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ELECTROCHEMISTRY OF COORDINATION COMPOUNDS

XXII *. ELECTROGENERATION AND CHARACTERIZATION OF MONOMERIC IRIDIUM(II) ORGANOMETALLIC COMPLEXES $[Ir(R)(CO)(PPh_3)_3]^+$

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Summary

Vaska type organometallic complexes *trans*-$Ir(R)(CO)(PPh_3)_2$ (R = CH_3, CH_2CN, C_6H_5) are oxidized in 1,2-dichloroethane containing PPh_3 in two one-electron steps, the first involving addition of PPh_3 prior to reversible electron transfer. One-electron electrolysis produces quite stable d^7 species $[Ir(R)(CO)(PPh_3)_3]^+$, which have been characterized by IR and ESR spectroscopy. Further one-electron oxidation produces highly reactive d^6 dications, which upon addition of chloride ions yielded $Ir(Cl)_2(R)(CO)(PPh_3)_2$.

Introduction

Rhodium and iridium complexes are uncommon in the d^7 electronic configuration and this is especially true for monomeric species [1–7]. During our investigations on transition metal complexes in unusual oxidation states we obtained d^7 monomeric hydrido cations of formula $[HM(CO)(PPh_3)_3]^+$ (M = Rh, Ir) [6]. As great importance is currently attributed to this type of unpaired electron species in the mechanisms operating in homogeneous catalysis [8], we decided to prepare the related species in which the hydride ligand is replaced by a σ-bonded organic group. We therefore examined the electrochemical oxidation of compounds of general formula $[Ir(R)(CO)(PPh_3)_2]$ (Vaska type), with R an alkyl (CH_3), substituted alkyl (CH_2CN), or aryl (C_6H_5) group. The results are presented below.

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* For part XXI see ref. 15.

Experimental

Chemicals and reagents

The following compounds were prepared by published procedures: $Ir(CH_3)(CO)(PPh_3)_2$ [9], $Ir(CH_2CN)(CO)(PPh_3)_2$ [10] and $Ir(C_6H_5)(CO)(PPh_3)_2$ [11,12]. These d^8 square-planar complexes have the *trans* configuration according to data in the literature for the cyanomethyl [10] and phenyl derivatives [12], and from ^{1}H NMR measurements for the methyl adduct (1/2/1 triplet at τ 10.17, J(PH) 9 Hz in CD_2Cl_2). $HIr(CO)(PPh_3)_3$ and $DIr(CO)(PPh_3)_3$ were prepared as in ref. 13; $[Ir(CO)(PPh_3)_3](ClO_4)$ as in ref. 14. The previously unreported complex $IrCl(CH_2CN)_2(CO)(PPh_3)_2$ was obtained by oxidative addition of chloromethyl cyanide (Fluka) to $Ir(CH_2CN)(CO)(PPh_3)_2$ by to the following procedure.

Chloromethyl cyanide (0.8 ml, 12.7 mmol) was added to a solution of cyanomethylcarbonylbis(triphenylphosphine)iridium(I) (1.2 g, 1.53 mmol) in dichloromethane (40 ml) under argon. After 24 h pentane was added, and a pale yellow powder which separated was washed with pentane and dried under vacuum. Elemental analysis, IR spectroscopy (ν(CO) 2037 cm^{-1}, ν(CN) 2202 cm^{-1} in KBr) and ^{1}H NMR spectroscopy (two 1/2/1 triplets with the same integrated area at τ 8.09, J(PH) 7.1 Hz and τ 8.97, J(PH) 5.6 Hz in CD_2Cl_2) confirmed the suggested formulation, at the same time indicated the phosphines were mutually *trans* and the cyanomethyl groups mutually *cis* in the octahedral structure.

The solvent, 1,2-dichloroethane (DCE), was purified as described previously [6], and the supporting electrolyte, tetrabutylammonium perchlorate (TBAP), and triphenylphosphine were purified by standard procedures. All other chemicals were reagent grade and used as received. Experiments were carried out under 99.999% argon.

Apparatus and procedures

The electrochemical apparatus and procedures have been described previously [15]. The reference electrode was silver/0.1 *M* silver perchlorate in acetonitrile (−0.12 V vs. ferrocene/ferricinium in DCE 0.2 *M* TBAP). All potentials are referred to the ferrocene/ferricinium couple.

IR and UV-VIS spectra were run on Perkin–Elmer mod. 580B and Cary mod. 17D spectrometers, respectively.

ESR spectra were obtained on a Bruker mod. ER 100D X-band spectrometer, NMR spectra on a Varian mod. FT-80A spectrometer.

Results and discussion

Voltammetry of $Ir(R)(CO)(PPh_3)_2$

Cyclic voltammograms of solutions of $Ir(R)(CO)(PPh_3)_2$ on a Pt microelectrode in DCE 0.2 *M* TBAP at 25°C (exemplified in Fig. 1 by the cyanomethyl derivative) are strongly dependent on the presence of extra phosphine in the solution. A single two-electron irreversible oxidation peak is displayed in the absence of free PPh_3 (peak I in Fig. 1a, E_p^I values in Table 1), but addition of the free ligand gives rise to an oxidative wave at less positive potentials (II in Fig. 1b) coupled with a reduction peak on reversal of the scan. As the phosphine concentration is increased and/or the scan rate v is decreased, wave II is transformed into a peak, its peak current ($i_p v^{-1/2}$

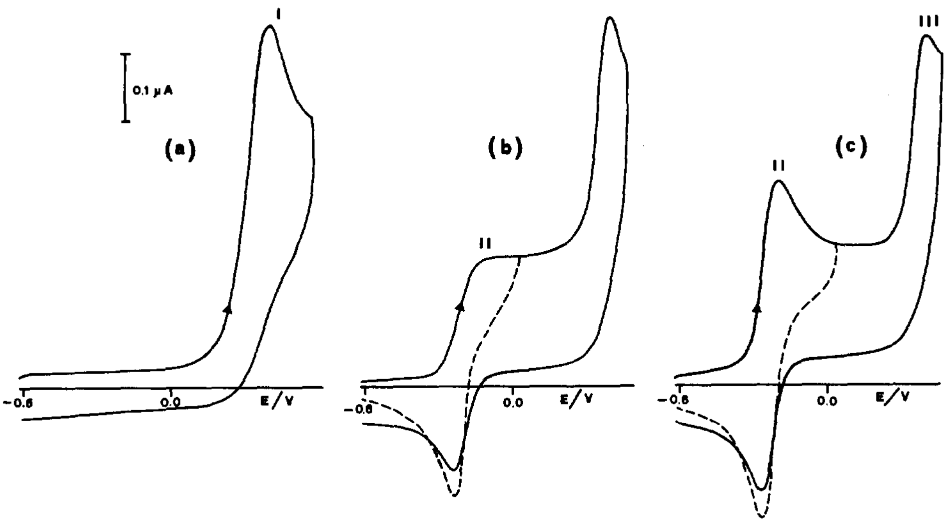


Fig. 1. Cyclic voltammograms for oxidation of $Ir(CH_2CN)(CO)(PPh_3)_2$ 0.44 m*M* in DCE 0.2 *M* TBAP at 25°C at various concentrations of PPh_3. Scan rate: 250 mV s^{-1}. (a) 0.0; (b) 5.0; (c) 50.0 m*M*.

value) increases, and the peak potential shifts cathodically until a well-defined one-electron reversible response is obtained (Fig. 1c). At the same time, peak I is transformed into a new peak (III in Fig. 1c), the characteristics of which are those expected for a fast one-electron oxidation process coupled with a subsequent fast irreversible reaction [16] (E_p^{III} values in Table 1).

The voltammetric behavior of process II suggests that the d^8 square-planar complex coordinates an extra phosphine ligand in a moderately fast equilibrium (eq. 1) before electron transfer (eq. 2):

$$Ir(R)(CO)(PPh_3)_2 + PPh_3 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ir(R)(CO)(PPh_3)_3 \qquad (1)$$

$$(K = k_f/k_b)$$

$$Ir(R)(CO)(PPh_3)_3 \underset{+e}{\overset{-e}{\rightleftharpoons}} [Ir(R)(CO)(PPh_3)_3]^+ \qquad (2)$$

This indication is not purely qualitative, since numerical analysis of the dependence of $i_p v^{-1/2}$ on v and phosphine concentration according to the proposed

TABLE 1

ELECTROCHEMICAL AND CHEMICAL DATA FOR OXIDATION OF *trans*-$Ir(R)(CO)(PPh_3)_2$ IN DCE 0.2 *M* TBAP AT 25°C

R	E_p^I (V) [a]	E_p^{III} (V) [a]	E_0 (V)	K^* (M^{-1})	$k_f \times 10^{-4}$ ($M^{-1}\ s^{-1}$)	$k_b \times 10^{-4}$ (s^{-1})	ν(CO) (cm^{-1})
CH_3	0.24	0.16	−0.495	14	71	5.1	1935
C_6H_5	0.18	0.26	−0.475	0.13	–	–	1938
CH_2CN	0.44	0.42	−0.350	0.42	9.05	21.5	1957

[a] Scan rate: 200 mV s^{-1}.

TABLE 2

TYPICAL EVALUATION OF KINETIC PARAMETER $K(k_f+k_b)^{1/2}$ FOR REACTION 1 FROM SCAN RATE v, DEPENDENCE OF PEAK CURRENT i_p (case III in ref. 16) (Conditions: 1.3 mM [Ir(CH$_2$CN)(CO)(PPh$_3$)$_2$] in DCE 0.2 M TBAP at 25°C in the presence of 27.5 mM PPh$_3$)

v (V s^{-1})	i_p (μA)	$K(k_f+k_b)^{1/2}$ (s$^{-1/2}$)
0.1	0.52	5.4
0.4	0.90	5.1
0.6	1.06	5.5
1.0	1.24	5.3
2.5	1.63	5.2
4.0	1.97	6.0

mechanism (case III in ref. 16) results in a satisfactory fit, as exemplified for R = CH$_2$CN in Tables 2 and 3.

The occurrence of the reaction shown in eq. 1 was predictable, as d^8 iridium complexes containing phosphorus ligands are known to be prone to pentacoordination, as in the case of the analogous HIr(CO)(PPh$_3$)$_3$, which is stable towards phosphine dissociation [17]. Furthermore, the voltammetric indication was confirmed by UV-VIS and NMR measurements. The three absorption bands in the electronic spectrum of Ir(R)(CO)(PPh$_3$)$_2$ [18] decrease progressively and reversibly on addition of PPh$_3$ by amounts depending on R, and this allows evaluation of the equilibrium constants for eq. 1. From the equilibrium constant values ($K^\star = K/[\text{PPh}_3]$ in Table 1) it appears that the formation of the phosphine adduct is more pronounced in the case of the methyl derivative, so that at high concentrations of PPh$_3$, it is the predominant species in solution. Thus, the ^{1}H NMR spectrum in CD$_2$Cl$_2$ containing 0.5 M PPh$_3$, run at −60°C to overcome the non-resolution resulting from fast exchange processes [13,19], displays a 1/3/3/1 quartet at τ 10.76 (J(PH) 11 Hz) assignable to the methyl group coupled with three equivalent phosphines; under the same conditions, the ^{31}P NMR signal of the coordinated phosphines appears as a single line at δ_p 6.5 (downfield from external 85% H$_3$PO$_4$).

These findings indicate unequivocally that one PPh$_3$ ligand adds to the d^8 square-planar complex, producing in the case of R = CH$_3$ (and presumably also in the other cases) a trigonal bipyramidal species with the three phosphines in the equatorial plane. Such an arrangement of ligands is also present in HIr(CO)(PPh$_3$)$_3$ [13].

TABLE 3

DEPENDENCE OF $K(k_f+k_b)^{1/2}$ (see Table 2) ON PPh$_3$ CONCENTRATION

[PPh$_3$] (mM)	$K(k_f+k_b)^{1/2}$ (s$^{-1/2}$)	$k_c{}^a = K(k_f+k_b)^{1/2}\,[\text{PPh}_3]^{-1}$ (M^{-1} s$^{-1/2}$)
12.8	2.4	190
27.5	5.4	195
39.0	7.7	200
57.5	11.0	190

[a] For $K \ll 1$, $k_c = k_f^\star k_b^{-1/2}$, where $k_f^\star$ is the second order rate constant $k_f/[\text{PPh}_3]$.

The voltammetric data for the reversible oxidation of $Ir(R)(CO)(PPh_3)_2$ measured under equilibrium (reversible half-wave potentials, $E^{\frac{1}{2}}$) and non-equilibrium (kinetic parameters, $K(k_f + k_b)^{1/2}$) conditions, coupled with the equilibrium constant values, allowed evaluation of the formal potential for the couple $[Ir(R)(CO)(PPh_3)_3]^+/[Ir(R)(CO)(PPh_3)_3]$ by use of eq. 3:

$$E^{\frac{1}{2}} = E_0 + (RT/nF) \ln(1 + 1/K^\star[PPh_3]) \tag{3}$$

along with the rate constant values $k_f^\star$ $(= k_f/[PPh_3])$ and k_b for eq. 1 (data summarized in Table 1). Examination of the table shows that the sequence of the formal redox potentials parallels that of the electron-donor properties of the organic moieties as indicated by the relative positions of the $\nu(CO)$ frequencies in the square-planar precursors [20].

We can conclude that the potential required for the oxidation of the d^8 square-planar species, which is so high that requires a straightforward two-electron process, is substantially lowered by the presence of an additional phosphorus ligand in the coordination shell, allowing oxidation to be performed in two well-separated one-electron steps so that formation of d^7 species is feasible.

Electrogeneration of $[Ir(R)(CO)(PPh_3)_3]^+$

In the light of the results described in the preceding section, oxidation of $Ir(R)(CO)(PPh_3)_2$ was performed in the presence of excess PPh_3 (0.1 *M*). Exhaustive electrolysis at 25°C at potentials on the first oxidation wave require one electron/mol and produce a light brown solution showing the voltammetric pattern of the d^8 precursor, except for a one-electron shift of the current scale (Fig. 2). In some cases, however, the limiting currents are lower, depending on R and the time of electrolysis. Thus, while the phenyl derivative is stable for at least several days, the cyanomethyl and methyl homologues decay by a first-order process during several hours ($t_{1/2} = 4$ and 19 h, respectively). The cyanomethyl d^7 complex produces the d^8 cation $[Ir(CO)(PPh_3)_3]^+$, identified voltammetrically [21] and spectrophotometrically by comparison with an authentic sample, and an iridium carbonylated complex ($\nu(CO)$ 2065 cm^{-1}) showing bands at 2215 and 2250 cm^{-1}, attributable to pendant and bridging nitrile groups, respectively, as found in dimeric bis-cyanomethyl complexes [22]. Addition of chloride ions to the solution causes the $\nu(CO)$ band to shift to 2043 cm^{-1} and the two CN bands to merge into one another at 2209 cm^{-1}, to give the same spectrum as the d^6 complex $IrCl(CH_2CN)_2(CO)(PPh_3)_2$ (see Experimental), and thus the CN-bridged species can be formulated as $[Ir(CH_2CN)_2(CO)(PPh_3)_2]^+{}_2$. Quantitative analysis of the spectra indicate that equimolar amounts of the d^6 and d^8 species are formed in the decay of the cyanomethyl d^7 complex. Likewise, for $R = CH_3$ the complex $[Ir(CO)(PPh_3)_3]^+$ is produced, but the amount is > 50% (75–80%) and the rest of the metal is mostly present as $IrCl(CO)(PPh_3)_2$; GC-MS analysis of the evolved gas reveals that methane is formed.

These findings suggest that the d^7 species decompose by a mechanism involving slow radical dissociation, followed by fast attack by the formed $R^\cdot$ on the solvent in the case of the more reactive methyl group or on the d^7 parent species in the case of the cyanomethyl radical, which is stabilized by conjugation. The unusual stability of the phenyl complex can be attributed to the higher carbon–metal bond energy [23],

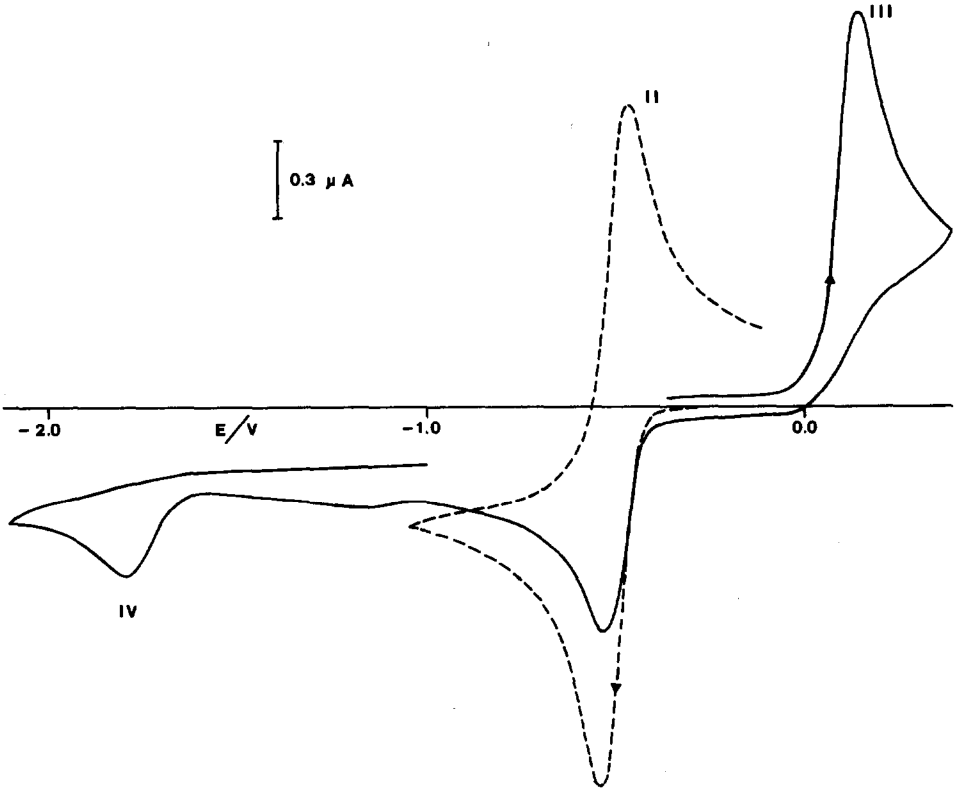


Fig. 2. Cyclic voltammogram for a solution of $[Ir(CH_3)(CO)(PPh_3)_3]^+$ 4.3 m*M* in DCE 0.2 *M* TBAP, 0.1 *M* PPh_3 at −20°C. Scan rate: 200 mV s^{-1}.

which is at a minimum in the studied series for the cyanomethyl radical because of the electron withdrawal by the CN group.

As the decomposition of the d^7 complexes, even in the case of $R = CH_2CN$, is relatively slow, electrolysis at low temperature (−20°C) allows satisfactory spectral characterization of the species and their further oxidation, as reported below.

Characterization of $[Ir(R)(CO)(PPh_3)_3]^+$

The d^7 species was characterized by IR and ESR spectroscopy. The IR spectra show a single $\nu(CO)$ band at about 2010 cm^{-1} (see Table 4) with a sequence of values along the series which follows that for and d^8 square-planar precursors, although the discrimination is lower in the higher frequency region.

The ESR spectra confirm the paramagnetic nature of the complexes, and the signal is consistent with the presence of one unpaired electron. Whatever the nature of *R* (including R = H or D), the spectrum at room temperature (Fig. 3a) consists of a doublet but on couling to 120 K this is transformed into a triplet of doublets (Fig. 3b) (a fourfold splitting of the high-field component, due to coupling with the Ir nucleus, is also shown). Thus, the unpaired electron appears to couple with one phosphorus atom in an anisotropic non-axial system (g and *A* values are shown in Table 4, together with data for the homologous hydride). The fact that the coupling involves only one phosphine ligand is surprising, since in the d^8 precursor, the PPh_3

TABLE 4

IR AND ESR[a] DATA FOR $[Ir(R)(CO)(PPh_3)_3]^+$ IN DCE 0.2 *M* TBAP, 0.1 *M* PPh_3

R	ν(CO) (cm^{-1})	g_1	g_2	g_3	A_1 (G)	A_2 (G)	A_3 (G)	A_{Ir}[b] (G)
CH_3	2008	2.22	2.19	1.97	163	163	226	31
C_6H_5	2010	2.25	2.16	1.97	171	171	227	31
CH_2CN	2015	2.24	2.15	1.97	173	173	232	38
H	1990	2.22	2.15	1.98	147	147	200	38
D	2017	2.22	2.15	1.98	147	147	200	38

[a] In frozen samples at 120 K. [b] Hyperfine coupling constant with iridium nucleus of g_3 component.

ligands, arranged in the equatorial plane of a trigonal bipyramid, are equivalent, and since the oxidation process is reversible retention of the original structure would be expected in the oxidized form. The conclusion was checked by IR measurements of ν(CO) in $[HIr(CO)(PPh_3)_3]^+$ and $[DIr(CO)(PPh_3)_3]^+$, electrogenerated as in ref. 6, in order to see whether a substantial isotope effect [19] could be observed and hence whether a mutual *trans* disposition of CO and R (H in this case) could be assigned to the d^7 configuration too. The carbonyl stretching frequency was shifted by 27 cm^{-1} towards higher frequencies upon deuteration, the shift also observed for the unoxidized parent compounds.

The apparent disagreements in the structural data can be resolved if it is assumed that the one-electron oxidation induces two phosphines in the trigonal plane to assume a mutual *trans* disposition, thus making the third distinct. This would result in a flat tetragonal pyramid with one phosphine in the apical position and the unpaired electron located in the d_{z^2} orbital. From another point of view, the structure could be regarded as a distorted octahedron with a vacant site, conceivably occupied by a counter-anion in a tight ion-pair. On the other hand, similar involvement of even less weakly coordinating ("innocent") anions (e.g., PF_6^-) in octahedral geometry are known [24], although in those cases true coordination, rather than ion-pairing, is present because of the even (d^6) electronic configuration.

These observations permit better understanding of some features of the further one-electron oxidation of the d^7 species, considered in the next section.

Electro-oxidation of $[Ir(R)(CO)(PPh_3)_3]^+$

Exhaustive controlled potential electrolysis of the d^7 complexes at −20°C (one electron/mol) produces colorless solutions which show ill-defined two-electron irreversible reduction processes, already evident in the cyclic voltammogram of the d^7 species on reversal of the scan after oxidative process III (process IV in Fig. 2). It was not possible to isolate the products because there is decomposition at room temperature. For the methyl compounds it was found that PPh_3 attacks the strongly electrophilic species to give $[CH_3PPh_3]^+$ and $[Ir(CO)(PPh_3)_3]^+$. The nature of these products could be determined by inhibiting the decomposition by coordination with chloride ions. Thus, when tetrabutylammonium chloride was added to the cold anolyte and the solution heated to room temperature then evaporated to dryness, and the white residue washed with methanol (to dissolve the supporting electrolyte and the excess of phosphine) then dried under vacuum, the products were identified as $Ir(Cl)_2(R)(CO)(PPh_3)_2$ (elemental analysis, IR and ^1H NMR spectra). In particu-

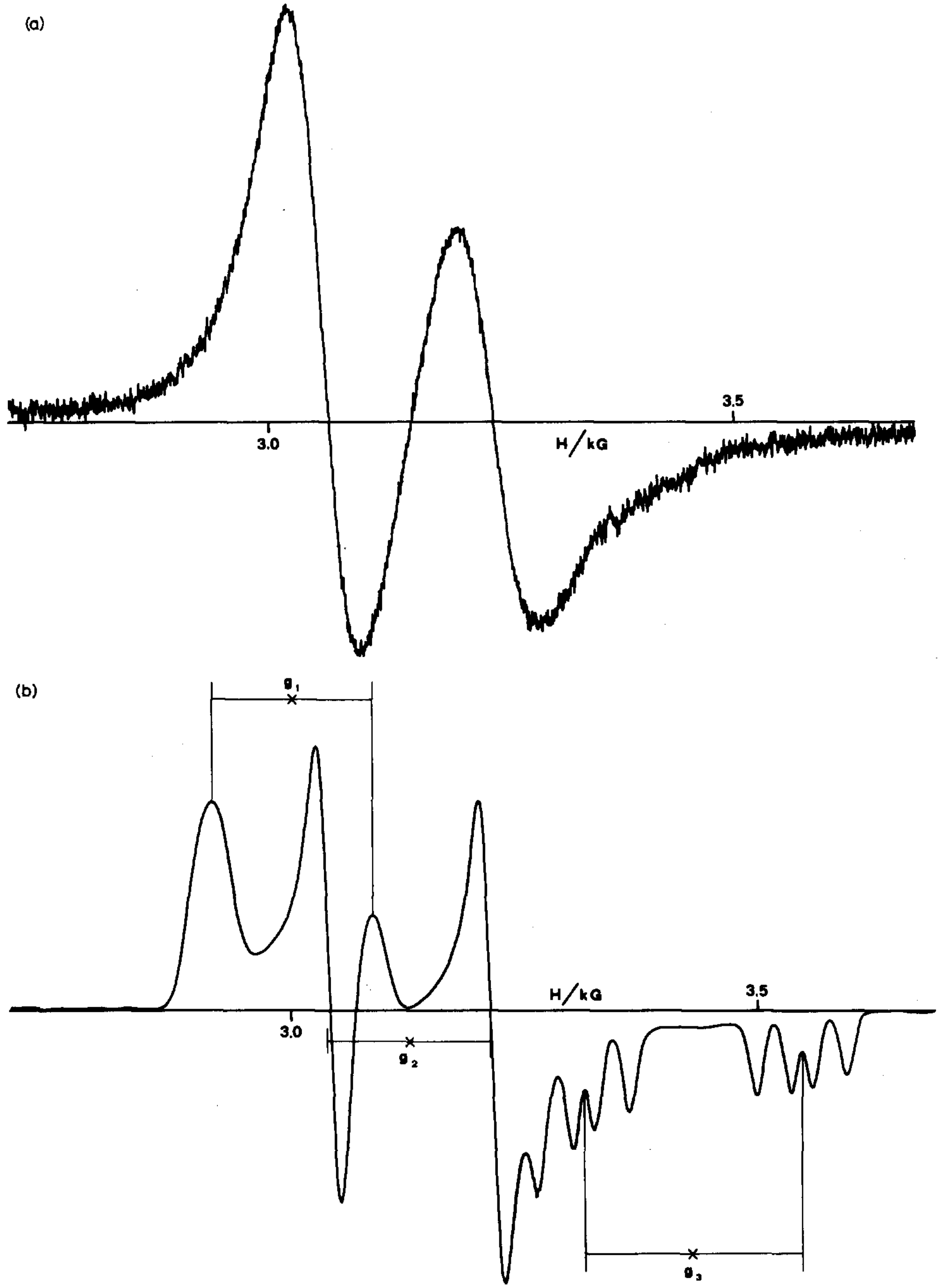
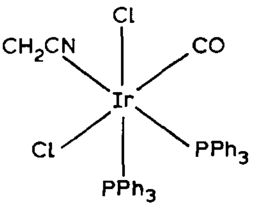
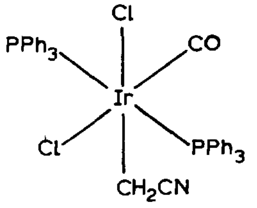


Fig. 3. ESR spectrum of $[Ir(C_6H_5)(CO)(PPh_3)_3]^+$ 1.0 m*M* in DCE 0.2 *M* TBAP, 0.1 *M* PPh_3 at 298 K (a) and 120 K (b).

lar, in addition to signals attributable to coordinated PPh_3 and to the organic radical, the IR spectra showed a single $\nu(CO)$ band centered around 2050 cm^{-1} and two bands in the low-frequency region (350–250 cm^{-1}) assigned to Ir–Cl stretching modes.The values for the methyl and phenyl derivatives agree with those reported in the literature [25]. For the previously unknown cyanomethyl compound the values are 2062 (ν(CO)), 2209 (ν(CN)), 310 and 293 (ν(IrCl)) cm^{-1} in a KI disc. The band at 310 cm^{-1} is readily assigned to the stretching mode of a chlorine atom *trans* to the carbonyl group [26], but attribution of the other band to Cl *trans* to PPh_3 (structure) A) or CH_2CN (**B**) is uncertain. The ^{1}H NMR data do not help since the 1/2/1 triplet observed for the methylene group (τ 7.91, J(PH) ca. 4 Hz) suggests that the phosphines are *cis* to CH_2CN (**B**), whereas the presence of only one signal in the aromatic region suggests a mutual *cis* disposition (A) [27,28].



(A)



(B)

The observation of slow isomerization in the electrolyte solution, indicated by the IR spectra, suggested that the initially formed complex is in configuration A, which is unstable because of the *cis* disposition of the bulky phosphines. Thus the compound isolated after complete transformation (1 h at 80°C) had the IR bands at 2053, 2211, 310 and 272 cm^{-1}, and the NMR spectrum displayed not only a 1/2/1 methylene triplet (τ 8.50, J(PH) 5.6 Hz) but also two phenyl signals at τ 2.10 and 2.56, consistent with *trans* structure **B** [27,28].

The main conclusion is that oxidation of the d^7 complex produces a d^6 species with retention of the organometallic (CO and R) and, conceivably, the phosphine environment. Hence, the fast chemical reaction following electron transfer (which cannot be assigned to attachment of PPh_3 to the formed d^6 species since the voltammetric response was wholly independent of the phosphine concentration) could tentatively be identified as the transformation of the tight ion-pair between the d^7 cation and the perchlorate counter-anion into a coordinatively bonded species.

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References

1 W.A. Bennett and P.A. Longstaff, J. Am. Chem. Soc., 91 (1969) 6266.
2 F.G. Moers, J.A.M. De Jong and P.M.H. Beaumont, J. Inorg. Nucl. Chem., 35 (1973) 1915.
3 R. Mason, K.M. Thomas, H.D. Empsall, S.R. Fletcher, P.N. Heys, E.M. Hyde, C.E. Jones and B.L. Shaw, J. Chem. Soc. Chem. Comm., (1974) 612.
4 A. Araneo, F. Morazzoni and T. Napoletano, J. Chem. Soc. Dalton Trans., (1975) 2039.
5 H.L.M. Van Gaal, J.M.J. Verlaak and T. Posno, Inorg. Chim. Acta, 23 (1977) 43.
6 G. Pilloni, G. Schiavon, G. Zotti and S. Zecchin, J. Organomet. Chem., 134 (1977) 305.
7 G. Valentini, G. Braca, G. Sbrana and A. Colligiani, Inorg. Chim. Acta, 69 (1983) 221.
8 G.W. Parshall, Homogeneous Catalysis, Wiley, New York, 1980, p. 13.
9 L. Dahlenburg and R. Nast, J. Organomet. Chem., 71 (1974) C49.
10 S. Zecchin, G. Zotti and G. Pilloni, J. Organomet. Chem., 235 (1982) 353.

11 M.D. Rausch and G.A. Moser, Inorg. Chem., 13 (1974) 11.
12 L. Dahlenburg and R. Nast, J. Organomet. Chem., 110 (1976) 395.
13 G. Yagupsky and G. Wilkinson, J. Chem. Soc. A, (1969) 725.
14 C.A. Reed and W.R. Roper, J. Chem. Soc. Dalton, (1973) 1365.
15 G. Zotti, S. Zecchin and G. Pilloni, J. Electroanal. Chem., 175 (1984) 241.
16 R.S. Nicholson and I. Shain, Anal. Chem., 36 (1964) 706.
17 M. Drouin and J.F. Harrod, Inorg. Chem., 22 (1983) 999.
18 F. Mirzaei and L. Dahlenburg, J. Organomet. Chem., 173 (1979) 325 and ref. therein.
19 J.P. Jesson in Transition Metal Hydrides, Marcel Dekker, New York, 1971, Chap. 4.
20 L. Vaska and J. Peone, Jr., Chem. Comm., (1971) 418.
21 G. Zotti, S. Zecchin and G. Pilloni, J. Organomet. Chem., 246 (1983) 61.
22 G. Oehme, K.C. Rober and H. Pracejus, J. Organomet. Chem., 105 (1976) 127.
23 M.L.H. Green, in Organometallic Compounds, Methuen Ltd., London, 1968, Vol. 2, p. 220.
24 F.J. Regina and A. Wojcicki, Inorg. Chem., 19 (1980) 3803 and ref. therein.
25 M. Kubota and D.M. Blake, J. Am. Chem. Soc., 93 (1971) 1368.
26 J.M. Jenkins and B.L. Shaw, J. Chem. Soc., (1965) 6789.
27 J.H. Nelson, A.W. Verstuyft, J.D. Kelly and H.B. Jonassen, Inorg. Chem., 13 (1974) 27.
28 K. Suzuki, J. Ooyama and M. Sakurai, Bull. Chem. Soc. Jpn., 49 (1976) 464.