^- \quad (1)$$

$X = C_4F_6, (CCOOCH_3)_2$

After exhaustive reduction in CH_3CN at −1.7 V/SCE, the reduced solutions exhibit one ν_{CO} stretching band at 1960 cm^{-1}. This is not consistent with a trimetallic anionic species for which six ν_{CO} stretching bands are expected (about 50 cm^{-1} lower than for the starting material). The observed absorption band at 1960 cm^{-1} is quite compatible with a mononuclear carbonyl-iridium(I) moiety, like for instance $Ir(S^tBu)(CO)(CH_3CN)_2$, analogous to the Vaska's complex [8] which should be obtained in CH_3CN by a chemical step following the cathodic electron transfer. Moreover, when reductive electrolysis of the complexes is carried out in CH_2Cl_2, even at −60 °C, no carbonyl stretching band was observed in the resulting solutions whereas a complete decomposition of the initial product occurs: this behaviour may be ascribed to the lack of stabilisation of the mononuclear carbonyl-iridium(I) species by the CH_2Cl_2–THAP medium. Unfortunately this hypothetical $Ir(S^tBu)(CO)(CH_3CN)_2$ species could not be isolated nor characterized from the electrolysed solution [9]. However, this hypothesis is consistent with the observation that the electroreduction fragment is generated from complexes (*1*) and (*2*) and also from (*3*) and (*4*) (Ep. = 0.2 V, ν_{CO} = 1960 cm^{-1}). Thus, the above electrochemical step (1) is followed by a chemical step (2) of which the proposed reaction scheme is:

$$[Ir_3(\mu S^tBu)_3(\mu X)(CO)_6]^- \xrightarrow[-CO]{CH_3CN} Ir(S^tBu)(CO)(CH_3CN)_2 + \text{`}[Ir_2(S^tBu)_2(X)(CO)_4]^-\text{'} \quad (2)$$

The 'Ir_2' species is not likely to be stable, and its decomposition leads to unidentified products without detectable ν_{CO} frequencies.

The reduction potentials of complexes (*3*) and (*4*) seem unaffected by the presence of the triply linked S atom to the three metals; the one electron reduction leads to the destruction of the trimetallic unit with the retention of the same carbonyl-iridium fragment (ν_{CO} = 1960 cm^{-1}). It may be speculated that the anionic species $[Ir_3(\mu_2\text{-}S^tBu)_2(\mu_3\text{-}S^tBu)(\mu\text{-}C_4F_6)(CO)_5(\pi\text{-}C_4F_6)]^-$, electrogenerated by controlled potential electrolysis of (*3*), reacts with the solvent CH_3CN according to the proposed scheme 3:

$$Ir_3(\mu_2S^tBu)_2(\mu_3\text{-}S^tBu)(\mu\text{-}C_4F_6)(CO)_5(\pi\text{-}C_4F_6)^- \xrightarrow{CH_3CN} Ir(S^tBu)(CO)(CH_3CN)(C_4F_6) + \text{`}[Ir_2(S^tBu)_2(C_4F_6)(CO)_4]^-\text{'} \quad (3)$$

The species $Ir(S^tBu)(CO)(CH_3CN)(C_4F_6)$ then reacts with CH_3CN to give $Ir(S^tBu)(CO)(CH_3CN)_2$ and C_4F_6 evolution. Indeed, free C_4F_6 was observed electrochemically in the solution and these results support the hypothesis made above.

The presumed species $Ir(S^tBu)(CO)(CH_3CN)_2$, only stable in CH_3CN, is not yet reducible at potential near −1.7 V at which the exhaustive coulometric reduction of (*3*) was carried out, and this absence of reduction is based on the following IR arguments:

i) The presence of the fragment $Ir(S^tBu)(CO)(CH_3CN)_2$ is assumed in the above reaction scheme (2) on the basis of close analogies between IR spectra of this fragment (with $\nu_{CO} = 1960\ cm^{-1}$) and of the known mononuclear species [4a] $Ir(SPh)(CO)(PPh_3)_2$ (with $\nu_{CO} = 1980\ cm^{-1}$).

ii) The non-reducibility of $Ir(S^tBu)(CO)(CH_3CN)_2$ up to −1.7 V is evidenced from the lack of variation (with time) of the corresponding ν_{CO} at 1960 cm^{-1}, as it is known [4a] that the reduction of the analogous $Ir(SPh)(CO)(PPh_3)_2$ results in a considerable shift of its ν_{CO}.

The binuclear complex (*5*) is reduced in an irreversible one-electron step, according to:

$$[Ir(\mu\text{-}S^tBu)(CO)_2]_2 + e \longrightarrow [Ir(\mu S^tBu)(CO)_2]_2^-$$

Surprisingly, the reductive potentiostatic coulometry of (*5*) led to a carbonyl derivative with ν_{CO} = 2005, 1925 cm^{-1} (Table I). This derivative could not be isolated, but on the basis of previous results [6] this derivative may reasonably be identified as $Ir(S^tBu)_2(CO)_2]^-$, which implies destruction of the bimetallic unit*. Therefore, the anionic dinuclear iridium species may be considered as undergoing a disproprotionation along the scheme:

$$[Ir(\mu\text{-}S^tBu)_2(CO)_2]_2^- \longrightarrow [Ir(S^tBu)_2(CO)_2]^- + \text{'}Ir(CO)_2\text{'}$$

The hypothetical 'Ir(CO)₂' fragment decomposes in CH_3CN.

The electrochemical oxidation of all the studied complexes (*1*) to (*5*) can be written as a one-electron process, as shown in 4:

$$[Ir_3(\mu S^tBu)_3(\mu X)(CO)_6] \longrightarrow e + [Ir_3(\mu S^tBu)_3(\mu X)(CO)_6]^+ \quad \text{(a)}$$

$$\text{or } [Ir(\mu S^tBu)(CO)_2]_2 \longrightarrow e + [Ir(\mu S^tBu)(CO)_2]_2^+ \quad \text{(b)} \qquad (4)$$

After controlled potential coulometry in CH_3CN at +1.7 V, all the oxidized solutions exhibited the same ν_{CO} stretching band at 2070 cm^{-1}. This is not compatible with the trimetallic cationic species from (*1*) and (*2*) as well as from (*4*), nor with a dinuclear cation $[Ir(\mu S^tBu)(CO)_2]_2^+$ from (*5*), for which respectively six, five and three ν_{CO} stretching bands are expected (about 50 cm^{-1} higher than the corresponding initial compound). The observed frequency at 2070 cm^{-1} (Table I) is in agreement with an iridium(II) species. Moreover the lack of e.s.r. signals suggests that this Ir(II) species has a dimetallic structure. This should result in the case of (*5*) from a chemical reaction according to 5:

$$[Ir^I(\mu S^tBu)(CO)_2]_2^+ \xrightarrow{L = CH_3CN} [Ir^{II}(S^tBu)(CO)_{2-n}L_{n+1}]^+ + [Ir^I(S^tBu)(CO)_{2-n'}L_{n'+1}] \qquad (5)$$

(c)

followed by dimerisation of the monocationic species and by decomposition of the Ir(I) species. In the case of (*1*) and (*2*), the cationic trimetallic species (a) should be split into a dimetallic Ir(II) species and a monocationic species (c) which would give by dimerisation the same dimetallic Ir(II) species (ν_{CO} = 2070 cm^{-1}). This hypothesis is in agreement with an oxidation of the Ir(I) metal center easier than that of the Ir(II) centers. Nevertheless this hypothesis does not account for the experimental value of n obtained by coulometry (n = 1.2); on the contrary it is possible to account for it by the reverse hypothesis in which the Ir(I) center is unaffected according to 6:

$$[Ir_3(\mu S^tBu)_3(\mu X)(CO)_6]^+ \xrightarrow[-CO]{CH_3CN} Ir(S^tBu)(CO)(CH_3CN)_2 + \text{'}[Ir_2(S^tBu)_2(X)(CO)_4]^{+}\text{'} \qquad (6)$$

after which the reoxidation of the presumed $Ir(S^tBu)(CO)(CH_3CN)_2$ occurs. Indeed, previous electrochemical oxidation studies on Vaska complexes $IrCl(CO)L_2$ [10] ($L = PPh_3$, PPh_2Et, $PPhEt_2$, PEt_3) show that at potential values near +1.5 V/S.C.E., $Ir(S^tBu)(CO)(CH_3CN)_2$ should be easily oxidized into a dimetallic Ir(II) metal–metal bonded compound (lack of e.s.r. signal) with $\nu_{CO} = 2070\ cm^{-1}$ for (*1*), (*2*), (*4*) and (*5*), according to 7, in agreement with Vlcek's [4b] conclusions:

$$Ir(S^tBu)(CO)(CH_3CN)_2 \longrightarrow e + \text{dimetallic Ir(II) species} \qquad (7)$$

At the same time '$[Ir_2(S^tBu)_2(X)(CO)_4]^+$' and '$[Ir(S^tBu)(CO)_2]^+$' should decompose rapidly and lead to our (unidentified) species without ν_{CO}

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*Reoxidation of $[Ir(S^tBu)_2(CO)_2]^-$ (obtained by reduction of $[Ir(\mu S^tBu)(CO)_2]_2$) at 0.0 V/SCE in CH_3CN gives $[Ir(\mu S^tBu)(CO)_2]_2$ yield < 100% and $(S^tBu)_2$ identified by HPLC.

stretching bands in CH_3CN. This second hypothesis implies a value of 1.33 for n.

By cyclic voltammetry (Fig. 2), after initial oxidation of (*1*), (*2*), (*4*) and (*5*), the reverse scan at rapid rate (>0.5 V/s) shows common cathodic peaks at −0.3 V and −0.9 V/S.C.E. (in CH_3CN + 0.1 *M* TEAP) which might correspond to the reduction of that cationic species. The electro-oxidation products of (*1*) to (*5*) in reaction (4)–(7) exhibit no e.s.r. signal in CH_3CN solvent, nor any carbonyl stretching bands (in CH_2Cl_2), owing to decomposition of the electrogenerated species.

Further studies on cluster electrochemistry are in progress.

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