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Electrochemistry of $[M_6(CO)_{15}]^{2-}$ anionic clusters (M = Co and Ir). Preparation and chemical characterization of $[Ir_6(CO)_{14}(NCO)]^-$ and of the radical anion $[Ir_6(CO)_{15}]^{-}$. Proposed mechanism of formation of the hexanuclear substituted cluster $[Ir_6(CO)_{15}Cl]^-$

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Abstract

Electrochemical studies performed on $[Ir_6(CO)_{15}]^{2-}$ show that the dianion undergoes stepwise oxidation to the congeners $[Ir_6(CO)_{15}]^n$ ($n = -1$ or 0); only the monoanion is notably long-lived. By contrast the electrochemical oxidation of $[Co_6(CO)_{15}]^{2-}$ shows that both the corresponding monoanion and neutral clusters are transient species. Information gained on the oxidation of $[Ir_6(CO)_{15}]^{2-}$ in the presence of halide ions has enabled establishment of the mechanism of formation of the anion $[Ir_6(CO)_{15}Cl]^-$, previously characterized by an X-ray study. This process of oxidation of $[Ir_6(CO)_{15}]^{2-}$ can be also initiated by treating the hexanuclear complex with chemical oxidants such as $[Fe(C_5H_5)_2]^+$ and $FeCl_3$. The characterization of $[N(PPh_3)_2][Ir_6(CO)_{14}(NCO)]$, obtained by chemical oxidation of $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ in the presence of $[N(PPh_3)_2]N_3$, is also reported.

Introduction

Since the discovery of the metal carbonyl clusters $M_6(CO)_{16}$ (M = Co [1], Rh [2], or Ir [3]) and the related dianionic species $[M_6(CO)_{15}]^{2-}$ (Co [4a], Rh [4b], and Ir [4c]) a variety of neutral and anionic derivatives have been obtained [5], and in many cases the reaction has been found to proceed without breakdown of the octahedral metal cage of the parent cluster. In spite of the stability of this metal framework there is little information on the redox aptitude of such metal carbonyl clusters, and this is confined to $[Rh_6(CO)_{15}]^{2-}$ [6].

Some recent reviews have focused on the application of electrochemistry in characterization of metal-carbonyl clusters [7–11], and in continuation of an interest in metal-carbonyl cluster chemistry we present here the results of an electrochemical investigation of the dianionic derivatives $[M_6(CO)_{15}]^{2-}$ (M = Co or Ir). In particular, the oxidation of $[Ir_6(CO)_{15}]^{2-}$ in the absence of coordinating ligands has allowed the characterization of the radical anion $[Ir_6(CO)_{15}]^{-}$, which survives in solution for a few hours, as well as of the notably shorter-lived neutral unsaturated species $Ir_6(CO)_{15}$. Such behaviour is rather unusual for octahedral carbonyl clusters, especially in the light of the very low stability of the analogous redox congeners of $[Co_6(CO)_{15}]^{2-}$ described here and $[Rh_6(CO)_{15}]^{2-}$.

Results and discussion

Electrochemical studies

The redox behaviour of $[Ir_6(CO)_{15}]^{2-}$ can be recognised from the cyclic voltammetric response in tetrahydrofuran (THF) solution shown in Fig. 1.

It can be seen that the dianion undergoes two consecutive anodic processes in correspondence to peaks A and B, each of which in the reverse scan displays a directly associated reduction peak (peaks C and D, respectively).

Controlled potential coulometric studies at the first anodic step ($E_w = +0.15$ V) reveal that it involves the removal of one electron/molecule.

Analysis of the cyclic voltammetric responses relating to the peak-system A/D, with scan rates v varying from 0.02 Vs^{-1} to 1 Vs^{-1} (at higher scan rates the response becomes ill defined), indicates that: (i) the peak current ratio $i_{p(D)}/i_{p(A)}$ is always unity; (ii) the current function $i_{p(A)} \cdot v^{-1/2}$ is essentially constant; (iii) the peak-to-peak separation $\Delta E_p = E_{p(A)} - E_{p(D)}$ increases from 80 to 115 mV [12]. Taking into account that under the same experimental conditions the one-electron oxidation of ferrocene displays almost the same variation of ΔE_p with the scan rate, we can assume that the first oxidation step of the dianion under study proceeds through a substantially reversible electron transfer. Confirmation that such an oxidation is also chemically reversible is provided by the finding that cyclic voltammetric studies performed after exhaustive one-electron removal reveal the same profile as that in Fig. 1, except for the peak system A/D, which now appears as a cathodic step.

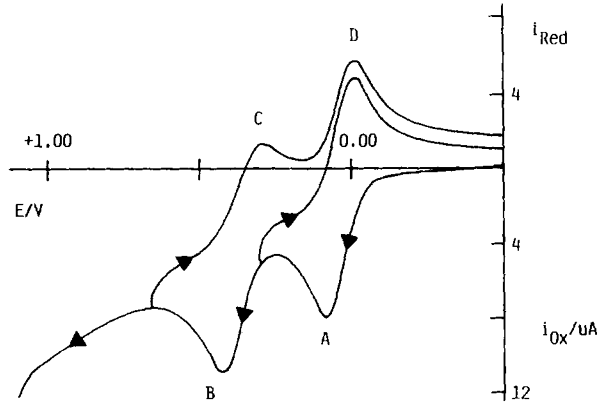


Fig. 1. Cyclic voltammogram recorded at a platinum electrode for a deaerated THF solution containing $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ (9.2×10^{-4} mol dm^{-3}) and $[NBu_4]ClO_4$ (0.1 mol dm^{-3}). Scan rate 0.2 Vs^{-1}.

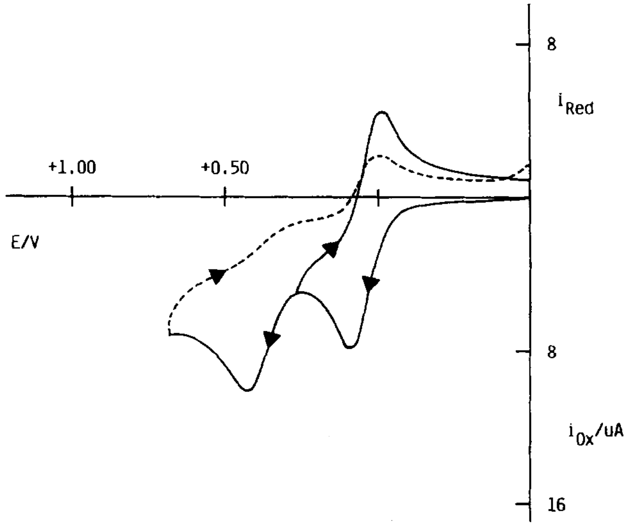


Fig. 2. Cyclic voltammogram recorded for a THF solution of $[Ir_6(CO)_{15}]^{2-}$ (experimental conditions of Fig. 1) under CO atmosphere.

The X-band EPR spectrum, at liquid nitrogen temperature, of the electrogenerated monoanion $[Ir_6(CO)_{15}]^-$ shows an absorption pattern characteristic of a metal-centered paramagnetic system ($S = 1/2$) with axial structure ($g_\parallel < g_\perp$), at $g_\parallel = 2.101 \pm 0.004$ and $g_\perp = 2.151 \pm 0.004$. Probably because of line-broadening caused by the solvent, the parallel region is poorly resolved. The peak-to-peak line width ΔH_{tot} is 150 ± 2 G. Increasing the temperature causes a rapid fall in the intensity of the signal, which disappears completely at about 200 K. During the one-electron oxidation, the initially brown solution turns green-brown, as in the chemical oxidation (see later).

The substantial reversibility of the electron transfer allows us to predict [7,10,11] that the structure of the molecular framework of $[Ir_6(CO)_{15}]^-$ is not significantly different from that of the parent dianion [4c].

As far as the second anodic step 1 − /0 is concerned, the electrochemical features indicate that it is followed by chemical reactions; thus, over the scan-range mentioned the $i_{p(C)}/i_{p(B)}$ ratio increases, from 0.5 to 0.7. This means that the neutral species $Ir_6(CO)_{15}$ is only transient; assuming a pseudo-first-order chemical complication, we can calculate that it has a half-life of about 2 sec.

Evidence of these complications comes also from controlled potential coulometry ($E_w = +0.5$ V), which slowly consumes more than 5 Faradays/mole, indicating that by-products (which are in turn oxidized) are produced. Furthermore, the high reactivity of the unstable $Ir_6(CO)_{15}$ is readily revealed by cyclic voltammetry under an atmosphere of CO which, as can be seen from Fig. 2, shows only the disappearance of the reduction peak directly associated in the reverse scan with the 1 − /0 oxidation (peak C in Fig. 1). It seems reasonable to assume that the coordinatively-unsaturated $Ir_6(CO)_{15}$ can react with CO to form $Ir_6(CO)_{16}$ [6]. $[Ir_6(CO)_{15}]^{2-}$ displays qualitatively similar redox behaviour in dichloromethane and in acetone solutions. In contrast, in acetonitrile there is a fully irreversible single-

Table 1

Redox potentials (vs SCE) and peak-to-peak separation for the electron transfers exhibited by $[Ir_6(CO)_{15}]^{2-}$ in various non-aqueous solutions

Solvent	$E°$ (2−/1−) (V)	ΔE_p [a] (mV)	$E°$ (1−/0) [b] (V)	ΔE_p [a] (mV)
THF	+0.04	96	+0.36	140
CH_2Cl_2	+0.01	96	+0.26	94
Me_2CO	+0.12	108	+0.50	230
MeCN	+0.17 [a,c]			

[a] Measured at 0.2 Vs^{-1}. [b] Estimated at high scan rates, so that the i_{pc}/i_{pa} ratio approximates as much as possible the unity. [c] Peak potential value for an irreversible two-electron step.

stepped two-electron oxidation. Table 1 summarizes the electrode potentials for the redox changes illustrated.

Figure 3 depicts the redox behaviour exhibited by $[Co_6(CO)_{15}]^{2-}$ in dichloromethane solution. Like $[Ir_6(CO)_{15}]^{2-}$, it undergoes two successive oxidation steps, which, from their peak heights, can confidently be assigned to two separate one-electron removals. In contrast to $[Ir_6(CO)_{15}]^{2-}$, the most anodic step completely lacks any directly associated response in the reverse scan, even at a scan rate of 1 Vs^{-1}. In addition, the first anodic process displays an i_{pc}/i_{pa} ratio increasing from 0.85 at 0.02 Vs^{-1} to 1 at 0.5 Vs^{-1} (concomitantly ΔE_p increases from 90 to 120 mV). These results suggest that the oxidation $[Co_6(CO)_{15}]^{2-/1-}$ proceeds through a quasireversible electron transfer complicated by subsequent chemical reactions. Such a picture implies that both $[Co_6(CO)_{15}]^-$ and $Co_6(CO)_{15}$ are transient species, the monoanion being longer-lived ($t_{1/2} \approx 2$ sec) than the neutral congener ($t_{1/2} < 1$ msec).

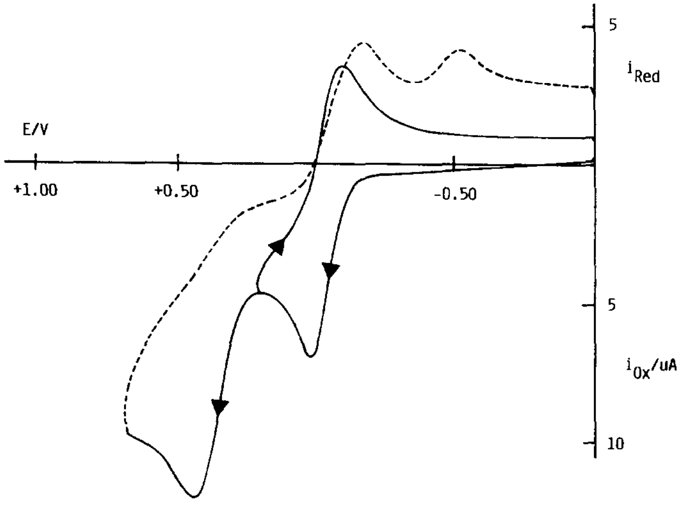


Fig. 3. Cyclic voltammogram recorded at a platinum electrode for a deaerated CH_2Cl_2 solution containing $[NEt_4]_2[Co_6(CO)_{15}]$ (1.01×10^{-3} mol dm^{-3}) and $[NBu_4]ClO_4$ (0.1 mol dm^{-3}). Scan rate 0.2 Vs^{-1}.

Table 2
Redox potentials for the two one-electron oxidation processes exhibited by $[Co_6(CO)_{15}]^{2-}$

Solvent	$E°$ (2−/1−) (V)	ΔE_p [a] (mV)	E_p (1−/0) [a] (V)
CH_2Cl_2	−0.05	120	+0.44
THF	−0.08	320	ill-defined

[a] Measured at 0.2 Vs^{-1}.

Qualitatively similar behaviour is found in tetrahydrofuran solution, but the two oxidation steps are decidedly less well defined. Table 2 summarizes the redox characteristics of the two oxidation processes. Further evidence for the existence of chemical complications coupled with the 2−/1− redox change comes from electrolysis experiments. Controlled potential coulometric studies in dichloromethane corresponding to the first anodic process (E_w = +0.1 V) show that the current falls abruptly after the consumption of one-electron/molecule but remains higher than the background current up to the overall consumption of three Faradays/mole. This means that species subsequently oxidizable at the working poten-

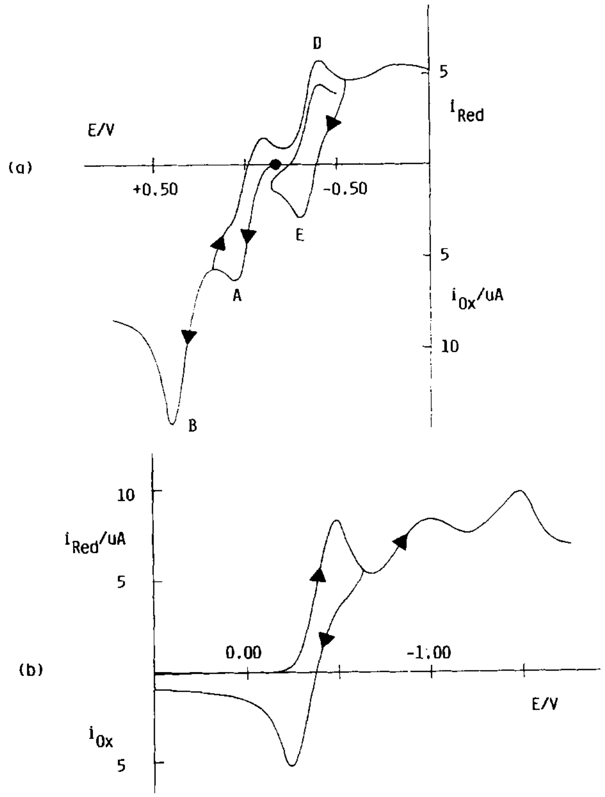


Fig. 4. Cyclic voltammograms recorded at a platinum electrode for deaerated CH_2Cl_2 solutions under the following conditions: (a) after consumptions of 0.8 Faradays/mole in electrolysis of $[NEt_4]_2[Co_6(CO)_{15}]$; (b) $Co_4(CO)_{12}$. $[NBu_4]ClO_4$ (0.1 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 Vs^{-1}.

tial arise from side-reactions accompanying the 2 − /1 − redox change. Figure 4a shows the cyclic voltammogram recorded after the consumption of 0.8 electrons/molecule. The peak system D/E is coincident with the first one-electron reduction exhibited in dichloromethane by an authentic sample of $Co_4(CO)_{12}$, Fig. 4b, which was previously investigated in dichloroethane [13]. This indicates that the main decomposition pathway following the one-electron removal produces $Co_4(CO)_{12}$.

Confirmation of the instability of $[Co_6(CO)_{15}]^-$ was also obtained by EPR studies. Thus even when the electrolysis was performed at −25 °C in order to reduce the rate of the subsequent chemical reactions, we were unable to detect the presence of paramagnetic species. Finally, $[Co_6(CO)_{15}]^{2-}$ undergoes a series of closely spaced irreversible reductions at potentials more negative than −1.4 V.

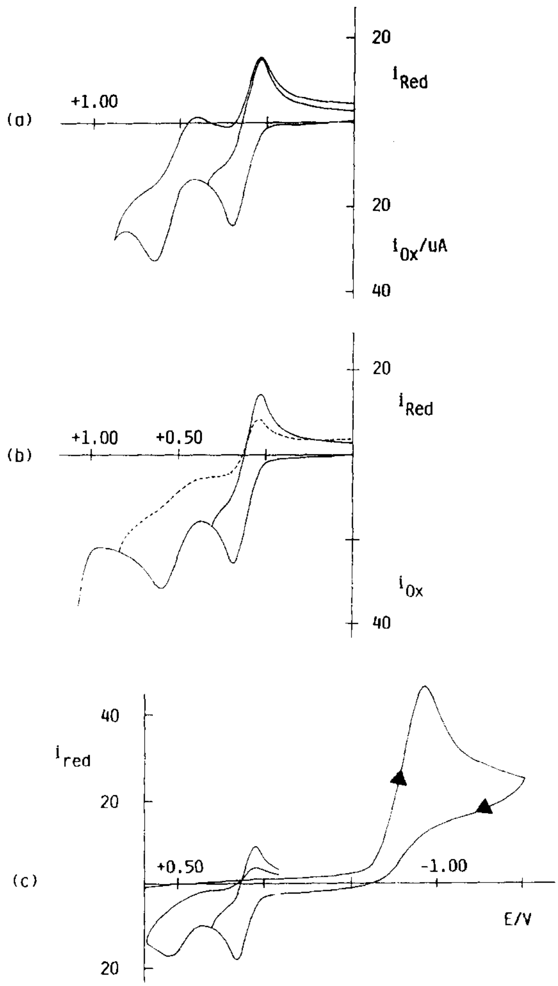


Fig. 5. Cyclic voltammograms recorded at a platinum electrode for a deaerated THF solution containing $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ (3.6×10^{-3} mol dm^{-3}) and $[NBu_4]ClO_4$ (0.2 mol dm^{-3}): (a) initial; (b) in the presence of $[NEt_3(CH_2Ph)]Cl$ (5.1×10^{-3} mol dm^{-3}); (c) after exhaustive two-electron oxidation at +0.7 V. Scan rate 0.2 Vs^{-1}.

It is relevant to recall that $[Rh_6(CO)_{15}]^{2-}$ undergoes two, near overlapping, one-electron removals, at all irreversible in character, because of the extremely fast decomposition of the oxidized species [6,10]. This shows that the stabilities of the congeners $[M_6(CO)_{15}]^{n-}$ (n = 1, 0; M = Co, Rh, or Ir) fall in the order: Ir ≫ Co ≫ Rh.

The redox behaviour of $[Ir_6(CO)_{15}]^{2-}$ *in the presence of halides*

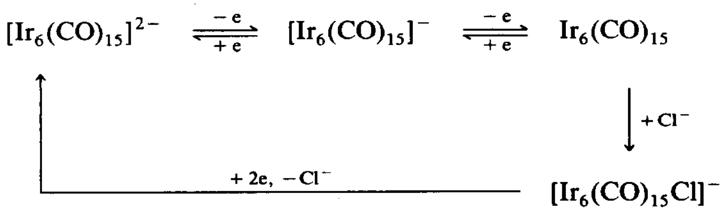
We have been intrigued by the elusiveness of the complex $[Ir_6(CO)_{15}X]^-$ (X = Cl, Br, or I), which we observed as an intermediate in the reaction between $Ir_6(CO)_{16}$ and halides to give $[Ir_6(CO)_{14}X]^-$ (X = Cl, Br, I, SCN) [14]. The electrochemistry of $[Ir_6(CO)_{15}]^{2-}$ in the presence of halides now makes clear the nature of the route to $[Ir_6(CO)_{15}X]^-$.

Figure 5b shows the cyclic voltammogram recorded for a tetrahydrofuran solution of $[Ir_6(CO)_{15}]^{2-}$ in the presence of an excess of Cl^- ions (about 1 : 2 ratio). Compared with the response of Fig. 5a, it can be easily seen that the presence of Cl^- suppresses the reduction peak directly associated with the oxidation step $[Ir_6(CO)_{15}]^{-/0}$ while not affecting the $[Ir_6(CO)_{15}]^{2-/-}$ redox change. This observation, reminiscent of the redox behaviour under a CO atmosphere discussed above, suggested that the electrogenerated $Ir_6(CO)_{15}$ might react with Cl^- to produce $[Ir_6(CO)_{15}Cl]^-$. In fact, after exhaustive two-electron oxidation at $E_w = +0.7$ V the solution which has turned from brown to reddish-brown displays an IR spectrum identical to that previously described for $[Ir_6(CO)_{15}Cl]^-$ [14]. The relevant cyclic voltammogram is illustrated in Fig. 5c. It can be seen that the oxidized product undergoes an irreversible reduction at $E_p = -0.93$ V, which in the reverse scan exhibits a voltammetric profile similar to that of $[Ir_6(CO)_{15}]^{2-}$. Final confirmation comes from the fact that exhaustive reduction at −1.1 V consumes two Faradays/mole, and the resulting solution gives again the voltammogram shown in Fig. 5b.

It is evident that the overall mechanism is that depicted in Scheme 1.

Chemical oxidation of $[Ir_6(CO)_{15}]^{2-}$

The radical anionic species $[Ir_6(CO)_{15}]^-$, obtained by electrochemical oxidation, can also be obtained by treating the dianion $[Ir_6(CO)_{15}]^{2-}$ with the bis-cyclopentadienyliron(III) cation $[FeCp_2]^+$ in 1 : 1 molar ratio in THF. The reaction is almost instantaneous, and as soon as the reagents are mixed the IR spectrum of the solution shows complete absence of the starting compound and the presence of new stretching bands at 2020s, 2010s, 1825m cm^{-1}, a pattern very similar to that of the starting dianion but shifted to higher wavenumbers ($[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ shows



Scheme 1

ν(CO) IR bands at 1985vs, 1975vs, 1925w, 1775m cm^{-1}, THF solution) [4c]. On standing, the THF solution undergoes change, and judging from the infrared spectrum some $[Ir_6(CO)_{15}]^{2-}$ is regenerated, together with a new, uncharacterized species that is presently under investigation [15]. The IR spectrum of this species (ν(CO) at 2025s, 1820m cm^{-1}) does not correspond to that of $[Ir_{12}(CO)_{26}]^{2-}$ [16], which we regarded as the most probable oxidation product from this reaction. All attempts to isolate the final oxidation product or the intermediate radical anion in pure form have so far failed. Opposite to what would be expected from the relevant redox potentials (see Table 1 and Experimental section), the presence of an excess of ferrocenium ions (1 : 2 molar ratio) does not seem to induce any further reaction.

The oxidation of $[Ir_6(CO)_{15}]^{2-}$ with $FeCl_3$ in THF proved to be of synthetic value in that such an oxidation, carried out in a solution containing a lot of halide, allows the quantitative transformation of $[Ir_6(CO)_{15}]^{2-}$ into the chloride-substituted cluster $[Ir_6(CO)_{15}Cl]^-$. We previously [14b] proposed a possible mechanism for the formation of this cluster on the basis of IR evidence and in keeping with the molar ratio of the two reactants. Further support for the proposed mechanism comes now from the electrochemically elucidated oxidation pathway.

Synthesis of $[Ir_6(CO)_{14}(NCO)]^-$

In order to confirm the generality of the synthetic approach adopted in the case of the reaction between $[Ir_6(CO)_{15}]^{2-}$ cluster and $FeCl_3$ [14] we examined the reaction of $[Ir_6(CO)_{15}]^{2-}$ with a different oxidant and in the presence of other ligands. Thus, we treated $[Ir_6(CO)_{15}]^{2-}$ with two moles of $[Fe(C_5H_5)_2]PF_6$ and 1 mole of $[N(PPh_3)_2]N_3$ in THF, at 0 °C. The reaction proceeds according to the following equation:

$$[Ir_6(CO)_{15}]^{2-} + N_3^- + 2[Fe(Cp)_2]^+ \rightarrow [Ir_6(CO)_{14}(NCO)]^- + N_2 + 2Fe(Cp)_2$$

After about 30 min, a black solution is formed that displays infrared absorptions bands at 2176m, 2066m, 2024vs, 1972m, 1824ms cm^{-1}. This spectrum is almost coincident in the shapes and intensities of the bands with that of $[Ir_6(CO)_{14}(\mu\text{-}X)]^-$ (X = Cl, Br, I, SCN) [14], but with an additional band at 2176 cm^{-1} typical of a bridging NCO group [17]. The compound was recovered by filtering off the insoluble $[N(PPh_3)_2]PF_6$ and removing the solvent in vacuum. Well shaped crystals of $[N(PPh_3)_2][Ir_6(CO)_{14}(NCO)].CH_2Cl_2$ were obtained by the slow diffusion technique from dichloromethane/pentane; in order to limit any decomposition the solvents were allowed to diffuse at −20 °C. X-ray data were collected [18], and the nature of the compound was established without any uncertainty, but unfortunately the structural parameters could not be refined with acceptable accuracy, probably because of crystallographic disorder or absorption anisotropy.

Experimental

The materials and the apparatus for electrochemical and EPR measurements have been described elsewhere [19]. All potential values reported here refer to an aqueous saturated calomel electrode (SCE). Under the experimental conditions used the ferrocenium/ferrocene coupled was located at: +0.55 V in THF solution, +0.53 V in CH_2Cl_2 solution, +0.51 V in acetone solution, +0.38 V in MeCN solution. $[M_6(CO)_{15}]^{2-}$ (M = Co [4a], and Ir [4c]), $[N(PPh_3)_2]N_3$ [20] and $[Fe(C_5H_5)_2]PF_6$ [21] were prepared by the reported procedure.

All reactions were carried out under nitrogen or carbon monoxide by Schlenk-tube and vacuum-line techniques [22].

Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer using calcium fluoride cells previously purged with nitrogen; (abbreviations: vs = very strong; s = strong; m = medium; w = weak).

Oxidation of $[Ir_6(CO)_{15}]^{2-}$ with ferrocenium ion

A Schlenk tube was charged under nitrogen with $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ (0.239 g, 0.09 mmol) and 8 cm^3 of THF. The resulting solution was cooled to 0 °C and $[Fe(Cp)_2]PF_6$ (0.030 g, 0.09 mmol) was added with stirring; monitoring of the solution by IR spectroscopy revealed complete disappearance of the starting material after 10 min. Twelve hours later the solution became greenish-brown, and contained small amounts of $[Ir_6(CO)_{15}]^{2-}$ and a new, unidentified, product.

Preparation of $[Ir_6(CO)_{14}(NCO)]^-$

A Schlenk tube was filled with nitrogen and cooled in an ice bath. $[N(PPh_3)_2]_2$-$[Ir_6(CO)_{15}]$ (0.380 g, 0.14 mmol) and $[N(PPh_3)_2]N_3$ (0.083 g, 0.14 mmol) were dissolved in 15 cm^3 of THF, then $[Fe(Cp)_2]PF_6$ (0.092 g, 0.27 mmol) was added in one portion. After 1 h complete conversion of the reagents was revealed by IR spectroscopy; the solution was warmed to room temperature, stirred for a further 1 h, then filtered through a sintered glass filter. The solvent was removed under vacuum and the dark residue washed with hexane (2 × 10 cm^3), to remove ferrocene, then dried again. The product was extracted with dichloromethane (2 × 4 cm^3), and the solution was layered with n-pentane and kept at −20 °C. After 15 days, the mother liquor was taken off by syringe and the crystals of $[N(PPh_3)_2][Ir_6(CO)_{14}$-$(NCO)] \cdot CH_2Cl_2$ were washed twice with cyclohexane and rapidly dried. The product always contained significant amounts of $[N(PPh_3)_2]PF_6$ as colourless large needles, and so gave unsatisfactory elemental analysis data.

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