Kinetics and Mechanism of the Reaction between Chromium(II) and 1,2-Bis(2-pyridyl)ethylene in Acidic Aqueous Solutions

Athinoula L. Petrou
Laboratory of Inorganic Chemistry, University of Athens, Panepistimiopolis, Kouponia, Athens 15701, Greece

The reduction of 1,2-bis(2-pyridyl)ethylene by chromium(II) perchlorate in aqueous perchloric acid to the corresponding dipyridylethane has been shown to take place through a σ-bonded organochromium intermediate. The acidolysis of this complex takes place in two stages, the first of which has an observed rate constant $k_{obs} = k_0 + k_1[H^+]$. The corresponding activation parameters are $\Delta H_0^‡ = 92.0 \pm 1.6$ kJ mol^{-1}, $\Delta S_0^‡ = -15.1 \pm 4.9$ J K^{-1} mol^{-1}, $\Delta H_1^‡ = 142 \pm 3$ kJ mol^{-1}, and $\Delta S_1^‡ = 142 \pm 7$ J K^{-1} mol^{-1}. The experimental results are discussed in terms of the nature of the lowest unoccupied molecular orbital of the substrate, which is 'ethylenic'.

Electron-transfer reactions through conjugated systems have been investigated for several substrates and metal ions[1a,b] and selective stoichiometric reductions of organic functional groups have been achieved.[1c] In some cases, in competition with electron transfer to the ligands, proton addition leads to stoichiometric or catalytic electron transfer to the solvent (water) and formation of dihydrogen, especially when accumulation of negative charge on the metal takes place.[1d]

Direct attack on the carbon of a double bond has been proposed,[2] leading to organometallic ion radicals during reactions of chromium(II), vanadium(II), europium(II) and titanium(III) ions with unsaturated carboxylic and α-keto-acids in acidic aqueous media. These ion radicals undergo transformations *via* nucleophilic attack on carbon by a second metal ion. Electron transfer from chromium(II) to a double bond has been studied for unsaturated compounds with a polar terminal group (mainly carboxylic) for promoting the attack of the metal ion at the substrate.[3] On the other hand it has been also proposed[4] that at least partial attack by chromium(II) directly on the carbon–carbon double bond leads to hydrogenation of olefinic compounds with polar substituents.

Previous studies on pyridineacrylic acids have shown that the reduction of the side-chain double bond takes place *via* the formation of σ-bonded organochromium complexes[3] and acidolysis of the chromium–carbon bond and subsequent metathesis produced an intermediate with a chromium–oxygen (carboxyl) bond.[5]

In order to investigate the role of the carboxylic group in the attack of chromium(II) at a substrate, I studied the reduction of 1,2-bis(2-pyridyl)ethylene (bpe).[6] This substrate is formally derived from pyridineacrylic acid whereby the carboxylic group is replaced by a pyridine. The reduction of isomeric dipyridylethylenes to the corresponding dipyridylethanes has been studied polarographically by Volke and Holubek.[7]

Experimental

Reagents and Materials.—All reagents used were of analytical grade. Stock solutions of chromium(II) (0.02–0.05 mol dm^{-3}) in 1 mol dm^{-3} perchloric acid were prepared by reduction of chromium(III) electrolytically at a mercury cathode. 1,2-Bis(2-pyridyl)ethylene (Aldrich), used as received, was dissolved in acidic ($HClO_4$) aqueous solutions in concentrations ranging from 0.007 to 0.01 mol dm^{-3}. These solutions were used shortly after preparation to avoid photochemically induced transformation and decomposition reactions.[8,9] All experiments were carried out under rigorously air-free conditions. The ionic strength was kept constant by addition of $NaClO_4$. The various chromium(III) complexes were isolated from the reaction mixture by ion-exchange chromatography using an SP-Sephadex C-25 resin.

Kinetic Experiments.—The acidolysis kinetics of the organochromium complex were followed at three different wavelengths (323, 290 and 265 nm) yielding identical results. The absorbances were recorded on a Hitachi Model 100–60 Spectrophotometer. First-order rate constants were estimated with a non-linear least-squares fit determining A_∞ and k. Analysis according to activated complex theory gives the activation parameters $\Delta H^‡$ and $\Delta S^‡$. Uncertainties were estimated by fitting the parametric equation to experimental k values which had the highest experimental errors. At times which are longer than three to four half-lives of the first reaction, a second reaction involving Cr–N bond hydrolysis sets in, causing further absorbance changes. The electronic spectra were recorded on a Cary-17 spectrophotometer.

Analytical Methods.—Chromium(III) was determined spectrophotometrically as chromate ($\varepsilon_{373} = 4815 \pm 15$ dm^3 mol^{-1} cm^{-1}), after decomposition of the complexes and oxidation with alkaline peroxide.[10]

Results and Discussion

At pH < 2.5 both nitrogens of bpe are protonated.[11] All the experiments in this work were conducted at pH < 2, hence the substrate exists as H_2bpe^{2+}. Its reaction with Cr^{II} proceeds through several steps during which formation and transformation of various intermediates * take place. However, because of protonation the pyridine nitrogens are effectively blocked and the first attack will not be on them.

The formation of a red complex, **1**, from an initially green

---

* The formation and subsequent transformation of the originally formed green intermediates proceeds through a complicated sequence of reactions.

solution is observed in the early stages of reaction (a few minutes). This complex undergoes acidolysis to give a violet species, shown to be nitrogen-bonded [1-(2-pyridinio)-2-(2-pyridyl)ethane]chromium(III) **2**, which hydrolyses in a slow step to produce Cr^{3+} and 1,2-bis(2-pyridyl)ethane.

Quantitative data from ion-exchange separations confirm a stoichiometry of 2:1 for the reaction of Cr^{2+} with H_2bpe^{2+}, in accord with the expected transfer of two electrons from Cr^{2+} to each unsaturated double bond. The red complex is eluted from the resin immediately after the Cr^{2+} and Cr^{3+} and before the violet species. The eluent acidity and total ion concentration indicates a species on the resin having a 3+ charge. The UV/VIS spectrum (Fig. 1) exhibits maxima at 550, 323 and 265 and a shoulder at 680 nm. The first peak and the shoulder are attributed to d $\longrightarrow$ d transitions and the other two peaks to metal-to-ligand charge-transfer. The acidolysis of this σ-bonded organochromium complex occurs in two stages. The first stage is characterised by an absorbance decrease at 323 nm and an absorbance increase at 265 nm (Fig. 2). These changes are attributed to the formation of a nitrogen-bound chromium(III)–dipyridylethane. This is followed by a very slow absorbance change which was not studied in detail. The formulation of the red complex as an organochromium compound is supported by the UV/VIS spectra, the decomposition kinetics, and the nature of the acidolysis product.

The qualitative characteristics of the spectra of the organochromium **1** and the [1-(2-pyridinio)-2-(2-pyridyl)ethane]chromium(III) species **2** do not change with changing hydrogen-ion concentration; only the values of the absorptivities change. It must be pointed out that there is no evidence for more than one reactant, protonated form or product. Fig. 3 shows the dependence of A^0_{265}/A^0_{323} and $A^\infty_{265}/A^\infty_{323}$ on acid concentration.

The kinetics of the first stage of the acidolysis followed a first-order rate law. The first-order rate constant, measured at 17.0, 20.0, 22.5, 25.0 and 30.0 °C (Fig. 4), was found to be acid dependent [equation (1)]. Below 17.0 °C the slope of the plot

$$k_{obs} = k_0 + k_1[H^+] \qquad (1)$$

Table 1 Kinetic data for the acidolysis of complex **1** *

10^3 [Cr^{2+}(aq)]/mol dm^{-3}	$10^4 k_{obs}$/s^{-1}
0.00	1.08
2.44	1.10
4.40	1.06
5.28	1.01
6.16	1.01
7.04	1.08

* Conditions: 25 °C, I = 3.70 mol dm^{-3}, [H^+] = 1 mol dm^{-3}, [Cr^{3+}(aq)] = 8.56 × 10^{-3} mol dm^{-3}.

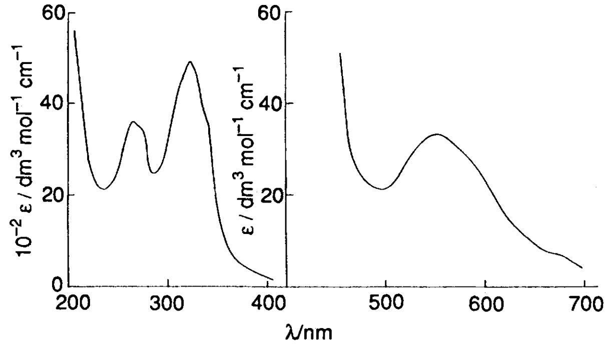


Fig. 1 The UV/VIS spectrum of the organochromium complex **1** formed during the reaction of H_2bpe^{2+} and Cr^{2+}(aq) in $HClO_4$

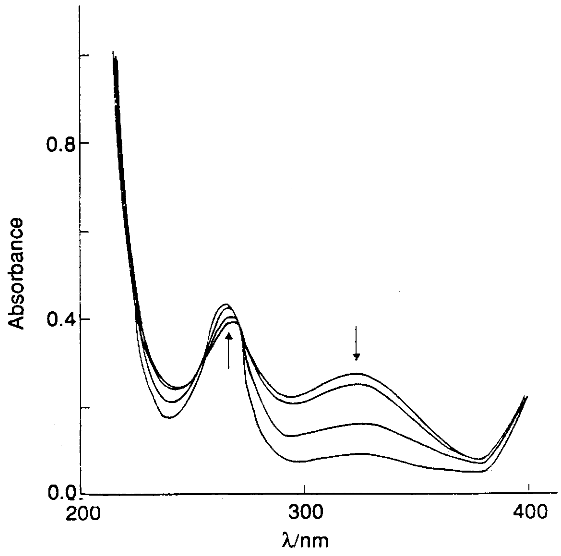


Fig. 2 Spectra taken at different reaction times showing acidolysis of the organochromium complex which results in a decrease in absorbance at 323 nm and an increase at 265 nm

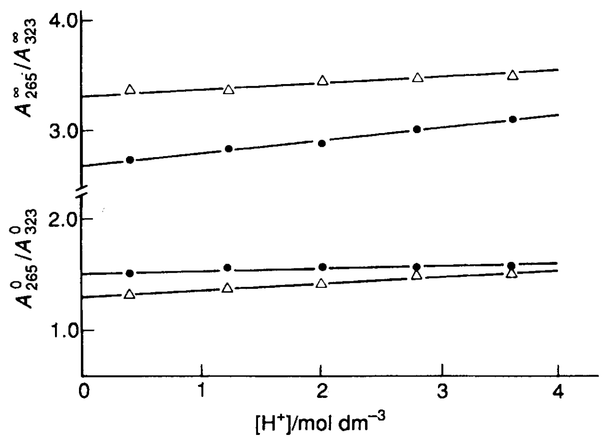


Fig. 3 Dependence on acid concentration of the absorbances A_{265}/A_{323} at 22.5 (△) and 30.0 °C (●)

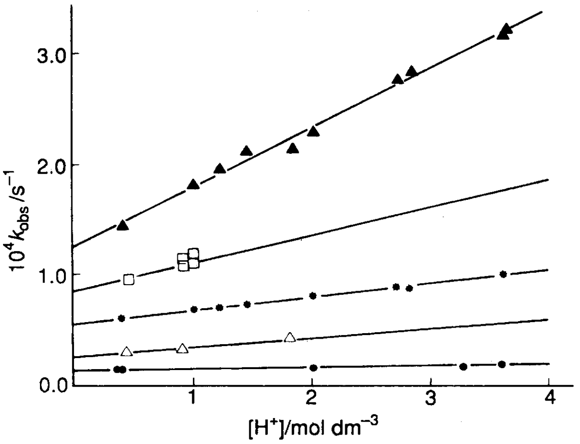


Fig. 4 Acid dependence of the first-order rate constant for the acidolysis of the organochromium complex at 17.0 (●), 20.0 (△), 22.5 (✱), 25.0 (□) and 30.0 °C (▲)

in Fig. 4 is almost zero, within experimental error, and above 30.0 °C the second reaction involving the Cr–N bond hydrolysis is significant, interfering with the first stage. The concentration of chromium(II) has no effect on the observed rate constants as shown in Table 1. From the acidolysis experiments at 25 °C and 1 mol dm^{-3} H$^+$, $k_{obs} = 1.08 \times 10^{-4}$ s^{-1}. This is in good agreement with the results obtained from the data in the presence of Cr^{2+}, where at 25 °C and 1 mol dm^{-3} H$^+$, $k_{obs} = (1.06 \pm 0.05) \times 10^{-4}$ s^{-1}. From the data in Fig. 4 the values for k_0, k_1 and the activation parameters were calculated. The results are summarised in Table 2 along with similar parameters for previously studied pyridineacrylic acid for comparison. The activation parameters for the two systems are roughly comparable.

At lower acid concentrations ($\leqslant$0.1 mol dm^{-3} HClO$_4$) the spectrum of the organochromium complex changes. The band at 550 nm shifts to 510 nm with a concomitant decrease in intensity. This process is at present not understood, but it did not interfere with the acidolysis experiments which were performed at higher acid concentrations. It is possible that at higher pH the complex exists partly in a chelated form.

When Cr^{2+}(aq) acts as a reducing agent an electron is removed from its σ-symmetry antibonding e$_g$* orbital (highest occupied molecular orbital, HOMO). The lowest excited states of dipyridylethylenes and of their conjugated acids have been found[12] by incomplete neglect of differential overlap (spectroscopy calculations) (INDO/S) to be of π-π* character, where the excitation is largely ethylenic. While the nature of the lowest unoccupied molecular orbital (LUMO) in these compounds was not explicitly reported, experimental results indicate that it should also be ethylenic in nature: the reaction of Cr^{2+}(aq) with H$_2$bpe^{2+} (ethylenic LUMO) leads to Cr–C bond formation (Scheme 1).[6] The HOMO–LUMO interaction between Cr^{2+}(aq) and the substrate should thus be an e$_g$*–'ethylenic' one and the first attack will necessarily be on carbon.

Table 2 Apparent activation parameters for the acidolysis

Complex		E/kJ mol^{-1}	ln A
a		106.3 ± 2.5	30.7 ± 0.9
1	^{b}(*i*)	94.0 ± 0.2	28.4 ± 0.1
1	^{b}(*ii*)	142.0 ± 8.9	46.6 ± 3.4

^{a} σ-bonded organochromium complex from the reaction of chromium(II) and pyridine-3-acrylic acid.[5] ^{b} $k_{obs} = k_0 + k_1$[H$^+$]; activation parameters calculated from the values of k_0 and k_1. (*i*) Acid-independent term; (*ii*) acid-dependent term.

The ion-exchange behaviour of the organochromium complex produced according to Scheme 1 and the nature of its acidolysis product are consistent with an overall charge on the molecule of 3+. This indicates that one nitrogen in the complex is deprotonated. Its physical and chemical properties such as UV/VIS spectra and the kinetic behaviour are typical of other known complexes containing a Cr–C bond.[13] Acidolysis of the complex (Scheme 2) produces an N-bonded chromium dipyridylethane species, characterised by its UV/VIS spectrum and overall charge (4+) as well as the final decomposition products. The quantitative data from the ion-exchange separations are also in agreement with the spectral and kinetic data, suggesting transformation of the red organochromium complex **1** to the N-bound violet species **2**, in accord with Scheme 2.

The presence of a violet band with 3+ charge on the ion-exchange column even in the very early stages of the reaction (a few minutes) before acidolysis takes place is consistent with the formation of Cr^{3+}(aq) and an organic radical as in Scheme 1. The free radical being very reactive is quickly captured by Cr^{2+}(aq). No violet band of charge 4+ exists in the very early stages and the chromium content of the Cr^{3+}(aq) band is approximately equal to that of the red band. At longer times a band of 4+ charge exists above the red one which first increases with time and then decreases. When the formation of the red organochromium species is complete and before hydrolysis of the violet species of 4+ charge, the sum of the chromium contents of the red and violet bands is equal to the chromium content in the Cr^{3+}(aq) band in accord with Schemes 1 and 2. When acidolysis of the red species is complete the violet band of 4+ charge evidently decreases in chromium content and the lower band of 3+ charge increases until the transformation is complete. Typical results are presented in Table 3.

The two-term rate equation (1) is similar to those observed earlier for organochromium complexes.[13]

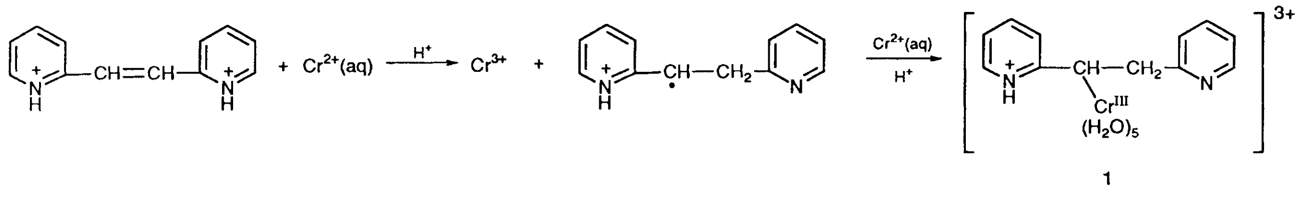
The formation of the 4+ species rather than Cr^{3+}(aq) is explained by Scheme 3 for the acid-catalysed path. Similarly, the acid-independent pathway could occur by a similar attack of H$_2$O at a Cr–C bond leading to complex **3** (Scheme 4) which in the acidic solution is easily transformed into **2**.

The postulated chelate formation in the transition state in Scheme 3 could occur both by a dissociative and associative mechanism. The latter has been found to be operative in reactions of Cr^{III}.[14] Alternatively, the original organochromium complex could be a chelate itself. This could easily explain

Table 3 Distribution of the various complexes from the chromium(II) reduction of H$_2$bpe^{2+} ^{a}

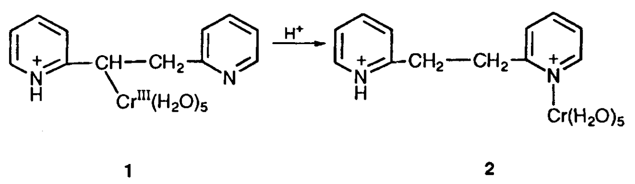
Reaction time/min	Unreacted Cr^{2+}(aq)^b	Cr^{3+}(aq)	Red species **1** (3+)	Violet species **2** (4+)	Green bands
30	25.5	27.5	27.3	0 (4)	19.7
60	25.5	34.5	18.7 (22)	9.8 (7)^c	11.5
2880	26.3	42.6		19.5	11.7

^{a} Conditions: 25 °C, [H$^+$] = 1 mol dm^{-3}, [Cr^{2+}]/[H$_2$bpe^{2+}] > 2. Yields are expressed in % Cr in the various bands. Values in parentheses are approximations from the kinetic parameters and from the proposed reaction schemes and equations, allowance having been made for the time of appearance of the red organochromium species **1**. ^{b} Sky-blue band of Cr^{2+}(aq) on the ion-exchange column appears only when [Cr^{2+}]/[H$_2$bpe^{2+}] > 2. ^{c} No hydrolysis has been assumed in the calculation.

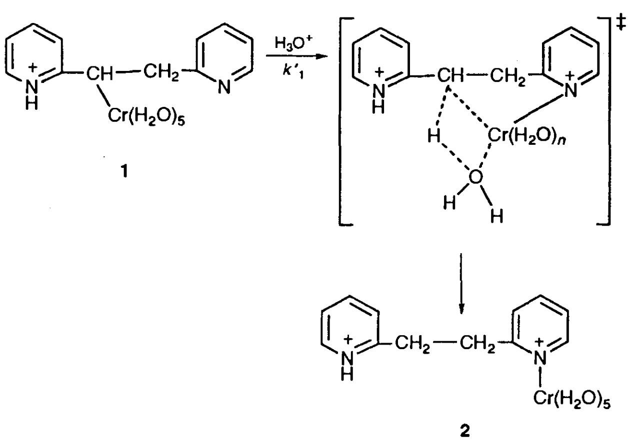


1

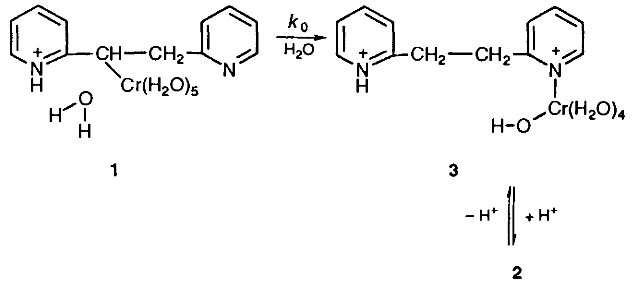
Scheme 1



Scheme 2



Scheme 3



Scheme 4

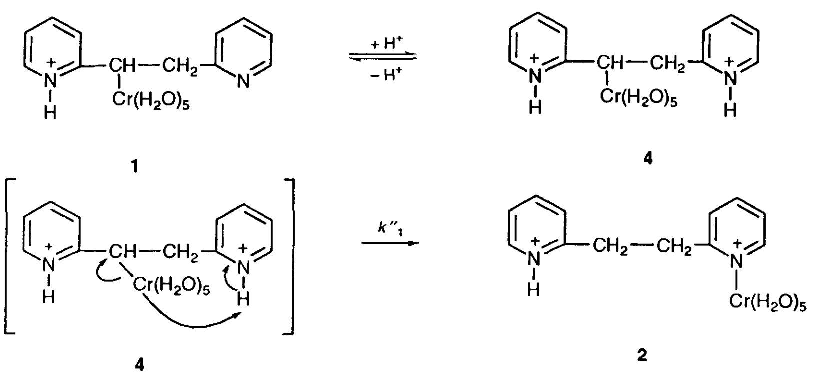
the formation of the product containing a Cr–N bond. The negative entropy of activation $\Delta S_0^\ddagger$ however suggests the formation of a more structured transition state from the less well organised reactants. Therefore, the organochromium complex is not in chelated form and the mechanism shown in Scheme 3 is preferred. If the acid-dependent path proceeds *via* electrophilic attack by an external H_3O^+ on the chromium-bound carbon atom, the k_1 path corresponds to the k_1' path shown in Scheme 3 and is analogous to the k_1 paths of other organochromium complexes. The positive value of $\Delta S_1^\ddagger$ suggests that the following k_1'' path predominates over k_1' where $k_1 = k_1' + k_1''Q$. The intimate mechanism of the k_1'' path is shown in Scheme 5. The quantity Q is the reciprocal of the acid dissociation constant of complex **4**. In this mechanism the protonated pyridine group acts as an internal electrophile to the chromium-bound carbon atom and supplies the proton to the ligand in the same complex.

The value of $\Delta S^\ddagger$ in the acidolysis of the chromium–pyridine-3-acrylic acid complex was attributed to loss of order in the solvation of H^+.[5] The activation parameters for the acidolysis of a number of organochromium complexes are shown in Table 4. Contrary to results obtained earlier for organochromium complexes containing carboxylic acids (maleic and succinic), there is no chromium(II)-catalysed pathway in the acidolysis of pyridine-containing organochromium compounds. This is probably a reflection of the high electron-donating ability of pyridine as discussed earlier.[5]

From the present results it is concluded that a carboxylic group is not necessarily needed for the transfer of electrons to a double bond and the only requirement is, as it is now known, positive overlap between the HOMO of the reducing agent and the LUMO of the oxidising agent.

Acknowledgements

I thank the University of Athens for financial support of the work. Thanks are also due to A. D. Koutselos for experimental work and to Dr. N. C. Bacalis for his help with the least-squares analysis.



Scheme 5

Table 4 Activation parameters[a] for acidolysis of some organochromium complexes

Complex[b]	$\Delta H_0^\ddagger$	$\Delta H_1^\ddagger$	$\Delta S_0^\ddagger$	$\Delta S_1^\ddagger$	Ref.
1	92.0 ± 1.6	142 ± 3	−15.1 ± 4.9	142 ± 7	This work
c		106.3 ± 2.5		2.34	5
$[Cr(CMe_2OH)(edta)]^{2-}$	80.9 ± 4.2	72.9 ± 2.7	−10 ± 14	43 ± 10	15
$[Cr\{CH(Me)OH\}(edta)]^{2-}$	81.9 ± 2.0	81.8 ± 5.5	−25 ± 7	65 ± 18	15
$[Cr(CH_2OH)(edta)]^{2-}$	74.2 ± 6.8	98.6 ± 0.8	−65 ± 22	132 ± 3	15

[a] $\Delta H^\ddagger$ in kJ mol^{-1}, $\Delta S^\ddagger$ in J K^{-1} mol^{-1}. [b] edta = Ethylenediamine tetraacetate. [c] See footnote *a* to Table 2.

References

1 (*a*) S. Zawacky and H. Taube, *J. Am. Chem. Soc.*, 1981, **103**, 3379; (*b*) P. K. Thamburaj, M. K. Loar and E. S. Gould, *Inorg. Chem.*, 1977, **16**, 1946 and refs. therein; (*c*) D. Katakis, Y. Konstantatos and E. Vrachnou, *Metal-promoted Selectivity in Organic Synthesis,* Kluwer, Amsterdam, 1991, pp. 223–235; (*d*) D. Katakis, *Pure Appl. Chem.*, 1988, **60**, 1285.

2 D. Katakis, J. Konstantatos and E. Vrachnou-Astra, *J. Organomet. Chem.*, 1985, **279**, 131.

3 A. Petrou, E. Vrachnou-Astra and D. Katakis, *Inorg. Chim. Acta*, 1980, **39**, 161.

4 D. Katakis, E. Vrachnou-Astra and J. Konstantatos, *J. Chem. Soc., Dalton Trans.*, 1986, 1491.

5 A. Petrou, E. Vrachnou-Astra, J. Konstantatos, N. Katsaros and D. Katakis, *Inorg. Chem.*, 1981, **20**, 1091.

6 A. Koutselos and A. Petrou, *Proceedings of the 23rd International Conference on Coordination Chemistry*, Boulder, CO, 1984.

7 J. Volke and J. Holubek, *Collect. Czech. Chem. Commun.*, 1962, **27**, 1777.

8 J. Vansant, S. Toppet, G. Smets, J. P. Declercq, G. Germain and M. V. Meerssche, *J. Org. Chem.*, 1980, **45**, 1565.

9 J. Vansant, G. Smets, J. P. Declercq, G. Germain and M. V. Meerssche, *J. Org. Chem.*, 1980, **45**, 1557.

10 G. W. Haupt, *J. Res. Nat. Bur. Stand.*, 1955, **48**, 2331.

11 G. Beggiato, G. Fevaro and V. Mazzucato, *J. Heterocycl. Chem.*, 1970, **7**, 583.

12 G. Orlandi, G. Poggi and G. Marconi, *J. Chem. Soc., Faraday Trans. 2*, 1980, 598.

13 H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1972, 320; *Inorg. Chem.*, 1974, **13**, 2434; N. Schmidt, J. H. Swinehart and H. Taube, *J. Am. Chem. Soc.*, 1971, **93**, 1117; J. K. Kochi and P. E. Mocaldo, *J. Org. Chem.*, 1965, **30**, 1134; R. G. Coombes, M. D. Johnson and N. Winterton, *J. Chem. Soc.*, 1965, 7029; F. L. Anet and E. Leblanc, *J. Am. Chem. Soc.*, 1957, **79**, 2649; R. S. Nohr and J. H. Espenson, *J. Am. Chem. Soc.*, 1975, **97**, 3392.

14 T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc.*, 1972, **94**, 8357; T. Ramasami and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 2885 and refs. therein.

15 H. Ogino, M. Shimura and N. Tanaka, *Inorg. Chem.*, 1982, **21**, 126.

Received 28*th April* 1993; *Paper* 3/02440G