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| CLASSIFICATION OF THIS PAGE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |       |                                                                                                                              | DOCUMENTATION PAGE                                                                |                                                                                               | Form Approved<br>OMB No 0704-0188 |                                 |
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| 12. PERSONAL AUTHOR(S)<br>Dr. Randy F. Johnston                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |       |                                                                                                                              |                                                                                   |                                                                                               |                                   |                                 |
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| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br>In this work several substituted-aryl-isocyanide ligands were synthesized. The corresponding isocyanidepentacarbonyl chromium complexes were synthesized photolytically to evaluate the electronic properties of the isocyanide ligands. The chromium compounds were characterized by elemental analysis, infrared, <sup>1</sup> H and <sup>13</sup> C NMR, and cyclic voltammetry. The infrared and <sup>13</sup> C NMR data contained only small differences between all the investigated ligands. This result indicated that only small perturbations in the electron density at the metal center had occurred. The cyclic voltammetry data had a larger variation with a oxidation potential range of 106mV. This range could prove to be important if a catalytic cycle of interest included an oxidative process. To completely determine the potential utility of these ligands more work needs to be done. |       |                                                                                                                              |                                                                                   |                                                                                               |                                   |                                 |
| DISTRIBUTION STATEMENT A<br>Approved for public release;<br>Distribution Unlimited                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |       |                                                                                                                              |                                                                                   |                                                                                               |                                   |                                 |
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| 22a. NAME OF RESPONSIBLE INDIVIDUAL                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |       |                                                                                                                              |                                                                                   | 22b. TELEPHONE (Include Area Code)                                                            |                                   | 22c. OFFICE SYMBOL              |

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### Final Report

In this work several aryl-isocyanide ligands were synthesized. They included: 2-chloroaryl isocyanide, 4-chloroaryl isocyanide, 4-nitroaryl isocyanide, 2-trifluoromethylaryl isocyanide, 4-trifluoromethylaryl isocyanide, 2,4-dichloroaryl isocyanide, 2,6-dichloroaryl isocyanide, and 2,4,6-trichloroaryl isocyanide. These ligands were expected to have a wide range of steric requirements at the metal center and to have a good range of sigma donating and accepting abilities. The C-N stretching frequency of these ligands were observed within a range of  $11\text{ cm}^{-1}$ .

The corresponding pentacarbonylchromium isocyanide compounds were synthesized by photolyzing the hexacarbonylchromium dissolved in tetrahydrofuran. The products of these photolyses were characterized by elemental analysis, infrared spectroscopy,  $^1\text{H}$  and  $^{13}\text{C}$  NMR. All of the chromium compounds contained a C-N stretch between  $2140$  and  $2130\text{ cm}^{-1}$ . There were two C-O stretches for the compounds except for the compound with the 2,4,6-trichloro substituted aryl isocyanide ligand. The  $^{13}\text{C}$  NMR spectra of these compounds contained two resonances for the carbonyl ligands which did not vary significantly (varied only  $0.6\text{ ppm}$ ). The NMR results seem to indicate that there is similar metal to carbonyl pi back bonding in all the compounds, since the observed chemical shifts are a function of this back donation and they remain fairly constant. The cyclic voltammograms of these compounds gave the largest variation of the characterization techniques. The potential for the Cr(0) to Cr(I) oxidation varied from  $695\text{ mV}$  to  $801\text{ mV}$  in the following order for the substituents: 4-chloro < 4-trifluoromethyl < 4-nitro < 2-chloro < 2,4-dichloro < 2-trifluoromethyl  $\leq$  2,6-dichloro < 2,4,6-trichloro. The ortho substitution of the aryl isocyanide ligand had the larger effect on the Cr(0)  $\rightarrow$  Cr(I) oxidation potential. The Cr(0)  $\rightarrow$  Cr(-I) reduction potential could not be studied since the reduction occurred less than  $-2.6\text{ V}$ .

This work has demonstrated that substituted isocyanide ligands do effect the physical properties of metals. Substituted isocyanide ligands are isoelectronic with carbonyl ligands but even with several electron withdrawing groups on the aryl ring they do not have similar electronic properties. The isocyanides still remain better sigma electron donors and weaker pi electron acceptors. The isocyanide ligands still could be used to "fine tune" the electron density on a metal center and most certainly the steric bulk. One drawback of the isocyanide ligands is their stability. The uncoordinated ligands are difficult to store for any length of time since they polymerize, but once they are coordinated they do become reasonably stable. The chromium compound with the 4-nitroaryl isocyanide did decompose in dry air and slowly in an inert atmosphere box which made it an exception. This observation might be utilized in obtaining a metal center which is coordinatively unsaturated if the metal complex loses an isocyanide ligand which then decomposes (polymerizes). Certainly more work can be done to examine these possibilities.

**Part I**

- a. **Papers Submitted to Refereed Journals**  
NONE
- b. **Papers Published in Refereed Journals**  
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- c. **Books (and sections thereof) Submitted for Publication**  
NONE
- d. **Books (and sections thereof) Published**  
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- e. **Technical Reports Published (including ONR Technical Reports) and  
Fapers Published in Non-Refereed Journals**  
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- f. **Patents Filed**  
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- g. **Patents Granted**  
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- i. **Contributed Presentations at Topical or Scientific/Technical Society  
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- j. **Honors/Awards/Prizes**  
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- k. **Number of Graduate Students Receiving Full or Partial Support on ONR  
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- l. **Number of Postdoctoral Fellows Receiving Full or Partial Support on  
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