Asian Journal of Chemistry Vol. 21, No. 7 (2009), 5337-5344

Substitution and Reduction Reactions Between Some *Tetrakis*(arylisocyanide)*bis*(perchlorato)cobalt(II) Complexes and Two Amines: Basicity and Steric Hindrance Effects

OLAYINKA A. OYETUNJI*, BANYALADZI D. PAPHANE and CLIFFORD A.L. BECKER
Department of Chemistry, University of Botswana, Private Bag UB 00704, Gaborone, Botswana
E-mail: oyetunji@mopipi.ub.bw

The kinetics of the reactions of two amines, 4-cyanopyridine (4-CNpy) and 4-methylpyridine (4-Mepy) with four *tetrakis*(arylisocyanide)cobalt(II) complexes, $[Co(CNR)_4(ClO_4)_2]$ {R = 2,6-$Me_2C_6H_3$ (**A**), 2,4,6-$Me_3C_6H_2$ (**B**), 2,6-$Et_2C_6H_3$ (**C**) and 2,6-*i*$Pr_2C_6H_3$ (**D**)}, have been studied in 2,2,2-trifluoroethanol medium. The amines reacted with each of the cobalt(II) complexes through an initial fast process, proposed to be substitution of the amine into the coordination sphere of the cobalt(II) complex, followed by a slow process, suggested to be reduction of the substituted Co(II) to Co(I). Each substitution process follows a rate law in which the pseudo first-order rate constant is linearly dependent on the concentration of the amine. Conversely, the subsequent reduction process for each reaction displays saturation kinetics at high amine concentrations. The reaction of each amine with the four Co(II) complexes exhibits significant steric hinderance by arylisocyanides in the order $k(A) > k(B) > k(C) > k(D)$. Comparison of the reactions of 4-CNpy and 4-Mepy with that of pyridine shows that the reaction rate increases with increasing basicity of the amines in the order $k(\text{4-CNpy}) < k(\text{py}) << k(\text{4-Mepy})$.

Key Words: Substitution, Reduction, Kinetics, Arylisocyanides, Cobalt(II), Amines, Steric, Basicity.

INTRODUCTION

The syntheses and characterization of alkylisocyanide and arylisocyanide cobalt(II) complexes have been widely reported either as dimers or as pentacoordinate monomeric complexes[1-10]. The five-coordinated alkylisocyanide complexes were known to generally react with tertiary phosphines to produce reduction/ligand substitution products of the type $[Co(CNR)_3(PR'_3)_2]X$, X = ClO_4 or BF_4[11-13], exceptions being reactions with tri-*n*-alkylphosphines which led to disproportionation/ligand substitution products of the types $[Co(CNR)_3(PR'_3)_2]X$ and $[Co(CNR)_3(PR'_3)_2]X_3$, X = ClO_4, BF_4[13-15]. On the other hand, the five-coordinated arylisocyanidecobalt(II) complexes can react with tertiary phosphines to give mono-substituted cobalt(I) products of the type $[Co(CNR)_4(PR'_3)]X$ or di-substituted cobalt(I) products of the type $[Co(CNR)_3(PR'_3)_2]X$ depending principally on the level of steric hindrance in the arylisocyanide ligand[10-12,16-18].

Conversely, triarylarsine ligands react with five-coordinated alkylisocyanidecobalt(II) complexes to produce primarily ligand-substituted six-coordinated Co(II) complexes of the type like *trans*-$[Co(CNR)_4(AsR'_3)_2]X_2$, X = ClO_4, BF_4; PR'_3 = $AsPh_3$, $As(C_6H_4Me\text{-}p)_3$[19]; although the Co(III) complex, $[Co(CNCH_2Ph)_4\{OAs(C_4H_4Me\text{-}P)_3\}_2](BF_4)_3$[6], has also been observed. Reactions of triphenylarsine with five-coordinated arylisocyanidecobalt(II) complexes have produced several different products, including $[Co(CNPh)_3(AsPh_3)_2]ClO_4$[20], $[Co(CNR)_4(ClO_4)_2]$, R = $C_6H_3Me_2$-2,6[21], $C_6H_4Me\text{-}o$[22] and $[Co(CNC_6H_3Me_2\text{-}2,6)]BF_4$[21].

Apart from the many *pentakis*(arylisocyanide)cobalt(II) complexes that have been prepared, the synthesis and characterization of a number of *tetrakis*(arylisocyanide)*bis*(perchlorato)cobalt(II) complexes have also been reported[21-25]. Earlier studies showed that these *tetrakis* complexes as well as the *pentakis*(arylisocyanide)cobalt(II) complexes react with amines to undergo reduction to their corresponding cobalt(I) complexes of the general formula $[Co(CNR)_5]X$. In some cases when R was sufficiently bulky, *e.g.* R = $CHMe_2$, CMe_3 and $C_6H_3iPr_2$, six-coordinate disubstituted intermediates like $[Co(CNR)_4(py)_2](ClO_4)_2$ were isolated[26-28]. It has also been observed that arylisocyanidecobalt(II) complexes are reduced in the presence of free arylisocyanide ligands or coordinating anions[1].

In spite of all the extensive information on the synthesis and characterization of these organoisocyanidecobalt(II) complexes, little is known about kinetic studies on their substitution/reduction reactions. In what might have been the first extensive kinetic study on such complexes, we recently reported results of kinetic studies on the reactions of pyridine with some six-coordinated *tetrakis*(aryliso-cyanide)cobalt(II) complexes, $[Co(CNR)_4(ClO_4)_2]$ {R = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 2,6-$Et_2C_6H_3$ and 2,6-$iPr_2C_6H_3$}[25]. All four complexes reacted with pyridine *via* a two-process mechanism involving a fast initial substitution of the perchlorate ions by pyridine, followed by slow reduction of the substituted intermediates to their corresponding *pentakis*(arylisocyanide)cobalt(I) complexes. The rates of both the substitution and reduction processes were controlled by steric hindrance of the arylisocyanide ligand in the order 2,6-$Me_2C_6H_3$ > 2,4,6-$Me_3C_6H_2$ > 2,6-$Et_2C_6H_3$ > 2,6-$iPr_2C_6H_3$.

This study is designed to explore the effect of the basicity of different amines on the kinetics of the substitution and reduction reactions of some *tetrakis*(arylisocyanide)*bis*(perchlorato)cobalt(II) complexes and thus provide further insight into the mechanisms of these reactions.

EXPERIMENTAL

The arylisocyanides RNC (R = 2,6-$Me_2C_6H_3$; 2,4,6-$Me_3C_6H_2$; 2,6-$Et_2C_6H_3$ and 2,6-$iPr_2C_6H_3$) were prepared either by Becker's modification[29] of the Hertler and Corey synthetic procedure[30] or through the method described by Appel *et al.*[31]. The corresponding cobalt(II) complexes of these ligands were prepared as reported elsewhere[21,23-25]. The pyridines and 2,2,2-trifluoroethanol were of analaR grade and were used as supplied. The complexes were characterized by their electronic and infrared spectra as well as by elemental analysis. The results agree with literature values. Percentage cobalt was determined using a flame atomic absorption spectrophotometer, model SpectrAA 220FS Varian.

Kinetics: The two amines, 4-CNpy and 4-Mepy were reacted with the four *tetrakis*(arylisocyanide)cobalt(II) complexes (**A**, **B**, **C** and **D**) in 2,2,2-trifluoroethanol. All reactions were monitored using a Shimadzu UV-2501PC UV/Vis spectrophotometer for the slow reactions and a Hi-Tech SF-61DX2 stopped-flow spectrophotometer for the fast reactions. Constant temperatures (± 0.1 ºC) were maintained either by circulating water from a Neslab RTE7 thermocirculator to the cell compartment of the stopped-flow equipment or by using a Shimadzu thermoelectric temperature controller, TCC-240A with the UV-2501PC UV/Vis spectrophotometer.

All of the reactions were studied under pseudo-first order conditions with the pyridine concentrations in at least 10-fold excess over those of the Co(II) complexes. All reactions were monitored to more that 90 % completion. Pseudo-first order rate constants, k_s', were obtained from linear regression plots for the slow processes while k_s for the fast processes were obtained from the stopped-flow kinetic software (KinetAsystTM3) by fitting the decay curves to single exponential analysis. The k_s' or k_s value quoted for each amine concentration (Tables 1 and 2) is an average of 4 to 5 runs.

RESULTS AND DISCUSSION

Upon addition of each of the amines to the Co(II) complexes, a bathochromic shift of about 25 to 35 nm was observed. This shift is attributed to the formation of a substituted 6-coordinate complex, $[Co(CNR)_4L_2]^{2+}$, where L is the added amine ligand and is similar to observations reported by earlier workers[25,32-35]. Some of these substituted complexes have actually been isolated as in the reactions of cobalt(II) protoporphyrin complexes with some amine ligands[32-35] and in the reaction of $[Co(CNR)_4(ClO_4)_2]$ (R = 2,6-$i$$Pr_2C_6H_3$) with pyridine[28].

At fixed wavelengths, the reaction of each amine with the Co(II) complexes showed a fast initial rise in absorbance followed by a slow decrease in absorbance (Fig. 1). The fast initial rise in absorbance is attributed to the substitution process and the slow absorbance decrease to a reduction process. For the fast substitution process monitored using the stopped-flow technique, the pseudo-first order rate constants k_s, were found to increase with increasing concentration of the amines (Table-1). Plots of k_s against [L] (L = 4-CNpy or 4-Mepy) were linear with intercepts for the four Co(II) complexes and similar to our earlier observation[25]. A typical plot for the reaction of 4-CNpy with **A**, **B**, **C** and **D** is shown in Fig. 2. This observation suggests substitution in an octahedral complex which involves a two-step ligand-ligand replacement and is consistent with the following mechanism:

TABLE-1

PSEUDO FIRST-ORDER RATE CONSTANTS, k_s, FOR THE SUBSTITUTION PROCESSES BETWEEN THE FOUR ARYLISOCYANIDECOBALT(II) COMPLEXES, **A, B, C** and **D** AND L (L = 4-CNpy AND 4-Mepy) IN CF_3CH_2OH AT 298 K

10^3[4-CNpy] (M)	k_s (s^{-1})			
	A	**B**	**C**	**D**
3.30	21.9	18.9	16.4	12.2
4.63	23.8	21.0	18.2	12.9
6.61	27.1	23.2	19.7	15.7
7.60	28.7	24.6	21.3	16.3
9.25	30.9	27.0	23.1	17.6
12.14	38.6	32.9	27.5	20.4
15.18	40.2	34.3	29.8	24.5
19.80	48.1	40.7	35.1	28.1
k_1 (s^{-1})	16.6	14.8	12.7	8.7
k_2 (M^{-1} s^{-1})	1610	1331	1143	992
10^4[4-Mepy] (M)	k_s (s^{-1})			
	A	**B**	**C**	**D**
3.30	29.9	27.3	23.6	20.8
4.63	34.2	30.8	26.5	23.3
6.61	39.1	34.2	29.5	26.0
7.60	43.1	36.1	31.6	27.9
9.25	47.6	39.8	34.2	30.1
12.14	55.1	45.0	39.3	34.2
15.18	66.0	52.6	43.6	37.5
19.80	78.9	61.5	52.0	44.9
k_1 (s^{-1})	21.0	20.6	18.4	16.6
k_2 (M^{-1} s^{-1})	29751	20652	16909	14213

TABLE-2

PSEUDO-FIRST ORDER RATE CONSTANTS, k_s', FOR THE REDUCTION OF $[Co(CNR)_4(ClO_4)_2]$ COMPLEXES BY 4-CNpy IN CF_3CH_2OH AT 318 K

10^3[4-CNpy] (M)	10^5 k_s' (s^{-1})			
	A	**B**	**C**	**D**
3.30	1.23	0.67	0.24	0.079
4.63	1.44	0.85	0.27	0.094
6.61	1.90	0.94	0.30	0.106
7.60	1.98	1.08	0.31	0.112
9.25	2.20	1.13	0.33	0.131
12.14	2.27	1.24	0.34	0.138
15.18	2.43	1.29	0.35	0.150
19.80	2.59	1.33	0.35	0.162
K (M^{-1})	164.2	195.3	260.9	209.2
K_3 (s^{-1})	3.49	1.74	0.398	0.196

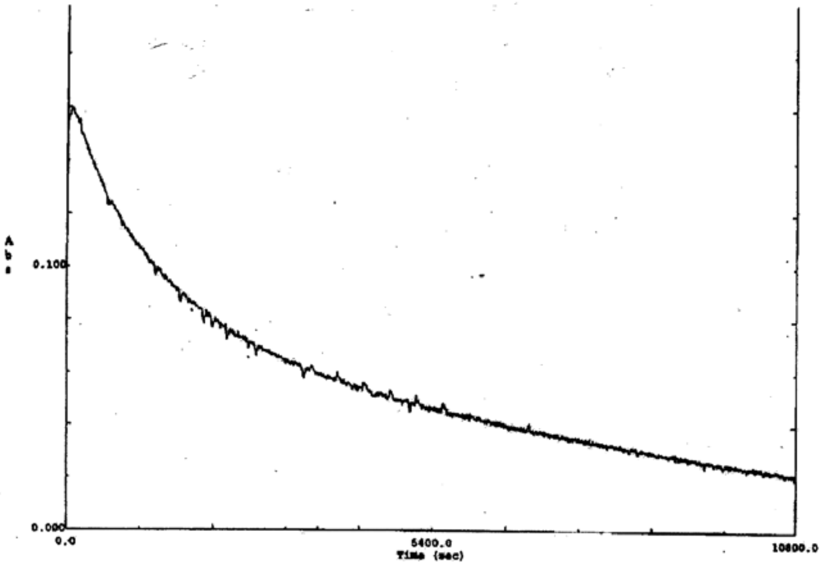

Fig. 1. Typical absorbance decay curve for the reduction of C by 4-CNpy at 298 K

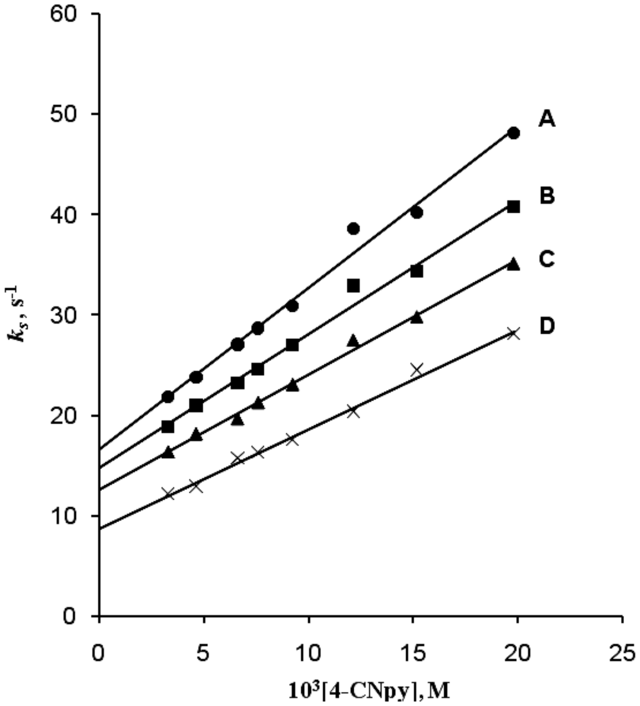

Fig. 2. Plots of the observed rate constant k_s against 4-CNpy concentration for the substitution process between the four isocyanidecobalt(II) complexes and 4-CNpy at 298 K

$$[Co(CNR)_4(ClO_4)_2] + L \xrightarrow{k_1} [Co(CNR)_4(L)(ClO_4)]^{2+} + ClO_4^- \qquad (1)$$

$$[Co(CNR)_4(L)(ClO_4)]^{2+} + L \xrightarrow{k_2} [Co(CNR)_4L_2]^{2+} + ClO_4^- \qquad (2)$$

for which the rate law is given as:

$$\text{Rate} = \frac{-d[Co(CNR)_4{}^{2+}]}{dt} = k_s[Co(CNR)_4{}^{2+}]$$

where, $k_s = k_1 + k_2[L]$ (3)

From plots of k_s *vs.* [L], values of k_1 and k_2 were obtained from the intercepts and slopes, respectively and are listed in Table-1.

In contrast, the slow reduction processes exhibited different kinetic behaviour as compared to the substitution process. Plots of k_s' *versus* [L] gave curves typical of saturation kinetics (Fig. 3). Similar observations have been reported in our earlier studies[25] as well as in both the aminolysis of sulfamate esters in chloroform[36] and in the reactions of Co(II) protoporphyrins IX dimethyl ester with pyridine and related compounds[32,35]. Such saturation kinetics is also typical of the formation of a precursor complex prior to electron transfer as observed in the electron transfer reactions of halopentacyanocobaltate(III) complexes[37]. The above observation fits well with the following mechanism:

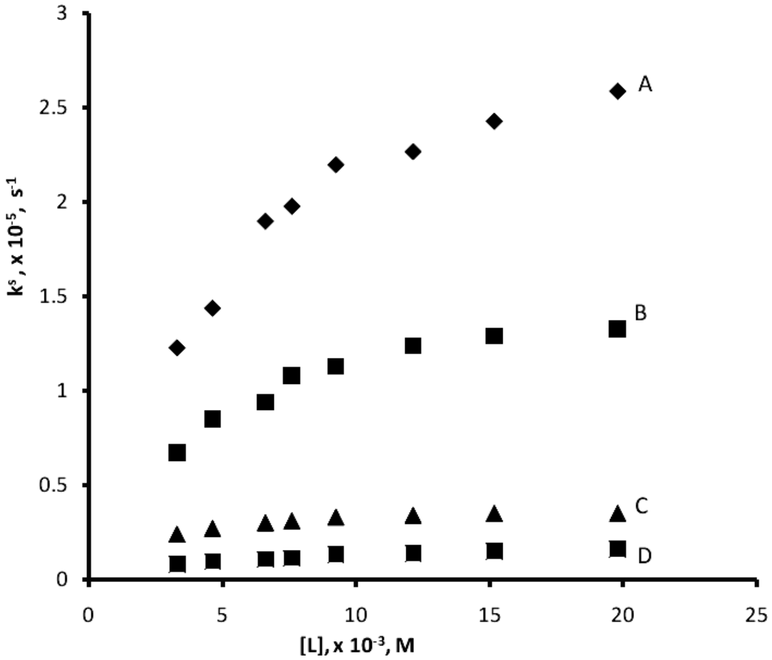

Fig. 3. Plots of observed rate constants against 4-CNpy concentration for the reduction of the four cobalt(II) complexes at 298 K

$$[Co(CNR)_4L_2]^{2+} \underset{fast}{\overset{K}{\rightleftharpoons}} [Co(CNR)_3L_2]^{2+} + :CNR \xrightarrow[slow]{k_3} Co(I)\ product \quad (4)$$

giving the rate law:

$$Rate = k_s' [Co(CNR)_4L_2]^{2+} \text{ where } k_s' = \frac{k_3K[L]}{1+K[L]} \quad (5)$$

Rearrangement of equation 5 gives:

$$\frac{1}{k_s'} = \frac{1}{k_3K[L]} + \frac{1}{k_3} \quad (6)$$

Values of k_3 and K are reported in Table-2. It is observed from Tables 1 and 2 that the rate constants k_2 and k_3, associated with the substitution by the amine ligand and the reduction of Co(II) to Co(I), respectively, decrease with increasing size of the arylisocyanide ligand, a clear evidence of steric hindrance.

The reactions of the four Co(II) complexes with 4-methylpyridine (4-Mepy) also involve both substitution and reduction processes. However, while the fast substitution process showed a regular dependence of rate constant on concentration of 4-Mepy, the slow reduction process exhibited some irregular behaviour in which a particular pattern of variation of k_s' with [L] cannot be established. However, there is clear evidence of steric hindrance as observed with the other amines and of importance is the fact that 4-Mepy reacted faster than pyridine and 4-CNpy. For example, at 298 K, the second order substitution rate constants for A are 1610, 1720 and 29751 for 4-CNpy, pyridine and 4-Mepy, respectively. While 4-CNpy reacted at a slower rate than pyridine, 4-Mepy reacted at a faster rate. This observation can be explained in terms of the basicity of the amines. The CN group is an electron withdrawing substituent and therefore reduces the electron density of the pyridine ring, making 4-CNpy a weaker electron donor and hence less basic than pyridine. On the other hand, the methyl substituent on pyridine increases the electron density of the ring such that 4-Mepy is a better electron donor and a more basic amine than pyridine. Since ligands usually coordinate to metal centres by acting as Lewis bases donating lone pairs of electrons to the empty metal *d*-orbitals, more basic amines will be better coordinating ligands and will form more stable complexes as compared to less basic amines. This can be used to explain the higher reactivity of 4-Mepy and lower reactivity of 4-CNpy when they are compared to pyridine.

In conclusion, both steric hindrance from the arylisocyanides and basicity of the amines have been observed to play significant roles in the reactions studied. The more bulky the arylisocyanide ligand, the slower the reaction for all the amines. For each of the amines, the order of reactivity is A > B > C > D. Similarly, the more basic the amine, the faster the reaction of the cobalt(II) complex. For the reaction of each of the amines with the four Co(II) complexes, the order is 4-Mepy >> pyridine > 4-CNpy.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the University of Botswana Research and Publications Committee for financial support. Financial grant from Royal Society of Chemistry to O.A.O to purchase some chemicals is also hereby acknowledged.

REFERENCES

1. L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, John Wiley, New York, Ch. 7 (1969).
2. E. Singleton and H.E. Oosthuizen, *Adv. Organomet. Chem.*, **22**, 209 (1983) and references therein.
3. F.A. Cotton, T.G. Dunne and J.S. Wood, *Inorg. Chem.*, **3**, 1495 (1964).
4. P.M. Boorman, P.J. Craig and T.W. Swaddle, *Can. J. Chem.*, **48**, 838 (1970).
5. C.A.L. Becker, *J. Coord. Chem.*, **28**, 147 (1993).
6. C.A.L. Becker, *Inorg. Chim. Acta*, **203**, 175 (1993).
7. J.M. Pratt and P.R. Silverman, *Chem. Commun.*, **117**, (1967); *J. Chem. Soc. A*, 1286 (1967).
8. F.A. Jurnak, D.R. Greig and K.N. Raymond, *Inorg. Chem.*, **14**, 2585 (1975).
9. C.A.L. Becker, *Inorg. Chim. Acta*, **27**, L105 (1978).
10. C.A.L. Becker, *Synth. React. Inorg. Met.-Org. Chem.*, **9**, 445 (1979).
11. J.W. Dart, M.L. Lloyd, R. Mason, J.A. McCleverty and J. Williams, *J. Chem. Soc., Dalton Trans.*, 1747 (1973).
12. E. Bordignon, U. Croatto, U. Mazzi and A.A. Orio, *Inorg. Chem.*, **13**, 935 (1974).
13. C.A.L. Becker, S.A. Al-Qallaf and J.C. Cooper, *Inorg. Chim. Acta*, **188**, 99 (1991).
14. C.A.L Becker, M.A.S. Biswas and J.C. Cooper, *Inorg. Chim. Acta*, **188**, 191 (1991).
15. C.A.L. Becker and M.A.S. Biswas, *J. Coord. Chem.*, **29**, 227 (1993).
16. S. Otsuka and M. Rossi, *Bull. Chem. Soc. (Japan)*, **46**, 3411 (1973).
17. C.A.L. Becker, *J. Inorg. Nucl. Chem.*, **42**, 27 (1980).
18. C.A.L. Becker and N.K. Homsy, *Inorg. Chim. Acta*, **89**, 93 (1984).
19. C.A.L. Becker, *J. Coord. Chem.*, **31**, 337 (1994)
20. C.A.L. Becker, *Inorg. Chim. Acta*, **36**, L441 (1979).
21. C.A.L. Becker and J.C. Cooper, *Inorg. Chim. Acta*, **158**, 141 (1989).
22. C.A.L. Becker, *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 1455 (1995).
23. C.A.L. Becker and J.C. Cooper, *Inorg. Chim. Acta*, **182**, 25 (1991).
24. C.A.L. Becker, *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 437 (1992).
25. O.A. Oyetunji, B.D. Paphane and C.A.L. Becker, *Transition Met. Chem.*, **31**, 951 (2006)
26. C.A.L. Becker and S. Odisitse, *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 1547 (2000).
27. C.A.L. Becker, *J. Coord. Chem.*, **26**, 231 (1992).
28. C.A.L. Becker and M.A.S. Biswas, *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 269 (1995).
29. C.A.L. Becker, *Synth. React. Inorg. Met.-Org. Chem.*, **4**, 213 (1974).
30. W.R. Hertler and E.J. Corey, *J. Org. Chem.*, **23**, 1221 (1958).
31. R. Appel, R. Kleinstuck and K.D. Ziehn, *Angew. Chem. Internat. Edit.*, **10**, 132 (1971).
32. D. Pavlovic, S. Asperger and B. Domi, *J. Chem. Soc., Dalton Trans.*, 2535 (1986).
33. D.V. Stynes, H.C. Stynes, B.R. James and J.A. Ibers, *J. Am. Chem. Soc.*, **95**, 179 (1973).
34. N. Datta-Gupta, *J. Inorg. Nucl. Chem.*, **33**, 419 (1972).
35. Z. Dokuzovic, X. Ahmeti, D. Pavlovic, I. Murati and S. Asperger, *Inorg. Chem.*, **21**, 1576 (1982).
36. W.J. Spillane, G. Hogan, P. McGrath and J. King, *J. Chem. Soc., Dalton Trans. II*, 309 (1998).
37. J. Ojo, J. Ige, G. Ogunlusi, O. Owoyomi and E. Olaseni, *Transition Met. Chem.*, **31**, 337 (2006).

(*Received*: 25 August 2008; *Accepted*: 30 April 2009) AJC-7474