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Electrochemical reduction of carbon dioxide in the presence of $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$

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Abstract

The electrochemical behaviour of $MCl(CO)(PPh_3)_2$ complexes (M = Rh and Ir) in dimethylformamide has been studied. The irreversible reduction of these complexes proceeds by a two-electron step. $IrCl(CO)(PPh_3)_2$ is an efficient homogeneous catalyst for the electrochemical reduction of CO_2 to CO and formic acid.

Introduction

Phosphine carbonyl-rhodium and -iridium complexes have been the subject of extensive studies largely because of their catalytic activity [1,2]. They are effective catalysts in reduction of C=C bonds, in hydroformylation, hydrosilylation etc. [2,3]. Carbon dioxide is one of the most promising substrates for the synthesis of the organic compounds [4,5]. The electrochemical reduction of CO_2 normally requires large negative overvoltages (e.g. in dimethylformamide -2.21 V and in MeCN -2.1 V vs. SCE [6]). There have been a few reports of the use of transition metal complexes as electrocatalysts for CO_2 reduction in homogeneous solutions involving $ReCl(CO)_3$ (bpy) (bpy = 2,2′-bipyridine) [7], $[Rh(diphos)_2]Cl$ [8], polypyridyl complexes of Rh and Ru [9], $[Ru(CO)_2(bpy)_2]^{2+}$ [10,11].

The phosphine-rhodium and -iridium complexes $M(OH)CO(PPh_3)_2$ react with carbon dioxide to produce the $[M(OH)CO(CO_2)(PPh_3)_2]$ complexes [4a]. In the presence of Lewis acids $[RhCl(CO)(PPh_3)_2]$ can catalyze the reduction of carbon dioxide [5], and so examination of the catalytic properties of $MCl(CO)(PPh_3)_2$ (M = Ir, Rh) in electrochemical reduction of CO_2 seemed to us to be of interest.

The complexes $MX(CO)(PPh_3)_2$ (M = Rh, Ir) undergo irreversible two-electron reduction [14–16] (eq. 1); the product of the reduction, a Rh^{-I} complex, reacts with

$$MCl(CO)(PPh_3)_2 + PPh_3 \xrightarrow{+(2e^-)} [M(CO)(PPh_3)_3]^- + Cl^- \qquad (1)$$

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the unreduced rhodium(I) complex to give a diamagnetic rhodium(0) dimer [14] (eq. 2 and 3).

$$[Rh(CO)(PPh_3)_2]^- + RhCl(CO)(PPh_3)_2 + PPh_3 \rightarrow Rh_2(CO)_2(PPh_3)_6 + Cl^- \quad (2)$$

$$2Rh(CO)(PPh_3)_3 \xrightarrow{+(2e^-)} 2[Rh(CO)(PPh_3)_2]^- \quad (3)$$

Electrochemical reduction of $[M(CO)(PPh_3)_3]^+$ (M = Rh, Ir) complexes [15] in weakly coordinating solvents ($MeOCH_2CH_2OMe$), in two one-electron processes produced $[M(CO)(PPh_3)_3]$ and then $[M(CO)(PPh_3)_3]^-$. In strongly coordinating solvents (MeCN) a two-electron reduction occurs to give $[M(CO)(PPh_3)_3]^-$. The half-wave potentials for the two-electron reduction of $MX(CO)(PPh_3)_3$ in CH_3CN in the presence of the excess of X^- are a linear function of the electron-donor abilities of ligands X^- [16].

The voltammetric measurements revealed that both the rhodium and iridium compounds in the presence of an excess of the phosphine undergo irreversible two-electron reduction to give $[M(CO)(PPh_3)_3]^-$ [14].

The electrochemical behaviour of $MX(CO)(PPh_3)_2$ complexes in DMF has not previously been investigated. Our results described below indicate that it is similar to that in the other solvents.

Experimental

$RhCl(CO)(PPh_3)_2$ [12] and $IrCl(CO)(PPh_3)_2$ [13] were prepared by published methods. The supporting electrolyte, tetra-n-butylammonium tetrafluoroborate (Fluka) was recrystallized from acetone/ether and dried in vacuo. Triphenylphosphine (Fluka) was recrystallized from n-hexane. *N,N'*-Dimethylformamide (DMF) was dried over 4A molecular sieves and distilled over the CaH_2 under argon. Demineralized water was triply distilled. Analytical quality mercury was purchased from POCh (Gliwice) and used as received. The cyclic voltammetry measurements were carried out with a PA4 apparatus (Laboratorni Pristroje) in the three electrode mode. The working electrode was a static mercury electrode (m_{Hg} 0.136 g) or the planar platinum electrode ($s = 0.98$ mm^2) with the surface restored periodically. Platinum wire served as the counter-electrode. Potentials were measured relative to the saturated calomel electrode (SCE) which was separated from electrolyte by a bridge filled with DMF (0.1 *M* $n\text{-}Bu_4NBF_4$); the solution in the bridge was periodically exchanged. Concentrations of $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$ in the electrolyte were 2×10^{-4}–1×10^{-3} *M* and the potential sweep rate was varied within the range 20–500 mV s^{-1}. During the reduction of carbon dioxide the argon-deaerated solutions were saturated with carbon dioxide. The measurements were repeated after addition of 5 and 10% of H_2O to the electrolyte.

Coulometric measurements at the controlled potential of the working electrode were made with an OH-404 apparatus (Radelkis) The coulometric electrolysis and CO_2 reduction in the solutions were carried out in an electrolyzer with cells separated by a double glass sinter (G4). The cathode was the mercury ($s = 10$ cm^2) stirred magnetically; the anode was platinum foil ($s = 6$ cm^2). The working electrode (Hg) potential was measured relative to the SCE. The cathode cell was connected to the gas chromatograph. Before each measurement the electrolyte was saturated with argon for 30 min, the solid rhodium and iridium complexes were added, and argon was passed for another 30 min. The coulometric reduction of carbon dioxide was carried out after complete removal of argon by CO_2 (as in cyclic voltammetry experiments). The experiments were performed at 20 ± 1° C. The EPR studies of the coulometrically electrolyzed solutions were carried out under argon at room temperature and liquid nitrogen temperature on a JEOL 3JSMX spectrophotometer.

Results and discussion

The cyclic voltammograms revealed that two-electron reduction of $[RhCl(CO)(PPh_3)_2]$ and $[IrCl(CO)(PPh_3)_2]$ in DMF (peaks I, Fig. 1 and 2) leads to relatively kinetically stable Rh^{-I} and less stable Ir^{-1} complexes (Tables 1 and 2). Diagnostic criteria for cyclic voltammetry [17] indicate that two-electron reduction of $[MCl(CO)(PPh_3)_2]$ complexes is irreversible.

The rather similar behaviour in reduction of both complexes at the mercury and platinum electrode in the first stage of the reaction can be represented as shown in eq. 4.

$$[MCl(CO)(PPh_3)_2] + 2e^- \xrightarrow{+DMF} [M(CO)(PPh_3)_2DMF]^- + Cl^- \qquad (4)$$

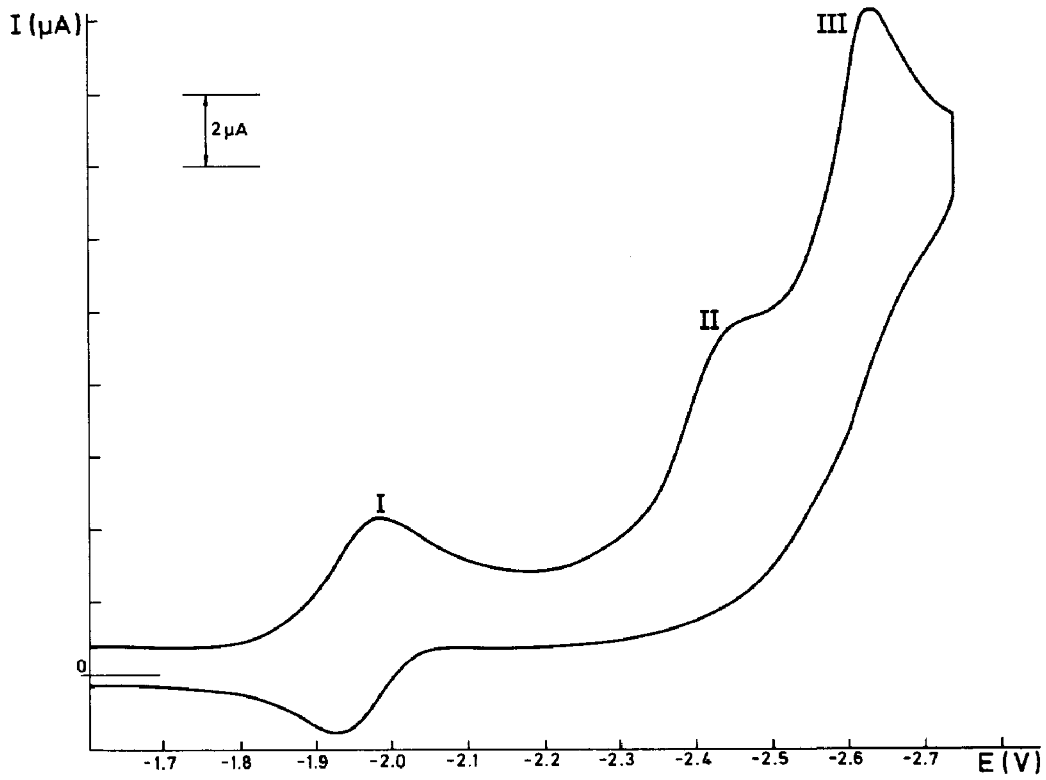

Fig. 1. Cyclic voltammogram for the reduction of 4×10^{-4} *M* $[RhCl(CO)(PPh_3)_2]$ in DMF (0.1 *M* $n\text{-}Bu_4NBF_4$) at Hg vs. SCE, v 0.2 V s^{-1}.

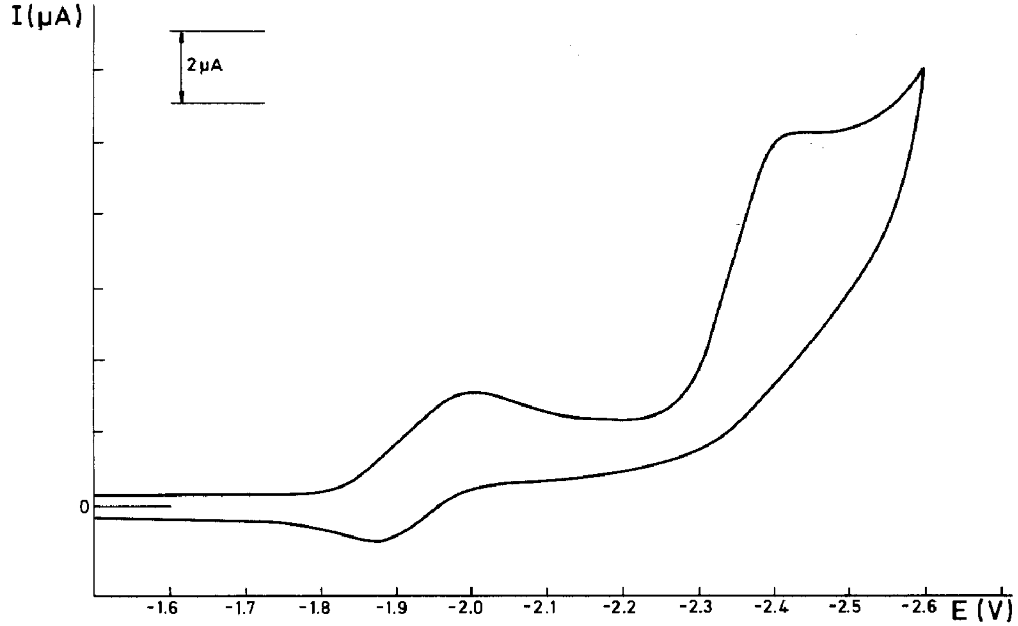

Fig. 2. Cyclic voltammogram for the reduction of 4×10^{-4} *M* [IrCl(CO)(PPh$_3$)$_2$] in DMF (0.1 *M* n-Bu$_4$NBF$_4$) at Hg vs. SCE, v 0.2 V s^{-1}.

Table 1

Voltammetric data for the reduction waves of [RhCl(CO)(PPh$_3$)$_2$] in DMF (0.1 *M* n-Bu$_4$NBF$_4$)

v (V s^{-1})	$-E^{\mathrm{I}}_{\mathrm{p,c}}$ (V)	$-E^{\circ\,a}$ (V)	$i_{\mathrm{p,c}}v^{-1/2}$ [μA V$^{-1/2}$s$^{1/2}$]	$i_{\mathrm{p,a}}/i_{\mathrm{p,c}}$	$-E^{\mathrm{II}}_{\mathrm{p,c}}$ (V)	$-E^{\mathrm{III}}_{\mathrm{p,c}}$ (V)
0.020	1.975	1.945	8.50	0.92	2.425	2.640
0.050	1.980	1.945	8.63	0.73	2.430	2.620
0.100	1.983	1.950	9.03	0.68	2.438	2.630
0.200	1.990	1.955	9.09	0.62	2.460	2.645
0.500	2.005	1.960	8.96	0.61	2.485	2.675

[a] E° = formal redox potential, obtained from $E_{\mathrm{p,c}}$ and $E_{\mathrm{p,a}}$ vs. SCE.

Table 2

Voltammetric data for the reduction waves of [IrCl(CO)(PPh$_3$)$_2$] in DMF (0.1 *M* n-Bu$_4$NBF$_4$)

v (V s^{-1})	$-E^{\mathrm{I}}_{\mathrm{p,c}}$ (V)	$-E^{\circ\,a}$ (V)	$i_{\mathrm{p,c}}v^{-1/2}$ (μA V$^{-1/2}$ s$^{1/2}$)	$i_{\mathrm{p,a}}/i_{\mathrm{p,c}}$	$-E^{\mathrm{II}}_{\mathrm{p,c}}$ (V)
0.020	1.980	1.940	6.12	0.98	2.438
0.050	1.987	1.940	5.90	0.77	2.440
0.100	1.993	1.943	5.80	0.61	2.448
0.200	2.005	1.950	5.90	0.44	2.477
0.500	2.015	1.960	5.80	0.41	2.495

[a] E° = formal redox potential, obtained from $E_{\mathrm{p,c}}$ and $E_{\mathrm{p,a}}$ vs. SCE.

The reactivity of the iridium complex is greater than that of its rhodium analogue. It reacts with a proton coming either from electrolytic decomposition of the n-Bu_4NBF_4 salt [9,18] or from the trace amounts of water absorbed by the electrolyte during the measurements, as indicated in eq. 5.

$$[Ir(CO)(PPh_3)_2DMF]^- + H^+ \rightleftarrows [IrH(CO)(PPh_3)_2(DMF)] \qquad (5)$$

The conclusion that $[M(CO)(PPh_3)_2DMF]^-$ was formed was confirmed by the coulometric reduction of both complexes at the controlled potential. Reduction of $RhCl(CO)(PPh_3)_2$ at E −2.2 V) gave an n_{app} value (Faradays per mole of reactant consumed) of 2.1, and the value for $IrCl(CO)(PPh_3)_2$ reduced at E −2.1 V was 1.9. The ESR spectra revealed the formation of paramagnetic species probably iridium(0) or iridium(II) complexes, during the coulometric reduction at E −2.1 V (in the presence of a signal with $g = 1.93$). The subsequent reduction of both complexes was observed below E −2.4 V (vs. SCE), (peaks II, Fig. 1, Table 1 and peak II, Fig. 2, Table 2). These processes probably involve irreversible reduction of both complexes, leading to the formation of Rh^{-III} and Ir^{-III} compounds.

The results of the electrochemical and EPR measurements revealed that during the reduction of $IrCl(CO)(PPh_3)_2$ reactions 6 and 7 take place

$$IrCl(CO)(PPh_3)_2 + 2e^- \xrightarrow{DMF} [Ir(CO)(PPh_3)_2(DMF)]^- + Cl^- \qquad (6)$$

$$\begin{array}{r}[Ir(CO)(PPh_3)_2(DMF)]^- + IrCl(CO)(PPh_3)_2 \rightarrow Ir_2(CO)_2(PPh_3)_4(DMF)_2 + Cl^- \\ \uparrow\downarrow \qquad\qquad \\ 2Ir(CO)(PPh_3)_2(DMF) \qquad \\ (7)\end{array}$$

The monomeric iridium(0) complex (electronic configuration d^9) could be formed in reaction between the Ir^{-I} compound and the excess of the Ir^I complex. The formation of the hydrido and hydroxo complexes may also involve reaction of the Ir^0 dimer with water (homolytic splitting of H_2O) or the result of protonation of the Ir^0 monomer and Ir^{-I} complex.

$$Ir(CO)_2(PPh_3)_4(DMF)_2 + H_2O \rightarrow$$
$$IrH(CO)(PPh_3)_2(DMF) + Ir(OH)(CO)(PPh_3)_2(DMF) \qquad (8)$$

$$Ir(CO)(PPh_3)_2(DMF) + H^+ \rightarrow [IrH(CO)(PPh_3)_2(DMF)]^+ \qquad (9)$$

$$[IrH(CO)(PPh_3)_2(DMF)]^+ + Ir(CO)(PPh_3)_2(DMF) \rightarrow$$
$$IrH(CO)(PPh_3)_2(DMF) + [Ir(CO)(PPh_3)_2(DMF)]^+ \qquad (10)$$

$$[Ir(CO)(PPh_3)_2(DMF)]^+ + OH^- \rightarrow Ir(OH)(CO)(PPh_3)_2(DMF) \qquad (11)$$

The hydroxo complex reacts readily with CO_2 to give the the complex $Ir(OH)(CO)(CO_2)(PPh_3)_2$, which has been reported previously [4a,5].

The cyclic voltammograms carried out under a carbon dioxide atmosphere showed that in DMF (0.1 M n-Bu_4NBF_4) the $RhCl(CO)(PPh_3)_2$ complex is not a catalyst for CO_2 reduction. In contrast, the $IrCl(CO)(PPh_3)_2$ complex does effectively catalyze the reduction of carbon dioxide to carbon monoxide. The voltammograms of $IrCl(CO)(PPh_3)_2$ in DMF (0.1 M n-Bu_4NBF_4) under CO_2 (Fig. 3, curve

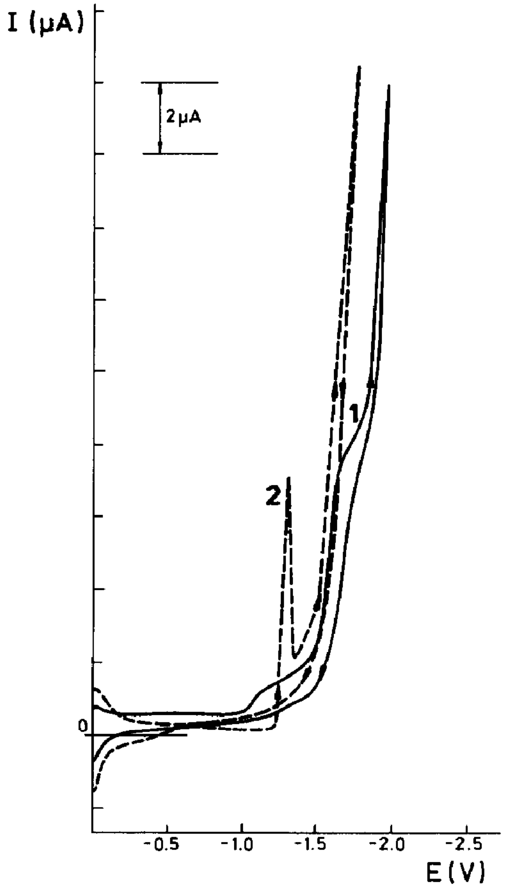

Fig. 3. The cyclic voltammograms for the reduction of CO_2 in DMF (0.1 *M* n-Bu_4NBF_4) at Hg electrode vs. SCE containing 4×10^{-4} *M* [$IrCl(CO)(PPh_3)_2$], at 20±1°C (———) (1); after 10% H_2O added (- - - -) (2), v 0.1 V s^{-1}.

1) showed a large increase in the cathode current in the region of the carbon dioxide reduction potential and a positive shift of the carbon dioxide reduction potential by c.a. 700 mV. Similar behaviour was observed in catalysis of CO_2 reduction by $Rh(dppe)_2Cl$ [8].

Replacement of CO_2 by argon caused the regeneration of a shape of voltammetric curves to the shape shown in Fig. 2. The CO_2 → Ar → CO_2 exchange process was repeated several times over several hours, during which the $IrCl(CO)(PPh_3)_2$ complex retained its catalytic activity. In the coulometric reduction of CO_2 in the presence of the iridium complex only carbon monoxide was chromatographically detetected in the gas phase (exp. 1, Table 3) and formic acid was found in the electrolyte. Its presence was confirmed by converting it into its methyl ester by treatment with methanol. The yield of the carbon dioxide reduction increased with increase in the water content (5 and 10% H_2O) of the solution (exp. 2, 3, Table 3, Fig. 3, curve 2). In this case, however, along with carbon monoxide, a trace of hydrogen was detected chromatographically. Hydrogen was detected when the electrolysis was conducted in the absence of CO_2 (Table 3, exp. 2, 3, under argon).

Table 3

Electroreduction of CO_2 catalyzed by $[IrCl(CO)(PPh_3)_2]^{a,b}$

Exp.	Solution composition	Electrolysis time (h)	Volume of CO produced (cm^3)	Coulombs consumed
1	DMF/0.1 *M* n-Bu_4BF_4	1	0.85	7.8
		2.5	1.9	13.1
		5.0	2.7	25.8
2	DMF/0.1 *M* n-Bu_4BF_4 +5% H_2O	1	1.5	12.9
		2.5	3.0	29.0
		5.0	5.5	58.2
3	DMF/0.1 *M* n-Bu_4BF_4 +10% H_2O	1	2.0	16.6
		2.5	3.5	45.0
		5.0	8.5	82.0

[a] CO_2 saturated solution (50 cm^3) containing 5×10^{-4} *M* $[IrCl(CO)(PPh_3)_2]$. The total volume occupied by the gas in the electrolysis cell was 120 cm^3. The gas phase were analysed by gas chromatography. [b] Carbon dioxide was reduced at potentials: −1.55 V (exp. 1); −1.45 V (exp. 2); −1.30 V (exp. 3) vs. SCE at 20±1° C.

Formation of the hydride and hydroxo Ir^I complexes during the electrolytic reduction of $IrCl(CO)(PPh_3)_2$ accounts for the effective electrocatalytic reduction of carbon dioxide because the hydroxo complex coordinates CO_2 while the hydrido complex gives the product of insertion of CO_2 into the Ir–H bond, $Ir(OOCH)(CO)(PPh_3)_2$. This provides a good explanation for the formation of formic acid as well as CO in the electrochemical reduction of CO_2 in the presence of $IrCl(CO)(PPh_3)_2$ (Table 3). Insertion of CO_2 into the M–H bond has been observed for many hydride transition metal complexes, especially elements of groups 8, 9, and 10 [4,5].

Acknowledgement

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References

1 R.P. Hughes, in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 5, Chapter 35; G.J. Leigh, R.L. Richards, ibid., Vol. 5, Chapter 36.

2 R.S. Dickson, Organometallic Chemistry of Rhodium and Iridium, Academic Press, London-New York, 1983.

3 C. Masters, Homogeneous Transition-metal Catalysis, Chapman and Hall, London, 1981; J. Falbe (Ed.), New Synthesis with Carbon Monoxide, Springer Verlag Berlin, 1980.

4 (a) D.A. Palmer, R. van Eldik, Chem. Rev., 83 (1983) 651; (b) M.E. Volpin, I.S. Kolomnikov, Organomet. React., 5 (1975) 313.

5 A.L. Lapidus, M.M. Savelev, Uspekhi Khimi, 53 (1984) 925.

6 C. Amatore, J.-M. Saveant, J. Am. Chem. Soc., 103 (1981) 5021.

7 J. Hawecker, J.-M. Lehn, R. Ziessel, J. Chem. Soc., Chem. Commun., (1984) 328.

8 S. Slater, J.H. Wagenknecht, J. Am. Chem. Soc., 106 (1984) 5367.

9 C.M. Bolinger, B.P. Sullivan, D. Conrad, J.A. Gilbert, N. Story, T.J. Mayer, J. Chem. Soc., Chem. Commun., (1985) 796.

10 H. Ishida, H. Tanaka, K. Tanaka, T. Tanaka, J. Chem. Soc., Chem. Commun., (1987) 131.

11 D.L. DuBois, A. Miedaner, J. Am. Chem. Soc., 109 (1987) 113.
12 J. McCleverty, G. Wilkinson, Inorg. Synth., 8 (1966) 214.
13 J. Peone Jr., L. Vaska, Angew. Chem. Int. Ed. Engl., 10 (1971) 511.
14 G. Pilloni, S. Valcher, M. Martelli, J. Electroanal. Chem., 40 (1972) 63.
15 G. Zotti, S. Zecchin, G. Pilloni, J. Organomet. Chem., 246 (1983) 61.
16 G. Schiavon, S. Zecchin, G. Pilloni, M. Martelli, J. Inorg. Nucl. Chem., 39 (1977) 115.
17 R.S. Nicholson, I. Shain, Anal. Chem., 36 (1964) 706.
18 (a) M. Tezuka, Y. Yajima, A. Tsuchija, J. Am. Chem. Soc., 104 (1982) 6834; (b) S. Meshitsuka, M. Ichikawa, K. Tamaru, J. Chem. Soc., Chem. Commun., (1974) 158.