= 6, $\Delta\nu_1$ = 4 cm^{-1} for P$_4$- -O$_3$ compared to $\Delta\nu_3$ = 6 and $\Delta\nu_1$ = 8 cm^{-1} for As$_4$- -O$_3$. This interaction between submolecules in the complex is responsible for the photochemistry and the resulting O atom transfer.

Mechanism. The proposed photochemical reaction mechanism (Scheme I) begins with the As$_4$- - -O$_3$ complex described above. The [As$_4$O]* product species is initially excited by the energy of the new terminal "As=O" bond, which can be approximated by the AsO diatomic thermochemical value (115 kcal/mol). This means that matrix relaxation of [As$_4$O]* must occur straight away or rearrangement and decomposition may occur. Only a small yield of terminal As$_4$O is trapped here. The formation of AsO directly from [As$_4$O]* requires that the As byproduct be bound to As$_2$ to give an As$_3$ species; otherwise, the reaction of As$_4$ + O to give AsO + As + As$_2$ is endoergic by 49 kcal/mol. In fact [As$_4$]O* can decompose directly to As$_3$ and AsO in the same matrix cage, and this (As$_3$)(AsO) complex is expected to photolyze to give other AsO species and bridged As$_4$O.

Bridged As$_4$O (**2**) can be formed directly by rearrangement of [As$_4$O]* during relaxation in the initial photochemical step or upon the insertion of O(^{1}D) into an As-As bond in As$_4$ in the UV photolysis studies. After one bridged oxygen is affixed to As$_4$, others can be added, leading to the formation of As$_4$O$_6$. Although specific As$_4$O$_x$ (x = 2-5) species cannot be identified with certainty, it is clear that stepwise addition of oxygen atoms to As$_4$ occurs, leading finally to the stable species As$_4$O$_6$. Support for this mechanism is found in mass spectroscopic evidence for As$_4$O$_3$, As$_4$O$_4$, and As$_4$O$_5$.[25] In addition it is believed that the As$_4$- -O$_3$ complex can also give As$_4$O$_3$ on photolysis and that two ozone molecules trapped in the same matrix site with As$_4$ can also give As$_4$O$_6$ on photolysis. Note that the reaction of As$_4$ and O$_3$ occurs on sample preparation as evidenced by As$_4$^{18}O$_6$ in the initial sample deposit for As$_4$ and ^{18}O$_3$.

Finally, the observation of weak bands for species **1** and **2** in a sample exposed only to the infrared examining radiation means that some As$_4$ and O$_3$ react spontaneously under the deposition conditions. The analogous reaction of As$_4$ and O$_2$ was not observed, but O atoms gave the same As$_4$ reaction products as ozone. The present observations attest to the great reactivity for As$_4$ with ozone.

Conclusions

The codeposition of As$_4$ and O$_3$ with excess argon at a low temperature produced sharp weak bands at 921.7 and 590.3 cm^{-1}. Red-light photolysis first increased the former more than the latter, but prolonged red-light photolysis decreased the former, increased the latter and produced a 565.4-cm^{-1} satellite, and formed a 952.0-cm^{-1} band. Scrambled isotopic ozone experiments revealed isotopic doublets for these bands, which is characteristic of the vibration of a single oxygen atom. Although it is difficult to be certain about the arsenic stoichiometry and structure, these single O atom species are believed to be due to (As$_3$)(AsO) complex, bridge-bonded As$_4$O, and perturbed AsO product species, respectively. Continued photolysis with visible and near-ultraviolet light produced a weak new band at 981.5 cm^{-1} and new bands in the 712-805-cm^{-1} region approaching that of As$_4$O$_6$. The latter are assigned to bridge-bonded As$_4$O$_x$ cage species (x = 2-5). On the basis of comparison with the P$_4$ + O system, the 981.5-cm^{-1} band is probably due to the terminally bonded As$_4$O species. The excited [As$_4$O]* species produced in the initial reaction is not relaxed as efficiently by the matrix as [P$_4$O]*, and decomposition and rearrangement products formed and trapped in the matrix cage dominate in the matrix spectra. Finally, As$_4$ is more reactive with O$_3$ than P$_4$ in matrix codeposition experiments.

Acknowledgment. We gratefully acknowledge financial support from NSF Grant CHE85-16611 and guidance from the first As$_4$ experiments performed by M. E. Boyle and R. Withnall.

Registry No. **1**, 118576-12-8; **2**, 118576-13-9; **3**, 118576-14-0; **4**, 12005-99-1; **5**, 118576-15-1; As$_4$, 12187-08-5; O$_3$, 10028-15-6; ^{18}O, 14797-71-8.

---

(24) Withnall, R.; Hawkins, M.; Andrews, L. *J. Phys. Chem.* **1986**, *90*, 575.

(25) Brittain, R. D.; Lau, K. H.; Hildenbrand, D. L. *J. Phys. Chem.* **1982**, *86*, 5072.

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

UV-Vis-IR Thin-Layer Spectroelectrochemical Studies of Hexakis(aryl isocyanide)chromium Complexes. In Situ Generation and Characterization of Four Oxidation States

John P. Bullock and Kent R. Mann*

Received March 30, 1989

Spectroelectrochemistry in the UV-vis and IR spectral regions has been used to characterize the Cr(0), Cr(I), Cr(II), and Cr(III) analogues of a series of chromium hexakis(aryl isocyanide) complexes. Controlled-potential bulk electrolyses in an improved thin-layer spectroelectrochemical cell were monitored with UV-vis and FT-IR spectrometers in separate experiments. All electrolyses proceeded isosbestically and were chemically reversible. IR data show that each sequential oxidation results in higher ν_{CN} stretching frequencies and lower absolute integrated intensities for the ν_{CN} absorption. This is related to the decrease in dπ-π^*_{CN} back-bonding in the more oxidized forms. Rough correlations between the electron-releasing ability of the aryl substituent and both the ν_{CN} stretching frequency and the absolute integrated intensities of the Cr(III) complexes are observed. This is attributed to varying degrees of $\sigma_{CNR} \rightarrow$ Cr donation, which become apparent only when the degree of dπ-π^*_{CN} back-bonding is small. UV-vis experiments show that for all compounds studied the ligand-to-metal charge-transfer (LMCT) band energy decreases upon successive oxidation, while the energy of the MLCT band increases. This is in accord with the increased oxidation strength of the central chromium ion. A correlation can also be made between the electron-releasing abilities of the aryl substituents and the energies of the LMCT electronic transitions in the Cr(II) and the Cr(III) complexes. This reflects the greater $\sigma_{CNR} \rightarrow$ Cr donation of aryl isocyanides with electron-donating substituents and is consistent with the trend in the absolute integrated intensities of Cr(III) species observed in IR experiments.

Introduction

The electrochemistry of hexakis(aryl isocyanide)chromium complexes has been studied by several groups in recent years.[1-6] These compounds undergo a series of reversible one-electron-transfer reactions at solid electrodes, resulting in formal chromium

---

* To whom correspondence should be addressed.

(1) Treichel, P. M.; Dirreen, G. E. *J. Organomet. Chem.* **1972**, *39*, C20.

(2) Treichel, P. M.; Essenmacher, G. J. *Inorg. Chem.* **1976**, *15*, 146.

(3) Essenmacher, G. J.; Treichel, P. M. *Inorg. Chem.* **1977**, *16*, 800.

oxidation states of 0, +1, +2, and +3.[7] Given the rich redox chemistry of these chromium complexes, we felt that they were ideal for demonstrating the utility of an improved thin-layer, spectroelectrochemical appratus that can be used in both the UV-visible and infrared spectral regions.

Spectroelectrochemistry, particularly in the UV-visible region, has become a standard technique for the characterization of electrogenerated species.[8-11] Recently the advantages of infrared spectroelectrochemistry as a structure determination tool have become apparent, and now it is becoming a more familiar experimental technique.[11b,12-18] We have developed a convenient thin-layer spectroelectrochemical cell that can be used in both spectral regions for water- and/or air-sensitive solutions. This allows more complete characterization of complexes than is achievable with either technique alone. In this work, we demonstrate the applicability of this cell to organometallic systems by measuring the UV-vis and IR spectra of several hexakis(aryl isocyanide)chromium compounds and their one-, two- and three-electron-oxidized analogues. Studying both spectral regions provided additional insights into the bonding in these complexes.

Experimental Section

Syntheses. All hexakis(aryl isocyanide)chromium complexes and their corresponding Cr^IPF_6 salts were synthesized by standard methods.[2-4,19] For ease of handling, the Cr^IPF_6 salts were used in all experiments.

Electrochemical Measurements. All electrochemical experiments were performed with a BAS 100 electrochemical analyzer unless otherwise noted.

Cyclic voltammetry (CV) was performed at ambient temperature (25 °C) with a normal three-electrode configuration consisting of a highly polished glassy-carbon-disk working electrode (A = 0.07 cm^2) and a AgCl/Ag reference electrode containing 1.0 M KCl. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 M solution of the supporting electrolyte.

The dichloromethane (Burdick and Jackson) and supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH) (Southwestern Analytical Chem., Inc.), were used without further purification.

Electrolyte solutions (0.1 M) were prepared and stored over 80–200-mesh activated alumina and activated 4-Å molecular sieves (Fisher Scientific Co.) prior to use in the experiments. In all cases, working solutions were prepared by recording background cyclic voltammograms of the electrolyte solution before addition of the complex. The working compartment of the cell was bubbled with solvent-saturated argon to deaerate the solution.

Potentials are reported vs aqueous AgCl/Ag and are not corrected for the junction potential. The standard current convention is used (anodic currents are negative). To allow future corrections and the correlation of these data with those of other workers, we have measured the $E°$ for the ferrocenium/ferrocene couple[20] under conditions identical with those used for the chromium hexakis(isocyanide) complexes. In CH_2Cl_2/TBAH, $E°$ = 0.460 V. No iR compensation was used.[21]

Table I. Redox Couple Potentials ($E°$) of Chromium Hexakis(aryl isocyanide) Complexes in CH_2Cl_2/TBAH As Determined by Cyclic Voltammetry (Scan Rate: 100 mV/s)

ligand	couple	$E°$, V
2,6-diisopropylphenyl isocyanide	+1/0	–0.49
	+2/+1	0.44
	+3/+2	1.54
2,6-dimethylphenyl isocyanide	+1/0	–0.47
	+2/+1	0.33
	+3/+2	1.19[a]
2-methylphenyl isocyanide	+1/0	–0.43
	+2/+1	0.29
	+3/+2	1.13
phenyl isocyanide	+1/0	–0.37
	+2/+1	0.25
	+3/+2	1.04
4-chlorophenyl isocyanide	+1/0	–0.23
	+2/+1	0.23
	+3/+2	1.02

[a] The 3+/2+ redox potential given for Cr(2,6-dimethylphenyl isocyanide)$_6$ is that of the anodic wave; this process was irreversible due to electrode passivation.

Spectroelectrochemical Experiments. Spectral changes in both the UV-visible and mid-IR ranges were observed by using a modified version of a flow-through spectroelectrochemical cell with an optically transparent thin-layer electrode as described elsewhere.[22] The original cell consisted of vapor-deposited platinum layers on quartz disks, which acted as working and pseudoreference electrodes, respectively, and a platinum wire outside the main cell assembly, which served as the auxiliary electrode. In the cell used for the current work, all three electrodes consisted of platinum layers deposited by vacuum evaporation on quartz or CaF_2 disks. The cell windows were separated by a 0.1-mm Teflon spacer. The deposition patterns of the three electrodes were designed to be nearly concentric with lateral spacings of about 2 mm. No adverse effects due to lateral diffusion during the time scale of our experiments were observed. Solutions were prepared and degassed under an inert atmosphere (Ar) and introduced into the cell via a gastight syringe through polyethylene tubing.

For UV-vis work, both plates of the cell were quartz, with the working electrode on one plate and the reference and auxiliary electrodes on the other. Bulk electrolyses were controlled by the BAS-100 thin-layer bulk electrolysis program. Spectra were collected with a Tracor Northern TN-6500 rapid-scan diode-array apparatus. The light source was a Xe arc lamp. Light passed through the working electrode platinum layer, which acted as a neutral density filter of about 1.5 absorbance units, before passing through the sample solution. The light beam did not sample the solution near either the axiliary or pseudoreference electrodes.

Infrared studies were carried out with a cell very similar to that described above, but the window upon which the platinum pseudoreference and auxiliary electrodes were deposited was CaF_2 instead of quartz. This cell was used in a specular reflectance mode, with the platinum working electrode acting as the mirror, rather than in a transmission mode as was done in the UV-visible work. The angle of incidence of the infrared beam was approximately 60°, resulting in a measured effective path length of 0.23 mm when a 0.1-mm spacer was used. The electrode arrangement was identical with that in the UV-visible cell. Infrared data were collected on a Mattson Sirius 100 mid-IR spectrometer equipped with a universal optics table, enabling the collection of specular reflectance data. All IR data were corrected for a stray light error (13%) that originates from the inadvertant collection of light reflected from the front face of the CaF_2 plate. Bulk electrolyses were controlled by an Electrosynthesis Co. (ESC) 410 potentiostatic controller and an ESC 420-A accessory power unit.

Results and Discussion

The measured $E°$ values for the 1+/0, 2+/1+, and the 3+/2+ redox couples of four chromium hexakis(aryl isocyanide) complexes are presented in Table I. These data are in good agreement with the observations of previous workers.[1-6] Double-potential step chronocoulometric experiments over each of these couples

---

(4) Treichel, P. M.; Firsich, D. W.; Essenmacher, G. P. *Inorg. Chem.* **1979**, *18*, 2405.

(5) Bohling, D. A.; Evans, J. F.; Mann, K. R. *Inorg. Chem.* **1982**, *21*, 3546.

(6) Plummer, D. T.; Angelici, R. J. *Inorg. Chem.* **1983**, *22*, 4063.

(7) Bohling, D. A.; Mann, K. R. *Inorg. Chem.* **1984**, *23*, 1426.

(8) Kuwana, T.; Heineman, W. R. *Acc. Chem. Res.* **1976**, *9*, 241.

(9) Heineman, W. R. *Anal. Chem.* **1978**, *50*, 390A.

(10) Heineman, W. R. *J. Chem. Educ.* **1983**, *60*, 305.

(11) For recent applications of UV-vis spectroelectrochemistry, see: (a) Berger, R. M.; McMillin, D. R. *Inorg. Chem.* **1988**, *27*, 4245. (b) Mu, X. H.; Kadish, K. M. *Inorg. Chem.* **1988**, *27*, 4720. (c) Boyd, D. C.; Matsch, P. A.; Mixa, M. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3331. (d) Ichimura, A.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 2134.

(12) Bullock, J. P.; Boyd, D. C.; Mann, K. R. *Inorg. Chem.* **1987**, *26*, 3084 and references cited therein.

(13) (a) Enger, S. K.; Weaver, M. J.; Walton, R. A. *Inorg. Chim. Acta* **1987**, *129*, L1. (b) Brisdon, B. J.; Enger, S. K.; Weaver, M. J.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3340.

(14) Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Cooney, R. P. *Rev. Sci. Instrum.* **1987**, *58*, 2071.

(15) Neckel, A. *Mikrochim. Acta* **1987**, *3*, 263.

(16) Nevin, W. A.; Lever, A. B. P. *Anal. Chem.* **1988**, *60*, 727.

(17) Ashley, K.; Pons, S. *Chem. Rev.* **1988**, *88*, 673.

(18) Flowers, P. A.; Mamantov, G. *Anal. Chem.* **1989**, *61*, 190.

(19) Malatesta, L.; Sacco, A.; Ghielmi, S. *Gazz. Chim. Ital.* **1952**, *82*, 516.

(20) Koepp, H. M.; Wendt, H.; Strehlow, H. Z. *Z. Elektrochem.* **1960**, *64*, 483.

(21) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(22) (a) Boyd, D. Ph.D. Thesis, Univ. of Minnesota, 1987; p 62. (b) Boyle, P. D.; Boyd, D. C.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 4424.

Table II. $\bar{\nu}_{CN}$ Stretching Frequencies and Absolute Integrated Intensities of Chromium Hexakis(aryl isocyanide)(n+) Complexes in CH_2Cl_2/TBAN

ligand	n	ν_{CN}, cm^{-1}	$A \times 10^{-4}$,[a] M^{-1} cm^{-2}
2,6-diisopropylphenyl isocyanide	0	2005 (sh), 1961	86
	1	2062	33
	2	2143	3.8
	3	2180	1.3
2,6-dimethylphenyl isocyanide	0	2021 (sh), 1950, 1869 (sh)	85
	1	2056, 1999 (sh)	36
	2	2139	4.2
	3	2205	*b*
2-methylphenyl isocyanide	0	1973, 1950, 1925 (sh)	76
	1	2064, 2045 (sh), 2012 (sh)	33
	2	2146	4.6
	3	2213	0.44
phenyl isocyanide	0	2013, 1966, 1956	110
	1	2069, 1986 (sh)	52
	2	2158	9.1
	3	2222	0.38
4-chlorophenyl isocyanide	0	2021, 1973 (sh), 1962	80
	1	2070, 2004 (sh)	36
	2	2159	6.1
	3	2223	0.35

[a] To convert these values to specific integrated intensities,[26] each value should be divided by the total number of C≡N oscillators in the complex (six in each case). A values are given to ±15%. [b] The passivation of the working electrode during the generation of Cr(2,6-dimethylphenyl isocyanide)$_6^{3+}$ prevented an accurate intensity measurement for this compound.

confirmed that each is a reversible one-electron process. The chemical equations describing each process are

$$Cr(CNR)_6^{+} + e^{-} = Cr(CNR)_6 \quad E°(1+/0)$$

$$Cr(CNR)_6^{2+} + e^{-} = Cr(CNR)_6^{+} \quad E°(2+/1+)$$

$$Cr(CNR)_6^{3+} + e^{-} = Cr(CNR)_6^{2+} \quad E°(3+/2+)$$

Controlled-potential bulk electrolyses were performed in the thin-layer spectroelectrochemical cell. In these experiments, the electrolysis potentials were set relative to the Pt pseudoreference electrode. The electrochemical behavior of the cell, in terms of electrolysis time, was highly dependent on the nature of the solvent/electrolyte combination used. Under forcing electrolysis conditions, the cell reached equilibrium much faster, (usually within 10–15 s) when a high dielectric constant solvent (e.g., acetone)[23] was used than with a low dielectric constant solvent (e.g., CH_2Cl_2). Electrolysis times when CH_2Cl_2/TBAH was used as the solvent/electrolyte ranged from 30 to 75 s.

Infrared Studies. The infrared spectral changes observed for the two one-electron oxidations and the one-electron reduction of Cr(2,6-diisopropylphenyl isocyanide)$_6$PF$_6$ in CH_2Cl_2/TBAH are shown in Figure 1. All three transitions proceed with the maintenance of excellent isosbestic points indicative of clean conversions. These electrochemical processes are all reversible, and subsequent reversal generally led to clean conversions regenerating the starting materials. The infrared spectral changes for the oxidations of the 2,6-dimethyl-, 2-methyl-, and 4-chlorophenyl and the unsubstituted aryl isocyanide complexes of chromium are similar to those shown in Figure 1. The only notable exception is that the oxidation of Cr(2,6-dimethylphenyl isocyanide)$_6^{2+}$ passivates the electrode before the electrolysis is complete. Table II lists the ν_{CN} stretching frequencies and the absolute integrated intensities of the four obtainable oxidation states of the chromium isocyanide complexes studied. Intensity measurements for the Cr(0) complexes are in good agreement with measurements made by Angelici et al. on similar compounds.[6] The observed frequencies are in good agreement with those previously determined.[24]

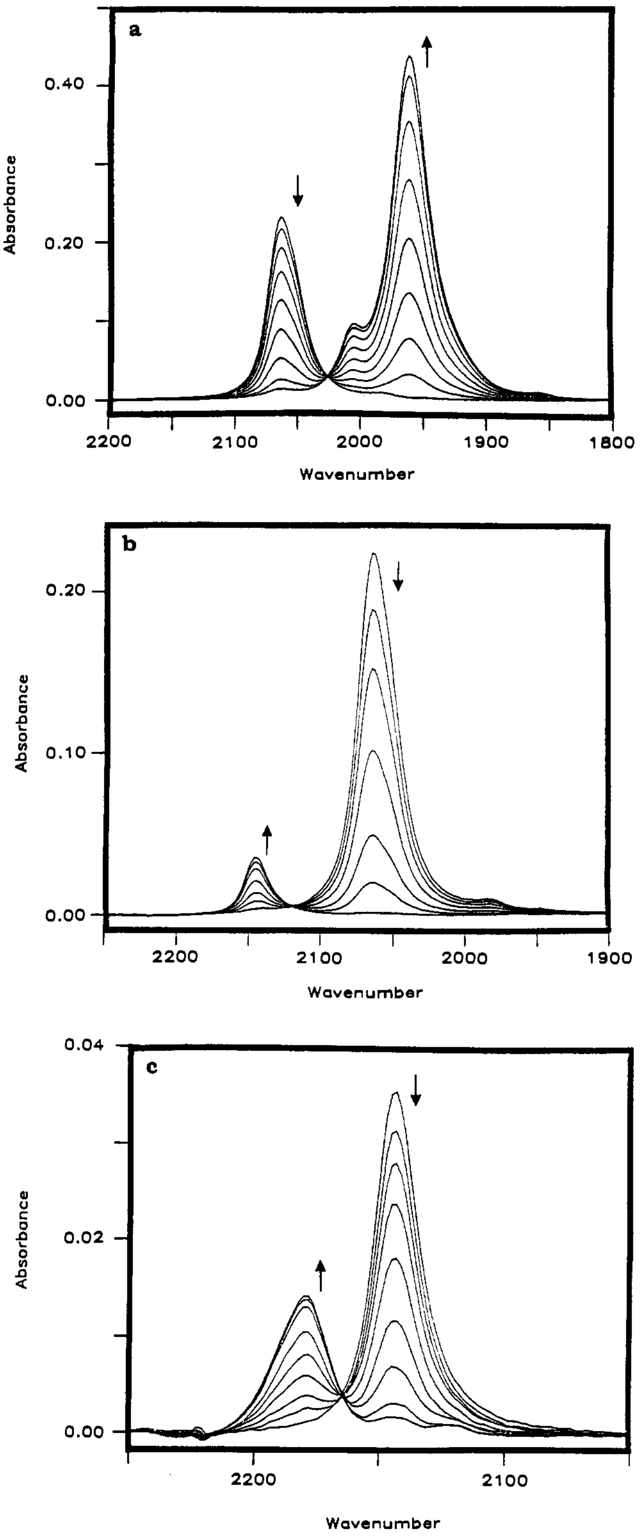

Figure 1. (a) Infrared spectral changes that result during the electrolysis of a 1.1 × 10^{-3} M solution of Cr(2,6-diisopropylphenyl isocyanide)$_6$PF$_6$ at −1.0 V vs a Pt pseudoreference electrode. The arrows indicate the direction of change. The peak at 2062 cm^{-1} decreases in intensity while that at 1961 cm^{-1} increases in intensity. Spectra shown were taken at 8-s intervals; total electrolysis time was about 65 s. (b) IR spectral changes resulting from electrolysis of the same solution at +1.0 V vs the Pt pseudoreference electrode. The peak at 2062 cm^{-1} decreases in intensity while that at 2143 cm^{-1} increases. Spectra were taken every 4 s; total electrolysis time was about 40 s. (c) IR spectral changes that result from the electrolysis of the solution generated in the experiment depicted in part b at +1.8 V vs the Pt pseudoreference electrode. The peak at 2143 cm^{-1} decreases in intensity while that at 2180 cm^{-1} increases in intensity. Spectra were taken at 4-s intervals; total electrolysis time was about 35 s.

---

(23) Bullock, J. P.; Sykes, A. G.; Mann, K. R. Work in progress.
(24) Bohling, D. A.; Mann, K. R. *Inorg. Chem.* **1983**, *22*, 1561.

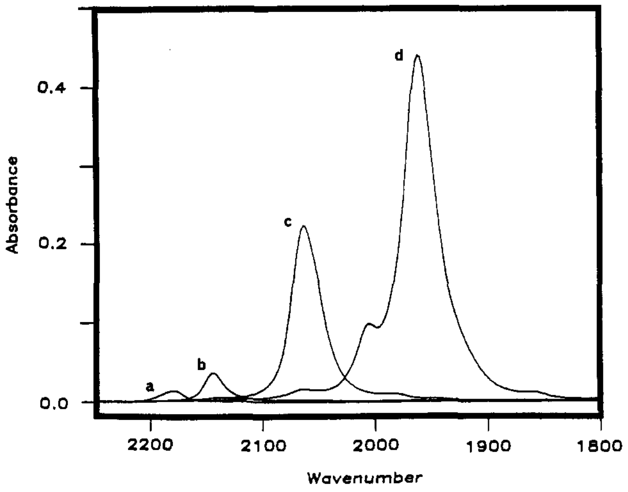

Figure 2. Infrared spectra of 1.1 × 10^{-3} M solutions of the tri- (a), di- (b), uni- (c), and zerovalent (d) analogues of Cr(2,6-diisopropylphenyl isocyanide)$_6$ in CH_2Cl_2/TBAH.

There are two primary changes in the infrared spectra as the metal becomes more highly oxidized. The first is the expected increase in the ν_{CN} stretching frequency, which results from a lower π^*_{CN} orbital electron density as the extent of back-bonding decreases with increasing Cr oxidation state.[25] The other effect is a dramatic decrease of the absolute integrated intensity of the ν_{CN} transition upon oxidation of the metal complex. This is illustrated more clearly in Figure 2. Here, the absorption spectra of the four oxidation states of Cr(2,6-diisopropyl isocyanide)$_6$ are superimposed. The absolute integrated intensity for the Cr(0) species is roughly 60 times that for the Cr(III) complex. The latter phenomenon is similar to that noted by Plummer and Angelici.[6] They reported that the absolute integrated intensities of a homoleptic series of d^6 isocyanide complexes (M(*t*-BuDiNC)$_3$ (*t*-BuDiNC = 1,2-bis(4-*tert*-butyl-2-isocyanophenoxy)ethane), where M = Cr^0, Mn^+, Fe^{2+}, and Co^{3+}) decreases with increasing metal atomic number, i.e., with increasing metal oxidation state. Moreover, the magnitude of the decrease for the homolepic series, from Cr^0 to Co^{3+}, is very similar to that observed by us for the series of chromium oxidation states, from Cr(0) to Cr(III). The absolute integrated intensity of Cr(*t*-BuDiNC)$_3$ is roughly 70 times that of Co(*t*-BuDiNC)$_3^{3+}$. The greatest difference in magnitude we observe between a Cr^0 and Cr^{3+} species was for the Cr(phenyl isocyanide)$_6$ complex, which has an absolute integrated intensity of 340 times that of its three-electron-oxidized analogue.

A similar study of a homoleptic series of d^6 metal carbonyls has also been reported[26] and shows a similar decrease in absolute integrated intensity with increasing oxidation state. The commonly accepted reason for the decrease is the reduction in $d\pi-\pi^*_{CO}$ back-bonding with increasing metal oxidation state. This decreases the amount of charge transferred to the CO during the vibrational transition, thereby reducing the net dipole moment change during that transition. The CO absorption intensity decreases as a result.[27,28] A similar decrease in $d\pi-\pi^*_{CN}$ back-bonding is responsible for the decrease in isocyanide peak intensities upon oxidation.

It should be noted that the greatest variability in integrated peak intensities through the series studied, for any single oxidation state, was in the Cr(III) compounds. For example, the absolute integrated intensity for the Cr(III) complex of 2,6-diisopropylphenyl isocyanide is nearly 5 times that of the 4-chloro-substituted aryl isocyanide. Moreover, the integrated ν_{CN} intensities of the Cr(III) compounds appear to increase with the electron-releasing ability (Hammett σ parameter) of the substituents on the aryl isocyanide ligand. A similar correlation between Hammett σ and the ν_{CN} stretching frequency of the Cr(III) complexes is also observed (ν_{CN} decreases with an increase in enhanced σ donation). A possible explanation for both of these relationships is that only when the degree of $d\pi-\pi^*_{CN}$ back-bonding is small do the differences in σ donation by the isocyanide become apparent. As the σ-donating ability of the aryl substituents increases, the electron density in the C lone pair (C–Nσ^*) orbital increases and the C–N σ bond weakens. This effect is also manifested in an increase in the absolute integrated intensities of the Cr^{3+} species. Although similar differences in σ donation probably exist for the other, more reduced species, they are not significant in comparison with the π contribution to the charge transfer during the vibrational transition.

UV–Visible Studies. Figure 3 shows the spectral changes that occur for a solution of Cr(2,6-diisopropylphenyl isocyanide)$_6$PF$_6$ upon reduction to the Cr(0) complex (Figure 3a) and oxidation to the Cr(II) complex (Figure 3b) and then to the Cr(III) complex (Figure 3c). The conditions under which these data were collected were identical with those under which the IR spectra in Figure 1 were observed. As was the case in the infrared experiments, the oxidations proceeded isosbestically. One problem unique to the UV–vis experiments was the photosensitivity of certain species, particularly some of the Cr^0 species, to UV–vis light in the interrogating beam. This caused appreciable decomposition during the electrolysis. In these cases, the electrolyses were performed in the dark, by shielding the cell from the Xe arc lamp, and only before and after spectra of the electrolyses were obtained.

The spectral changes observed upon the three sequential oxidations of Cr(2,6-diisopropylphenyl isocyanide)$_6$ all reflect the stabilization of the chromium d orbitals relative to both the π_b and π^* orbitals of the isocyanide. Thus the lowest energy band, at 479 nm, in the Cr(0) complex, which has been assigned as a $d\pi-\pi^*_v$ metal-to-ligand charge transfer (MLCT),[29] moves to higher energy after each oxidation. Similarly, the σ(CN)–$d\pi^*$ ligand-to-metal charge-transfer (LMCT) band at 369 nm in the Cr(I) complex is red-shifted upon oxidation to 476 nm in the Cr(II) species and finally to 594 nm in Cr(2,6-diisopropylphenyl isocyanide)$_6^{3+}$. These shifts are in accord with the increasing oxidation strength of the central metal ion in the complexes.

Table III presents the UV–vis data for the chromium aryl isocyanides studied and their oxidized analogues. Assignments for the zerovalent chromium complexes of the phenyl, 2,6-dimethylphenyl, and 4-chlorophenyl isocyanides and those for both the zero- and univalent compound of 2,6-diisopropylphenyl isocyanide have been reported elsewhere.[29,30] Assignments in Table III for the Cr(II) and Cr(III) complexes are based on the above d-orbital stabilization argument.

We also note the observation of a relationship between the lowest energy LMCT transition in the Cr(III) complexes (and to a lesser extent those of the Cr(II) complexes) with the electron-releasing ability of the aryl substituents. The isocyanides with the more electron-donating substituents, with the exception of 4-chlorophenyl isocyanide, have Cr(III) and Cr(II) complexes with lower energy LMCT transitions, as would be expected. For example, the LMCT band in Cr(phenyl isocyanide)$_6^{3+}$ is at 480 nm, whereas that for the 2,6-diisopropyl-substituted complex is at 594 nm. The LMCT bands in the Cr(II) complexes are at 428 and 476 nm, respectively. The corresponding transitions for the 2-methyl- and the 2,6-dimethyl-substituted aryl isocyanide complexes are at intermediate wavelengths. This observation of the enhanced importance of σ-donation effects in the Cr(aryl isocyanide) bonding in the high-valent compounds (Cr(II) and Cr(III)) is nicely consistent with the observed variation in ν_{CN} frequencies and integrated ν_{CN} intensities. We believe that the LMCT energy variation and ν_{CN} frequency intensity variations in the Cr(II) and especially the Cr(III) complexes arise from the same effect. The above-noted exceptional behavior of the 4-chlorophenyl isocyanide complex is thought to be due to the

---

[25] Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.
[26] Noack, K. *Helv. Chim. Acta* **1962**, *45*, 1847.
[27] Kettle, S. F. A.; Paul, I. *Adv. Organomet. Chem.* **1972**, *10*, 199.
[28] Brown, T. L.; Darensbourg, D. J. *Inorg. Chem.* **1967**, *6*, 971.
[29] Mann, K. R.; Cimolino, M.; Geoffroy, G. L.; Hammond, G. S.; Orio, A. A.; Albertin, G.; Gray, H. B. *Inorg. Chim. Acta* **1976**, *16*, 97.
[30] Mann, K. R. Ph.D. Thesis, California Institute of Technology, 1976.

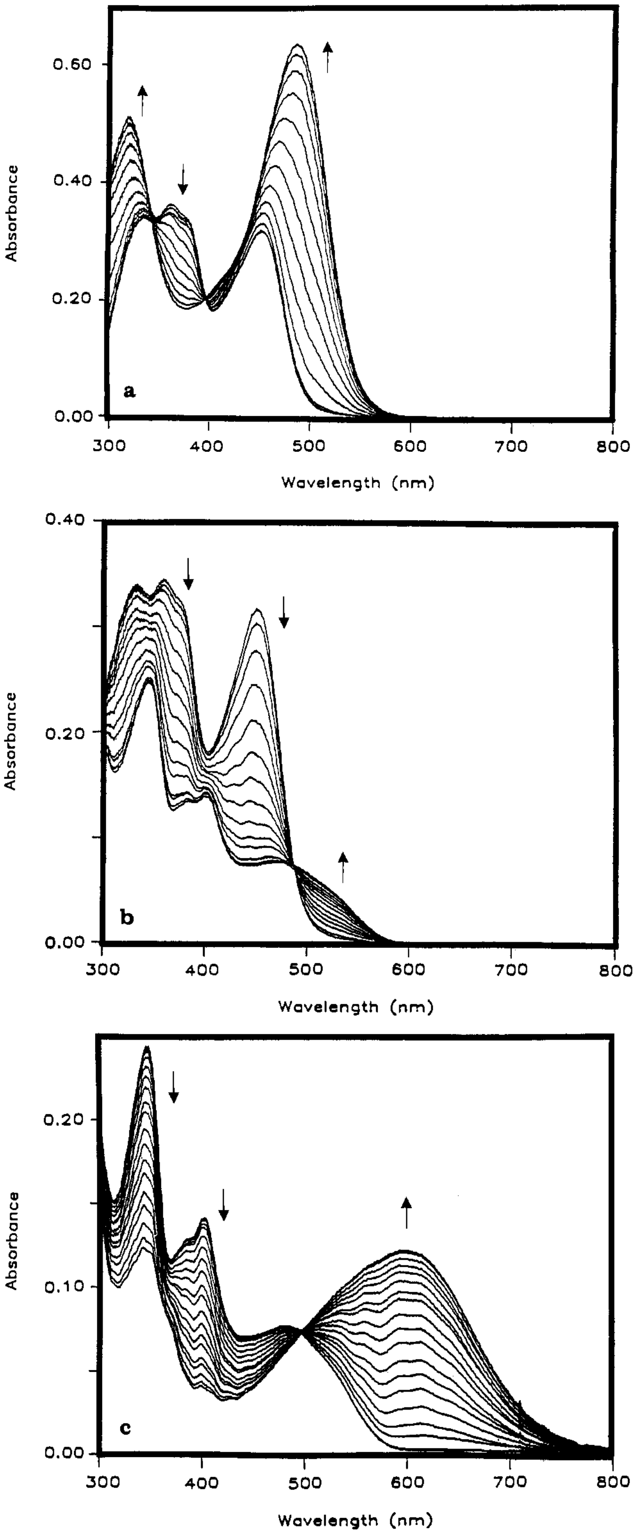

Figure 3. (a) UV-vis spectral changes that result during the electrolysis of a 0.82 × 10^{-3} M solution of Cr(2,6-diisopropylphenyl isocyanide)$_6$(PF$_6$) at −1.0 V vs the Pt pseudoreference electrode in CH_2Cl_2/TBAH. The arrows indicate the direction of change. The peaks at 445, 369, 355, and 330 nm decrease in intensity while those at 479 and 315 nm increase in intensity. Spectra were taken at 3.0-s intervals; total electrolysis time was about 45 s. (b) UV-vis spectral changes resulting from electrolysis of the same solution at +1.0 V vs the Pt pseudoreference electrode. The peaks at 445, 369, 355, and 330 nm decrease in intensity while those at 476, 397, 382, and 342 nm increase in intensity. Spectra were taken at 2.6-s intervals; total electrolysis time was about 45 s. (c) UV-vis spectral changes that result from the electrolysis of the solution generated in the experiment depicted in part b at +1.8 V vs the Pt pseudoreference electrode. The peaks at 476, 397, 382, and 342 nm decrease in intensity while those at 594, 362, and 344 nm increase in intensity. Spectra were taken every 2.6-s; total electrolysis time was about 65 s.

Table III. UV-Vis Absorbance Maxima and Extinction Coefficients for Hexakis(aryl isocyanide)chromium(*n*+) Complexes in CH_2Cl_2/TBAH

ligand	*n*	λ, nm	$\epsilon \times 10^{-3}$,[a] M^{-1} cm^{-1}	assgnt
2,6-diisopropylphenyl isocyanide	0	315	67	$d\pi \rightarrow \pi^*_h$
		415 (sh)	31	$d\pi \rightarrow \pi^*_v$
		479	85	$d\pi \rightarrow \pi^*_v$
	1	330	41	
		355	42	$d\pi \rightarrow \pi^*_v$
		369 (sh)	40	$\sigma(CNR) \rightarrow d\pi^*$
		445	39	$d\pi \rightarrow \pi^*_v$
	2	342	29	$d\pi \rightarrow \pi^*_v$
		382 (sh)	15	*b*
		397	17	$d\pi \rightarrow \pi^*_v$
		476	9.0	$\sigma(CNR) \rightarrow d\pi^*$
	3	344	15	$d\pi \rightarrow \pi^*_h$
		362 (sh)	13	*b*
		594	8.8	$\sigma(CNR) \rightarrow d\pi^*$
2,6-dimethylphenyl isocyanide	0	319	34	$d\pi \rightarrow \pi^*_h$
		410	58	$d\pi \rightarrow \pi^*_v$
		455	48	$d\pi \rightarrow \pi^*_v$
	1	355	38	$\sigma(CNR) \rightarrow d\pi^*$
		435	22	$d\pi \rightarrow \pi^*_v$
	2	334	24	$d\pi \rightarrow \pi^*_v$
		374 (sh)	11	*b*
		393	11	$d\pi \rightarrow \pi^*_v$
		445	6.6	$\sigma(CNR) \rightarrow d\pi^*$
2-methylphenyl isocyanide	0	318	31	$d\pi \rightarrow \pi^*_h$
		403	47	$d\pi \rightarrow \pi^*_v$
		448 (sh)	37	$d\pi \rightarrow \pi^*_v$
	1	330 (sh)	38	*b*
		353	46	$\sigma(CNR) \rightarrow d\pi^*$
		436	26	$d\pi \rightarrow \pi^*_v$
	2	329	29	$d\pi \rightarrow \pi^*_v$
		373 (sh)	13	*b*
		394	13	$d\pi \rightarrow \pi^*_v$
		435 (sh)	7.5	$\sigma(CNR) \rightarrow d\pi^*$
	3	332	12	$d\pi \rightarrow \pi^*_v$
		491	9.3	$\sigma(CNR) \rightarrow d\pi^*$
phenyl isocyanide	0	330 (sh)	36	$d\pi \rightarrow \pi^*_h$
		395	65	$d\pi \rightarrow \pi^*_v$
		450 (sh)	43	$d\pi \rightarrow \pi^*_v$
	1	321 (sh)	37	*b*
		353	47	$\sigma(CNR) \rightarrow d\pi^*$
		438	31	$d\pi \rightarrow \pi^*_v$
	2	325	29	$d\pi \rightarrow \pi^*_v$
		372 (sh)	14	*b*
		397	16	$d\pi \rightarrow \pi^*_v$
		428 (sh)	7.4	$\sigma(CNR) \rightarrow d\pi^*$
	3	338	12	$d\pi \rightarrow \pi^*_v$
		480	16	$\sigma(CNR) \rightarrow d\pi^*$
4-chlorophenyl isocyanide	0	332 (sh)	29	$d\pi \rightarrow \pi^*_h$
		407	53	$d\pi \rightarrow \pi^*_v$
		453 (sh)	40	$d\pi \rightarrow \pi^*_v$
	1	325 (sh)	30	*b*
		360	43	$\sigma(CNR) \rightarrow d\pi^*$
		448	27	$d\pi \rightarrow \pi^*_v$
	2	335	26	$d\pi \rightarrow \pi^*_v$
		388 (sh)	12	*b*
		406	13	$d\pi \rightarrow \pi^*_v$
		444 (sh)	5.9	$\sigma(CNR) \rightarrow d\pi^*$
	3	349	10	$d\pi \rightarrow \pi^*_v$
		509	15	$\sigma(CNR) \rightarrow d\pi^*$

[a] ϵ's are reported to ±15%. [b] Not assigned.

π-donating ability of the chloro substituent. None of the other substituents in the series studied is able to similarly donate electrons into the aryl π system; hence, the anomalous behavior is not necessarily in conflict with the established trend.

Acknowledgment. We thank Professors John Evans and Michael Weaver for several helpful discussions and John Evans for the use of his vapor deposition apparatus. J.P.B. thanks the University of Minnesota Graduate School for a Stanwood Johnson Memorial Fellowship and the University of Minnesota Chemistry Department for a departmental fellowship sponsored by 3M. The FT-IR spectrometer was purchased with funds provided by the

NSF (Grant No. CHE 8509325). This work was funded in part by an additional grant from 3M.

Registry No. Cr(2,6-diisopropylphenyl isocyanide)$_6$, 61770-86-3; Cr(2,6-diisopropylphenyl isocyanide)$_6^+$, 82456-69-7; Cr(2,6-diisopropylphenyl isocyanide)$_6^{2+}$, 82456-70-0; Cr(2,6-diisopropylphenyl isocyanide)$_6^{3+}$, 82456-71-1; Cr(2,6-dimethylphenyl isocyanide), 82456-65-3; Cr(2,6-dimethylphenyl isocyanide)$^+$, 82456-66-4; Cr(2,6-dimethylphenyl isocyanide)$^{2+}$, 82456-67-5; Cr(2,6-dimethylphenyl isocyanide)$^{3+}$, 82456-68-6; Cr(2-methylphenyl isocyanide), 57016-37-2; Cr(2-methylphenyl isocyanide)$^+$, 57016-38-3; Cr(2-methylphenyl isocyanide)$^{2+}$, 57016-40-7; Cr(2-methylphenyl isocyanide)$^{3+}$, 82469-01-0; Cr(phenyl isocyanide), 17375-15-4; Cr(phenyl isocyanide)$^+$, 57016-32-7; Cr(phenyl isocyanide)$^{2+}$, 57016-35-0; Cr(phenyl isocyanide)$^{3+}$, 70801-01-3; Cr(4-chlorophenyl isocyanide), 36732-52-2; Cr(4-chlorophenyl isocyanide)$^+$, 57016-50-9; Cr(4-chlorophenyl isocyanide)$^{2+}$, 57016-52-1; Cr(4-chlorophenyl isocyanide)$^{3+}$, 82456-73-3.

Supplementary Material Available: Plots of IR spectroelectrochemical data for each oxidation of all complexes and UV–vis spectroelectrochemical data for all oxidations involving nonphotosensitive complexes, UV–vis spectra of all oxidation states of each complex studied, and illustrations of the electrode arrangement (24 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Stereochemical Inhibition of Substitution in Simple Coordination Compounds. Experimental and Molecular Mechanics Evidence for Discrimination between Dissociative and Interchange Pathways in *trans*-Dichloro(*meso*- and *rac*-(*1,8*)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III)[1]

Carolyn L. Schwarz and John F. Endicott*

Received August 15, 1988

High-field ^{1}H NMR studies have shown that acid hydrolysis of the title complex gave a nonequilibrium mixture of aquo–chloro complexes when the macrocyclic ligand was in the racemic conformation. The cobalt center of this complex, Co(*rac*-(*N*)-Me_6[14]dieneN$_4$)Cl_2^+, has two different sites for substitution: one protected by axial geminal methyl and other functional groups of the macrocyclic ligand and one relatively unrestricted. The least favored aquo–chloro isomer could not be detected in equilibrated solutions, indicating that the substitution of water for chloride at the most congested site is thermodynamically favored by a factor of at least 10^2. Molecular mechanics calculations are in agreement with this thermodynamic selectivity. However, the thermodynamically least stable isomer is a major initial aquation product, and approximately equal amounts of the two chloro–aquo isomers were found to result from the first aquation of Co(*rac*-(*N*)-Me_6[14]dieneN$_4$)Cl_2^+. That substitution at the relatively uncongested site is kinetically, but not thermodynamically, favored implicates an interchange mechanism in which stereochemical protection of the coordination site from the entering water molecule countervails the stereochemical (macrocyclic ligand–Cl) repulsions that weaken the Co–Cl bond at this site. Such stereochemical protection of the coordination site is implied in the molecular mechanics calculations, which show that the weaker Co–Cl bond must be stretched more than 1.5 Å before the leaving group is free from the influence of the geminal methyl and other groups near the stereochemically congested site. The observations on several systems are in accord with a prevailing interchange mechanism for substitution, but with the interchange of ligands becoming increasingly dissociative as the substitution site becomes more congested.

Introduction

Ligand substitution reactions in cobalt(III) complexes have been so thoroughly investigated over the past 30 years[2,3] that their kinetic behavior has been described as paradigmatic of the dissociative interchange mechanism.[3b] This mechanistic assignment was in part based on the direct proportionality observed between the rate and equilibrium constants for Co(III) hydrolyses,[3] and it has been reasonably well supported by the small positive values found for volumes of activation.[4,5] Nevertheless, there are some peculiar features of the rate behavior in certain classes of cobalt(III) complexes, and different mechanistic pathways for substitution have sometimes been proposed. Most notably, there has been an almost universal postulation of a dissociative pathway for substitution in *trans*-Co^{III}(N$_4$)XY complexes in which the equatorial ligand is a tetraaza macrocycle.[6–9] Poon's work[6] has been especially systematic in its attempt to assess the effects of (a) the stereochemistry of alkyl substituents on the macrocyclic

---

(1) Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

(2) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1968.

(3) (a) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1965. (b) Langford, C. H.; Sastri, V. S. In *M. T. P. Reviews of Science*; Tobe, M. L., Ed.; Butterworths: London, 1972; Vol. 9, Series 2, p 203.

(4) Swaddle, T. W. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982.

(5) Palmer, A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89.

(6) (a) Poon, C.-K.; Lau, T.-C. L.; Kan, Y.-P. *J. Chem. Soc., Dalton Trans* **1983**, 1641. (b) Poon, C.-K.; Liaso, Sarah S. T. *J. Chem. Soc., Dalton Trans.* **1978**, 1180. (c) Poon, C.-K.; Mak, P.-W. *J. Chem. Soc., Dalton Trans* **1978**, 216. (d) Poon, C.-K.; Wong, C.-L.; Make, P.-W. *J. Chem. Soc., Dalton Trans.* **1977**, 1931. (e) Poon, C.-K.; Wan, W.-K.; Liaso, Sarah S. T. *J. Chem. Soc., Dalton Trans.* **1977**, 1247. (f) Poon, C.-K.; Wong, C.-L. *J. Chem. Soc., Dalton Trans.* **1977**, 523. (g) Poon, C.-K.; Wong, C.-L. *J. Chem. Soc., Dalton Trans.* **1976**, 966. (h) Chau, W.-K.; Lee, W. K.; Poon, C.-K. *J. Chem. Soc., Dalton Trans.* **1974**, 2419. (i) Poon, C.-K.; Tong, H.-W. *J. Chem. Soc., Dalton Trans.* **1974**, 930. (j) Poon, C.-K.; Tong, H.-W. *J. Chem. Soc., Dalton Trans.* **1974**, 1. (k) Poon, C.-K.; Tong, H.-W. *J. Chem. Soc., Dalton Trans.* **1973**, 1301. (l) Mak, P.-W.; Poon, C.-K.; *Inorg. Chem.* **1976**, *15*, 1949. (m) Poon, C.-K. *Proc. Int. Conf. Coord. Chem., XVI* **1974**, 3.47. (n) Lai, T. F.; Poon, C-K. *Inorg. Chem.* **1976**, *15*, 1562. (o) Poon, C.-K.; Wong, C.-L. *Inorg. Chem.* **1976**, *15*, 1562. (p) Poon, C.-K.; Wong, C.-L. *Inorg. Chem.* **1976**, *15*, 1573. (q) Lee, W.-K.; Poon, C.-K. *Inorg. Chem.* **1974**, *12*, 2016. (r) Poon, C.-K. *Coord. Chem. Rev.* **1973**, *10*, 1. (s) Mok, K.-S.; Poon, C.-K.; Tong, H.-W. *J. Chem. Soc. Dalton Trans.* **1972**, 1701. (t) Lui, C.-K.; Poon, C.-K. *J. Chem. Soc., Dalton Trans.* **1972**, 216. (u) Mok, K.-S.; Poon, C.-K. *J. Chem. Soc., Dalton Trans.* **1971**, 1358. (v) Poon, C.-K. *Inorg. Chim. Acta* **1971**, 2151. (w) Chau, W.-K.; Poon, C.-K. *J. Chem. Soc. A* **1971**, 3087. (x) Poon, C.-K.; Tong, H.-W. *J. Chem. Soc. A* **1971**, 2151. (y) Poon, C.-K. *Inorg. Chim. Acta Rev.* **1970**, *4*, 123. (z) Poon, C.-K.; Mok, K.-S. *Inorg. Chem.* **1971**, *10*, 225. (aa) Poon, C.-K.; Mok, K.-S. *J. Am. Chem. Soc.* **1970**, *92*, 4467. (bb) Poon, C.-K.; Tobe, M. L. *Inorg. Chem.* **1968**, *7*, 2398. (cc) Poon, C.-K.; Tobe, M. L. *Inorg. Chem.* **1968**, 1549. (dd) Poon, C.-K.; Tobe, M. L. *Chem. Commun.* **1968**, *3*, 156. (ee) Poon, C.-K.; Tobe, M. L. *J. Chem. Soc. A* **1967**, 2069. (ff) Bosnich, B.; Poon, C.-K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

0020-1669/89/1328-4011$01.50/0