

## Sulfur-Nitrogen-Bonded Metal Chelates. 18. 1,3-Dipolar Cycloadditions to Coordinated Azide in Nickel(II) Complexes of the Types $[\text{Ni}(\text{S}^{\ominus}\text{N}^{\ominus}\text{N})(\text{N}_3)]$ and $[(\text{S}^{\ominus}\text{N}^{\ominus}\text{N})\text{Ni}(\text{N}_3)\text{Ni}(\text{N}^{\ominus}\text{N}^{\ominus}\text{S})](\text{ClO}_4)$

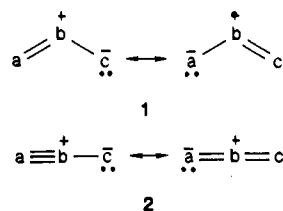
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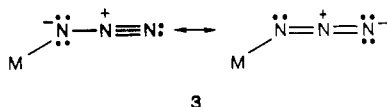
The reactions of nitriles, alkenes, alkynes, PhNCS, and  $\text{CS}_2$  with coordinated azide in nickel(II) chelates of the types  $[\text{NiL}(\text{N}_3)]$  ( $\text{L} = \text{L}^1\text{-L}^3$ ),  $[\text{L}^1\text{Ni}(\text{N}_3)\text{NiL}^1](\text{ClO}_4)$ , and  $[\text{L}^1\text{Ni}(\text{N}_3)\text{NiL}^3](\text{ClO}_4)$  (where  $\text{HL}^1 =$  methyl 2-((2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate,  $\text{HL}^2 =$  methyl 2-((2-(dimethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate,  $\text{HL}^3 =$  methyl 2-((2-(diethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate) have been investigated. In all of the cases [3+2] cycloaddition reactions take place, and the metal-bound heterocyclic anions produced are tetrazolates from nitriles, triazolines from alkenes, triazolates from alkynes, and phenyl tetrazolinethionate from PhNCS.  $\text{CS}_2$  reacts to produce thermally unstable thiothiazolates, which decomposes to isothiocyanate. With  $\mu$ -azido complexes either binuclear heterocyclic bridged compounds are obtained or mononuclear cycloaddition products are formed. The azido complexes do not react with carbon monoxide at ambient temperature and pressure. The nature of linkage isomerism in  $[\text{NiL}(\text{heterocycle})^-]$  complexes has been established from  $^1\text{H}$  NMR spectra. The kinetics of cycloaddition reactions have been investigated as a function of temperature and solvent ( $\text{NO}_2\text{Me}$ ,  $\text{NO}_2\text{Ph}$ , DMF). The reactivity of the dipolarophile increases with an increase in the electron-withdrawing power of its substituents. The reaction rate is also influenced by the electron-releasing power of the terminal nitrogen atom of the parent ligand and decreases in the order  $[\text{NiL}^1(\text{N}_3)] > [\text{NiL}^2(\text{N}_3)] > [\text{NiL}^3(\text{N}_3)]$ . The  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values indicate that the cycloaddition reactions are concerted.

### Introduction

1,3-Dipolar cycloaddition,<sup>1-6</sup> a common process in organic chemistry, involves the reaction between 1,3-dipoles having allyl (1) or propargylallenyl (2) type zwitterionic resonating structures



and multiple-bonded molecules, dipolarophiles. Among various 1,3-dipoles, organic azides<sup>3,6</sup> are particularly important for synthesizing heterocyclic compounds. By analogy, coordinated azide (3) in metal complexes can also undergo cycloaddition.<sup>7</sup>



Thus, azido complexes have been reported to react with nitriles<sup>8-20</sup> and isonitriles<sup>8,21-24</sup> to produce metal-nitrogen- and

metal-carbon-bonded tetrazolates, respectively. Similar reactions with alkynes<sup>12,16,18,19,25-27</sup> produce triazolates; alkenes, however, react very slowly and mostly afford impure products.<sup>18</sup> Azido complexes react with carbon disulfide<sup>8,12,14-16,28</sup> to produce thiothiazolates, but this being thermally and photochemically unstable often decomposes to the isothiocyanato complex. Several azido complexes have been found to react with organic isothiocyanates<sup>14,18,19,29</sup> and alkyl thiocyanates<sup>12,18,19</sup> to give tetrazolinethionates and 5-(thioalkyl)tetrazolates, respectively.  $\text{MeNCO}$ , on the other hand, reacts with  $[\text{M}(\text{PPh}_3)_2(\text{N}_3)_2]$  ( $\text{M} = \text{Pd}, \text{Pt}$ )<sup>12</sup> to form  $[\text{M}(\text{PPh}_3)_2(\text{NCO})_2]$ , presumably via decomposition of the cycloaddition product.

A survey of the azido complexes known to take part in cycloaddition reactions discloses several facts: (1) The majority of the reactions have been reported with palladium(II) and platinum(II) complexes, although compounds of other metals, viz. rhodium(I), iridium(I), gold(I), copper(I), mercury(II), lead(II), cobalt(III), gold(III), and tin(IV) have also been used. (2) Except for a few cobalt(III) complexes<sup>18</sup> derived from chelating ligands, other metal complexes are either phosphine-ligated species or organometallic derivatives. (3) While most of the reacting azido complexes have been mononuclear, in a few cases<sup>14,16,28b</sup> both 1,3- and 1,1-bridged

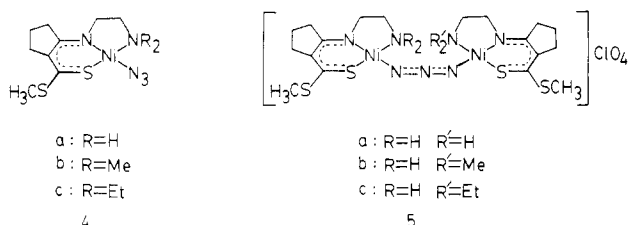
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azido binuclear complexes have been found to produce metal-bound bridged heterocycles.

We consider that the scope of cycloaddition reactions of azido complexes can be considerably widened by including metal chelates that provide substantial electron delocalization in the chelate ring and a suitable steric environment for uninhibited approach of a dipolarophile toward the azide. It can also be reasoned that an azide-coordinated square-planar nickel(II) complex will be more reactive than the corresponding palladium(II) and platinum(II) species because the  $Ni^{2+}$  ion will polarize the metal-bound azide more because of its greater charge density.

We have reported the thermodynamics of nucleophilic substitution of complexes  $[NiLX]$ ,<sup>30</sup> and augmented reactivities of coordinated nitriles in the complexes  $[NiL(NCR)](ClO_4)$ ,<sup>31</sup> where HL is methyl 2-((2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate or methyl 2-((2-dialkylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate. We now report cycloaddition reactions of the mononuclear azido complexes  $[NiL(N_3)]$  (4), and binuclear 1,3-bridged azido complexes,  $[LNi(N_3)NiL](ClO_4)$  (5). Characterization of the products of these reactions and their kinetics and mechanism are discussed.



## Experimental Section

**Materials.** All chemicals were reagent grade and were used as received. The ligands methyl 2-((2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate ( $HL^1$ ), methyl 2-((2-(dimethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate ( $HL^2$ ), and methyl 2-((2-(diethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate ( $HL^3$ ) were prepared as described earlier.<sup>32</sup>  $[NiL(NCMe)](ClO_4)$  ( $L = L^1-L^3$ ) complexes were obtained by a previously described procedure.<sup>30</sup>  $p$ - $NO_2C_6H_4CN$  and  $p$ - $ClC_6H_4CN$  were prepared from the corresponding aldehydes by a known method,<sup>33</sup> and  $PhCOC\equiv CCOPh$  was prepared by the literature method.<sup>34</sup> The solvents MeCN, MeNO<sub>2</sub>, PhNO<sub>2</sub>, and  $N,N$ -dimethylformamide (DMF) used for kinetic studies were purified and dried according to standard procedures.<sup>35</sup>

**Physical Measurements.** Infrared spectra in KBr pellets were recorded on a Perkin-Elmer Model 783 infrared spectrophotometer. Electronic spectra were obtained with a Pye-Unicam SP8-150 spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker 270 MHz spectrometer with  $CDCl_3$  or  $Me_2SO-d_6$  solutions;  $Me_4Si$  was used as the internal reference. A Philips PR9500 bridge was used for solution conductivity measurements. Magnetic measurements were carried out with a PAR Model 155 vibrating sample magnetometer. C, H and N analyses were performed on a Perkin-Elmer Model 240C elemental analyzer.

**Kinetic Measurements.** The reaction kinetics were followed spectrophotometrically between 10 and 60 °C. The temperature of the spectrophotometer cells were controlled to  $\pm 0.1$  °C with a Hakke K-Type thermostat. Spectral changes were monitored at 620 and 600 nm for the mononuclear and binuclear azido complexes, respectively. Kinetic measurements were carried out under pseudo-first-order conditions with ca.  $2 \times 10^{-3}$  M of each azido complex and 4 M dipolarophile. Kinetic runs were followed for at least 2 half-lives, and the completion of a reaction was ascertained by comparing the final molar absorptivity with that of an authentic product specimen.

**Synthesis and Reactions.** (1) Preparation of the Azido Complexes  $[NiL(N_3)]$  ( $L = L^1-L^3$  (I-III)). To a MeCN solution (25 mL) of

$[NiL(NCMe)](ClO_4)$  (5 mmol) an aqueous solution (5 mL) of  $NaN_3$  (0.33 g, 5 mmol) was slowly added with stirring. The azido complex formed was collected by filtration, washed successively with water and MeCN, and then recrystallized from  $Me_2CO$  for complex I or MeOH for complexes II and III. Typical yields were 95%.

$[L^1Ni(N_3)NiL^1](ClO_4)$  (IV),  $[L^1Ni(N_3)NiL^2](ClO_4)$  (V),  $[L^1Ni(N_3)NiL^3](ClO_4)$  (VI). A  $Me_2CO$  solution (100 mL) of  $[NiL(NCMe)](ClO_4)$  ( $L = L^1-L^3$ ) (5 mmol) was mixed with another  $Me_2CO$  solution (150 mL) of  $[NiL^1(N_3)]$  (1.58 g, 5 mmol). The resulting solution was heated under reflux for 0.5 h, concentrated to 50 mL, and filtered, and the filtrate was then kept overnight at ambient temperature. The reddish brown crystals that deposited were collected by filtration and recrystallized from  $Me_2CO$  (80%).

(2) Reactions with Nitriles.  $[NiL^1(N_4C-R)]$  ( $R = Me$  (VII), Et (VIII), Ph (IX)).  $[NiL^1(N_3)]$  (0.5 g) was mixed with MeCN (30 mL), EtCN (20 mL), or PhCN (10 mL) and heated on a steam bath (10 h for MeCN and EtCN and 15 h for PhCN). The solution was filtered, and the filtrate was concentrated on a rotary evaporator to half of the original volume. The crystals deposited from the solution on standing overnight were collected by filtration and recrystallized from MeCN (VII) or  $Me_2CO$  (VIII, IX) (80–85%).

$[NiL^1(N_4C-p-NO_2C_6H_4)]$  (X) and  $[NiL^1(N_4C-p-ClC_6H_4)]$  (XI). A mixture of  $[NiL^1(N_3)]$  (0.32 g, 1 mmol),  $CH_2Cl_2$  (80 mL), and  $p$ - $NO_2C_6H_4CN/p$ - $ClC_6H_4CN$  (4 mmol) was refluxed for 6 h. The product deposited during this period was collected by filtration. The compound was recrystallized from hot (ca. 100 °C) DMF (80%).

$[NiL^3(N_4C-R)]$  ( $R = Me$  (XII), Et (XIII)). Following the procedure adopted for VII and VIII, the reaction mixture in this case was concentrated to 5 mL, filtered, then diluted with 20 mL of  $Et_2O$ . The product obtained on standing was recrystallized from 1:3 MeOH– $Et_2O$  (70%).

$[NiL^3(N_4C-p-NO_2C_6H_4)]$  (XIV). The method of preparation was the same as for X; the product was recrystallized from MeOH (75%).

$[L^1Ni(N_4C-R)NiL^1](ClO_4)$  ( $R = Me$  (XV), Et (XVI), Ph (XVII)). Starting from  $[L^1Ni(N_3)NiL^1](ClO_4)$ , these compounds were prepared and recrystallized (80%) in the same way as described for VII–IX.

$[L^1Ni(N_4C-p-NO_2C_6H_4)NiL^1](ClO_4)$  (XVIII). The method of preparation was the same as for XIV; the product was recrystallized from  $Me_2CO$  (75%).

(3) Reactions with Alkenes.  $[NiL^1N_3C_2H_2(CO_2Me)_2]$  (XIX). Dimethyl fumarate (0.72 g, 5 mmol) was added to a suspension of  $[NiL^1(N_3)]$  (0.32 g, 1 mmol) in  $CH_2Cl_2$  (50 mL). The mixture on refluxing for 4 h gave a clear solution, which was concentrated to 10 mL and then filtered. The filtrate, on standing, slowly deposited crystals, which were collected after 6 h. The product was recrystallized from  $CH_2Cl_2$  (60%).

$[NiL(N_3C_2H_3-CN)]$  ( $L = L^1$  (XX),  $L = L^3$  (XXI)). A mixture containing  $[NiL(N_3)]$  (0.5 g),  $Me_2CO$  (50 mL), and  $CH_2=CHCN$  was refluxed for 8 h. The product obtained from the concentrated solution (15 mL) was recrystallized from  $Me_2CO$  (60–65%).

$[L^1Ni(N_3C_2H_2)(CO_2Me)_2]NiL^1](ClO_4)$  (XXII). This compound was obtained (60%) in the same way as described for XIX.

$[L^1Ni(N_3C_2H_3-CN)NiL^1](ClO_4)$  (XXIII). This compound was obtained (70%) by adopting the procedure described for XX. The product could not be recrystallized due to its insolubility.

(4) Reactions with Alkynes.  $[NiL^1N_3C_2(CO_2Me)_2]$  ( $L = L^1$  (XXIV),  $L = L^3$  (XXV)). A mixture of  $[NiL(N_3)]$  (0.5 g),  $CH_2Cl_2$  (50 mL), and  $MeO_2CC\equiv CCO_2Me$  (0.5 mL) was refluxed for 2 h. The product deposited from the concentrated solution (10 mL) was recrystallized from  $CH_2Cl_2$  (75%).

**Complex XXVI.** This compound was obtained (80%) in the same way as described for XXIV by using  $[NiL^1(N_3)]$  and  $PhCOC\equiv CCOPh$  as the reactants.

$[NiL^3N_3C_2(COPh)_2]$  (XXVII). The method of preparation was same as for XXV except that reactants were  $[NiL^3(N_3)]$  and  $PhCOC\equiv CCOPh$ .

$[L^1Ni(N_3C_2(CO_2Me)_2)NiL^1](ClO_4)$  (XXVIII) and  $[L^1Ni(N_3C_2(CO_2Me)_2)NiL^3](ClO_4)$  (XXIX). These compounds were obtained by refluxing a mixture of  $[L^1Ni(N_3)NiL^1](ClO_4)$  or  $[L^1Ni(N_3)NiL^3](ClO_4)$  and  $MeO_2CC\equiv CCO_2Me$  in  $CH_2Cl_2$  (similar to the preparation of XXIV and XXV). The products were recrystallized from  $CH_2Cl_2$  (75%).

(5) Reaction with PhNCS.  $[NiL(N_4C(S)Ph)]$  ( $L = L^1$  (XXX),  $L = L^3$  (XXXI)) and  $[L^1Ni(N_4C(S)Ph)NiL^1](ClO_4)$  (XXXII). About 0.5 g of the appropriate azido complex in 50 mL of  $Me_2CO$  was heated to boiling, and PhNCS (2 mL) was added dropwise. The reaction mixture was refluxed for 5–6 h; each product was isolated by concentrating the solution and was recrystallized from  $Me_2CO$  (70%).

(6) Reaction with  $CS_2$ .  $[NiL(NCS)]$  ( $L = L^1$  (XXXIII),  $L = L^3$  (XXXIV)). These compounds were obtained (90%) by refluxing a suspension of  $[NiL(N_3)]$  (0.5 g) in  $CS_2$  (25 mL). They were recrystallized from  $CHCl_3$ .

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**Table II.** Selected Infrared and Visible Spectral Data for the Azido Complexes and Their Cycloaddition Products

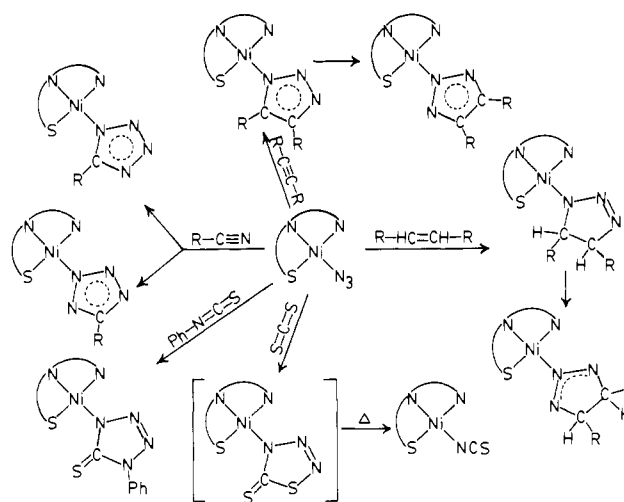
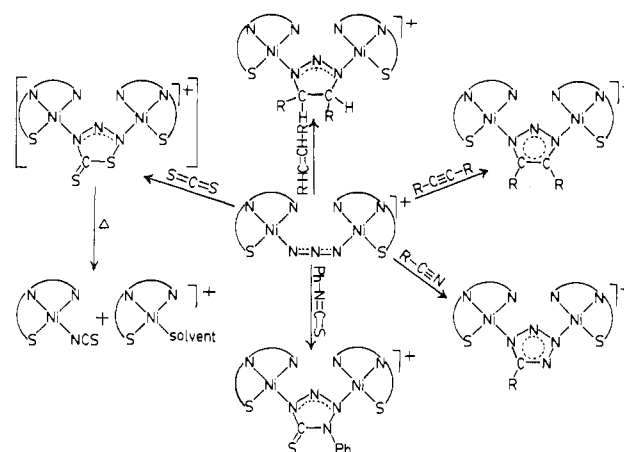
compd	IR, cm <sup>-1</sup>	$\tilde{\nu}_{\max}$ , cm <sup>-1</sup> ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> ) <sup>a</sup>
I	3295 m, 3270 m, 3220 m, 3135 w ( $\nu(\text{NH})$ ); 2040 s ( $\nu_{\text{as}}[\text{N}_3]$ ); 1350 m ( $\nu_{\text{s}}[\text{N}_3]$ )	17 250 (105)
IV	3300 m, 3220 m, 3140 w ( $\nu(\text{NH})$ ); 2085 s ( $\nu_{\text{as}}[\text{N}_3]$ ); 1350 w ( $\nu_{\text{s}}[\text{N}_3]$ )	17 550 (180)
VI	3300 m, 3220 m, ( $\nu(\text{NH})$ ); 2090 s ( $\nu_{\text{as}}[\text{N}_3]$ ); 1350 w ( $\nu_{\text{s}}[\text{N}_3]$ )	17 250 (190)
VIII	3250 m, 3220 m, 3120 w ( $\nu(\text{NH})$ ); 1235 m, 1160 m, 1128 m, 1065 m <sup>b</sup>	19 930 (100)
X	3290 m, 3235 m, 3120 w ( $\nu(\text{NH})$ ); 1175 w, 1110 s, 1040 m, 880 m <sup>b</sup>	18 520 (115)
XII	1228 m, 1110 w, 1085 m, 1020 m <sup>b</sup>	18 180 (80)
XVII	3300 m, 3250 m, 3220 w, 3140 w ( $\nu(\text{NH})$ ); 1225 w, 1015 w, 790 w <sup>b</sup>	18 530 (180)
XIX	3280 m, 3255 m, 3180 m, 3100 w ( $\nu(\text{NH})$ ); 1740 s, 1715 s ( $\nu(\text{C}=\text{O})$ ); 825 m, 795 m, 775 m <sup>b</sup>	18 520 (120)
XX	3220 m, 3110 m ( $\nu(\text{NH})$ ); 2120 ( $\nu(\text{C}\equiv\text{N})$ ); 790 m, 685 m <sup>b</sup>	18 180 (90)
XXI	2160 m ( $\nu(\text{C}\equiv\text{N})$ ); 795 m, 740 m, 690 <sup>b</sup>	18 200 (80)
XXII	3290 m, 3240 m, 3140 w ( $\nu(\text{NH})$ ); 1725 s ( $\nu(\text{C}=\text{O})$ ); 790 w <sup>b</sup>	17 850 (280)
XXIII	3290 m, 3250 m, 3230 w, 3140 w ( $\nu(\text{NH})$ ); 2160 ( $\nu(\text{C}\equiv\text{N})$ ); 790 w <sup>b</sup>	18 520 (200)
XXIV	3295 m, 3265 m, 3195 m, 3110 w ( $\nu(\text{NH})$ ); 1745 s, 1725 s ( $\nu(\text{C}=\text{O})$ ); 830 m, 800 m, 775 m <sup>b</sup>	18 870 (220)
XXVI	1650 s ( $\nu(\text{C}=\text{O} + \text{C}=\text{N})$ ); 810 m, 785 m, 760 m <sup>b</sup>	18 180 (490)
XXVII	1660 s, 1645 s ( $\nu(\text{C}=\text{O})$ ); 900 s, 800 m, 760 m <sup>b</sup>	17 850 (110)
XXVIII	3300 m, 3235 m, 3190 m, 3125 w ( $\nu(\text{NH})$ ); 1715 s, 1700 s ( $\nu(\text{C}=\text{O})$ ); 820 m, 800 m, 775 m <sup>b</sup>	18 520 (190)
XXIX	3300 m, 3240 m, 3180 w, 3110 w ( $\nu(\text{NH})$ ); 1750 s, 1725 s ( $\nu(\text{C}=\text{O})$ ); 820 m, 800 m, 765 m, 745 m <sup>b</sup>	17 550 (130)
XXX	3180 m, 3100 m ( $\nu(\text{NH})$ ); 1300 s ( $\nu(\text{C}=\text{S})$ ); 1235 w, 1150 m, 1090 m <sup>b</sup>	17 700 (270)
XXXII	3300 m, 3240 m, 3140 w ( $\nu(\text{NH})$ ); 755 m, 695 m <sup>b</sup>	17 550 (280)
XXXIII	3320 w, 3280 m, 3200 m, 3130 w ( $\nu(\text{NH})$ ); 2110 s ( $\nu(\text{NCS})$ )	17 700 (115)

<sup>a</sup>Spectra were recorded in DMF solution. <sup>b</sup>Heterocyclic ring vibrations.

**Caution!** Perchlorate salts are potentially explosive, especially when heated.

Analytical data for representative complexes are given in Table I (supplementary material).

**I. Synthesis, Reactivities, and Characterization.** Mononuclear azido complexes I–III were readily obtained by reacting  $[\text{NiL}(\text{NCMe})](\text{ClO}_4)$  complexes with  $\text{NaN}_3$ . Also reaction between stoichiometric amounts of  $[\text{NiL}(\text{NCMe})](\text{ClO}_4)$  ( $\text{L} = \text{L}^1\text{--L}^3$ ) and  $[\text{NiL}^1(\text{N}_3)]$  complexes led to the formation of binuclear  $\mu$ -azido complexes IV–VI. All these azido complexes are diamagnetic and their electronic spectra (see Table II) are consistent with square-planar geometries about nickel. Complexes I–III are nonelectrolytes, but IV–VI behave as 1:1 electrolytes ( $\Delta_M$  in DMF ca.  $70 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ). The IR spectra of I–III (Table II) exhibit  $\nu_{\text{as}}[\text{N}_3]$  and  $\nu_{\text{s}}[\text{N}_3]$  at about 2050 and 1350  $\text{cm}^{-1}$ , respectively. In complexes IV–VI  $\nu_{\text{as}}[\text{N}_3]$  is shifted to a higher frequency (2090  $\text{cm}^{-1}$ ), in conformity with the presence of an azido bridge.<sup>7</sup> The  $\nu_{\text{s}}[\text{N}_3]$  observed at 1350  $\text{cm}^{-1}$  in these compounds is of very low intensity. Although it is difficult to distinguish between 1,1 and 1,3 azido bridges on the basis of IR spectra, it has been pointed out<sup>36</sup> that  $\nu_{\text{s}}[\text{N}_3]$  in the 1,3-bridged azide is either IR inactive or of low intensity. On this basis we consider that 1,3 azido bridges are present in complexes IV–VI. Alternative 1,1 bridging appears unlikely on steric grounds. In the following sections we discuss the cycloaddition reactions of azido complexes that are outlined in Schemes I and II for mononuclear and binuclear nickel(II) complexes, respectively.

**Scheme I****Scheme II**

**1. Reactions with Nitriles.** Complexes I–III react with aliphatic and aromatic nitriles to produce tetrazolate complexes VII–XIV. It will be seen later (section II) that electron-deficient nitriles ( $p\text{-NO}_2\text{C}_6\text{H}_4\text{CN}$ ,  $p\text{-ClC}_6\text{H}_4\text{CN}$ ) react much more rapidly with the azido complexes than do electron-rich nitriles (MeCN, EtCN, PhCN). The reactivity patterns of the bridged azido complexes IV and VI showed some interesting differences.  $[\text{L}^1\text{Ni}(\text{N}_3)(\text{NiL}^1)]\text{ClO}_4$  (IV) reacted with nitriles to give the corresponding  $\mu$ -tetrazolate complexes XV–XVIII. However, the reaction between  $[\text{L}^1\text{Ni}(\text{N}_3)\text{NiL}^3]\text{ClO}_4$  (VI) and nitriles always gave monomeric  $[\text{NiL}^1(\text{tetrazolate})]$  complexes. The formation of tetrazole complexes can be followed easily by observing the disappearance of  $\nu_{\text{as}}[\text{N}_3]$  and  $\nu_{\text{s}}[\text{N}_3]$  and the appearance of new bands due to tetrazole ring vibrations in the range 1250–750  $\text{cm}^{-1}$  (Table II). In  $\mu$ -tetrazolate complexes some of these ring vibrations are obscured by perchlorate bands.

It should be noted that the tetrazole anion can be coordinated by a metal center through either its N(1) or N(2) nitrogen atom. Molecular orbital calculations<sup>37–39</sup> indicate that these two bonding modes are essentially isoenergetic. Evidence obtained to date indicates that either both N(1) and N(2) isomers are formed simultaneously<sup>12,18,19,37–39</sup> or that the N(2) isomer is produced exclusively.<sup>12,18,19</sup>

In Table III <sup>1</sup>H NMR spectra of  $[\text{NiL}^1(\text{tetrazolate})]$  complexes VII–X that are diagnostic of the nature of tetrazolate linkage are given. The <sup>1</sup>H NMR spectrum of VII (Figure 1, supplementary material) exhibits three singlets ( $\delta = 2.58, 2.66, 2.72$ ) due to the  $\text{CH}_3$  group of methyltetrazole and two broad signals ( $\delta = 4.1, 4.4$ ) due to the  $\text{NH}_2$  group of  $\text{L}^1$ . Two of the  $\text{CH}_3$  resonances (at  $\delta = 2.58$  and 2.72) and the two  $\text{NH}_2$  signals can be accounted for by the presence of both N(1)- and N(2)-bound tetrazoles. However, to account for the third  $\text{CH}_3$  singlet

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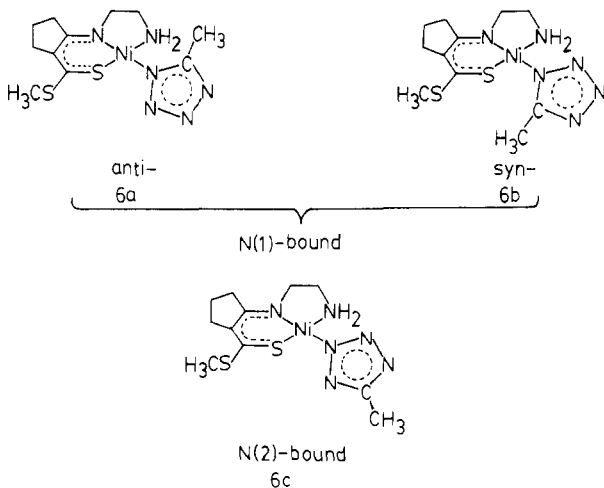
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**Table III.**  $^1\text{H}$  NMR Spectral Data for Tetrazolate, Triazolinate, and Triazolite Complexes

compd	heterocyclic ring	chemical shifts, $\delta$	comment
VII <sup>a</sup>		2.40 s (SCH <sub>3</sub> ); 2.58 s (CH <sub>3</sub> , N(2) tetrazole); 2.66 s (CH <sub>3</sub> , N(1) <i>syn</i> ); 2.72 s (CH <sub>3</sub> , N(1) <i>anti</i> ); 4.1, 4.4 br (NH <sub>2</sub> )	N(1):N(2) = 2:1
VIII <sup>a</sup>		1.18 t ( $\beta$ -CH <sub>3</sub> , N(2) tetrazole); 1.48 t ( $\beta$ -CH <sub>3</sub> , N(1) tetrazole); 2.40 s (SCH <sub>3</sub> ); 4.2, 4.5 br (NH <sub>2</sub> )	N(1):N(2) = 2:1
IX <sup>a</sup>		2.48 s (SCH <sub>3</sub> ); 4.45, 4.55 br (NH <sub>2</sub> ); 7.5 m (C <sub>6</sub> H <sub>5</sub> , N(2) tetrazole); 8.0 m (C <sub>6</sub> H <sub>5</sub> , N(1) <i>syn</i> ); 9.12 m (C <sub>6</sub> H <sub>5</sub> , N(1) <i>anti</i> )	N(1):N(2) = 2:3
X <sup>a</sup>		2.52 s (SCH <sub>3</sub> ); 4.55 br (NH <sub>2</sub> ); 8.35 m (C <sub>6</sub> H <sub>4</sub> )	N(2) isomer
XIX <sup>b</sup>		2.52 s (SCH <sub>3</sub> ); 3.86 s (CO <sub>2</sub> CH <sub>3</sub> ); 4.0 s, 4.12 s (CH=CH); 4.4 br (NH <sub>2</sub> )	N(2) isomer
XXIV <sup>b</sup>		2.52 s (SCH <sub>3</sub> ); 3.86 s (CO <sub>2</sub> CH <sub>3</sub> ); 4.66 (NH <sub>2</sub> )	N(2) isomer

<sup>a</sup> In Me<sub>2</sub>SO-*d*<sub>6</sub>. <sup>b</sup> In CDCl<sub>3</sub>.

at  $\delta = 2.66$ , it is necessary to consider the rotation of the tetrazole ring along the Ni-N bond in the two isomers. Molecular models indicate that while the N(2)-bound tetrazole is free to rotate, similar rotation of the N(1) isomer is restricted due to the steric interaction between CH<sub>3</sub> and NH<sub>2</sub> groups. Accordingly, the N(1)-bound tetrazole can exist in two conformations: *syn* (**6a**) and *anti* (**6b**). In the *anti* configuration the



CH<sub>3</sub> group of tetrazole is closer to the paramagnetic anisotropic influence of the metal center and therefore is most deshielded. By contrast, the CH<sub>3</sub> group of the N(2)-bound tetrazole (**6c**) is most shielded because it is farthest from the metal center. Thus, the three CH<sub>3</sub> singlets observed at  $\delta$  2.58, 2.66, and 2.73 can be attributed to N(2)-, *syn*-N(1)-, and *anti*-N(1)-bound tetrazole, respectively. From the position and intensities of the NH<sub>2</sub> resonances ( $\delta$  4.1 and 4.2, 2:1 ratio) it appears that the one appearing at the higher field is due to the N(1) isomer. This assignment

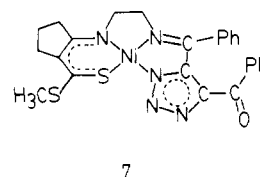
seems justified because the electron-releasing CH<sub>3</sub> renders the Ni-N(1) tetrazole bond stronger, which in effect causes shielding of the NH<sub>2</sub> group in this isomer. The determination of the relative abundances of **6a-c** by measuring the intensities of three CH<sub>3</sub> singlets, however, is prevented by the presence of overlapping signals due to L<sup>1</sup> and the solvent.

The same stereochemical consideration is applicable to complex VIII. However, this complex exhibits two triplets ( $\delta$  1.18 and 1.48), instead of three, due to the CH<sub>3</sub> group of ethyltetrazole. The most shielded one is obviously that of N(2)-bound ethyltetrazole. Molecular models suggest that the CH<sub>3</sub> group of N(1)-bound tetrazole in both *syn* and *anti* conformations will exhibit similar chemical shifts since the CH<sub>3</sub> group is remote from the metal center in both cases. The relative abundance of N(1)- and N(2)-bound tetrazoles in complex VIII is found to be 2:1 on the basis of both CH<sub>3</sub> and NH<sub>2</sub> resonances.

In complex IX the phenyl substituent of the tetrazole ligand exhibits three multiplets at  $\delta$  7.5, 8.0, and 9.1 (intensity ratio 16:10:1), and the NH<sub>2</sub> protons of L<sup>1</sup> appear as two broad peaks at  $\delta$  4.45 and 4.55. The point to note here is that rotation of the phenyltetrazole about the Ni-N(1) bond is severely restricted by steric interactions between the C<sub>6</sub>H<sub>5</sub> and NH<sub>2</sub> groups. Consequently, the *syn* isomer will be more abundant than the *anti* isomer. The observed intensity ratio (10:1) confirms this expectation. It is also evident that the relative proportion of the N(1)- and N(2)-bound phenyltetrazole is close to 3:2. We thus conclude that the proportion of the N(2) isomer increases with decreasing electron-releasing capacity of the tetrazole substituent. The effect becomes more striking in complex X, which exhibits (Figure 2; supplementary material) a single multiplet due to the aromatic ring ( $\delta$  8.35) and a broad signal ( $\delta$  4.5) due to NH<sub>2</sub>. Here the cycloaddition product is solely the N(2)-bound tetrazole.

**2. Reactions with Alkenes.** Most of the cycloaddition reactions of alkenes reported in the literature give impure products presumably because of thermal instability and base sensitivity of  $\Delta^2$ -triazoline.<sup>40</sup> We have investigated the reactions of complexes I, III, and IV with dimethyl fumarate and acrylonitrile and obtained stable [3+2] cycloaddition products, XIX-XXIII. The triazolite complexes formed were easily characterized from their IR spectra. The cycloaddition of CH<sub>2</sub>=CHCN to coordinated azide, in principle, can take place via C=C or C $\equiv$ N. The presence of  $\nu(\text{C}\equiv\text{N})$  at about 2150 cm<sup>-1</sup> in the reaction products XX, XXI, and XXIII clearly establishes that C=C adds to coordinated azide. Concerning N(1) vs. N(2) nickel-triazolite bonding, the  $^1\text{H}$  NMR spectrum of complex XIX shows a singlet at  $\delta$  3.86 for the six CO<sub>2</sub>Me protons, which is clearly indicative of the N(2) isomer because in the N(1) isomer two resonances are expected for anisochronous CO<sub>2</sub>Me groups.

**3. Reactions with Alkynes.** Dimethyl acetylenedicarboxylate and dibenzoylacetylene readily react with mono- and binuclear azido complexes to produce the triazolite complexes XXIV-XXIX. It is interesting to note that, unlike the nitriles, MeO<sub>2</sub>CC $\equiv$ CCO<sub>2</sub>Me reacts with [L<sup>1</sup>Ni(N<sub>3</sub>)NiL<sup>3</sup>](ClO<sub>4</sub>) to give the  $\mu$ -triazolite species XXIX. The triazolite complexes can be recognized by observing expected  $\nu(\text{C}=\text{O})$  and triazole ring frequencies (Table II). Although the IR spectrum of complex XXVI obtained by reacting [NiL<sup>1</sup>(N<sub>3</sub>)] with PhCOC $\equiv$ CCOPh clearly indicates the presence of a triazolite species, it does not indicate the presence of  $\nu(\text{N}-\text{H})$  in L<sup>1</sup> observed in all other cycloaddition products. The analytical data for this product indicate an anhydrous complex. It appears that one of the carbonyl groups of XXVI condenses with the NH<sub>2</sub> group of L<sup>1</sup> to form the complex XXVI (**7**). The  $^1\text{H}$  NMR



spectrum of complex XXIV (Table III) obtained by reacting [NiL<sup>1</sup>(N<sub>3</sub>)] with MeO<sub>2</sub>CC $\equiv$ CCO<sub>2</sub>Me shows it again to be an N(2) linkage isomer.

**4. Reactions with Heterocumulenes.** CS<sub>2</sub> reacts with azido complexes to give thiothiazolinate products; however, these could not be isolated in pure form due to their low thermal stability; instead, thiocyanato complexes were obtained after prolonged reaction. It is interesting to note that CS<sub>2</sub> reacts with [L<sup>1</sup>Ni(N<sub>3</sub>)NiL<sup>3</sup>]/ClO<sub>4</sub> to form [NiL<sup>1</sup>(NCS)], but with [L<sup>1</sup>Ni(N<sub>3</sub>)NiL<sup>3</sup>]<sup>+</sup> it gives [NiL<sup>3</sup>(NCS)]. On the other hand, PhNCS reacts with azido complexes to produce the stable tetrazolothionate complexes XXX-XXXII.

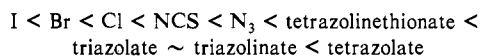
**Table IV.** Rates Constants for the Cycloaddition Reactions of Azido Complexes with Nitriles and Alkynes in Different Solvents<sup>a</sup> at Different Temperatures

complex	dipolarophile	solvent	T, °C	10 <sup>5</sup> k <sub>obsd</sub> , s <sup>-1</sup>	10 <sup>2</sup> k, <sup>b</sup> s <sup>-1</sup> M <sup>-1</sup> (50 °C)	ΔH <sup>‡</sup> , kJ mol <sup>-1</sup>	-ΔS <sup>‡</sup> , J mol <sup>-1</sup> K <sup>-1</sup>	
[NiL <sup>1</sup> N <sub>3</sub> ]	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CN	NB	60	61 ± 1	15.1	50 ± 3	107 ± 10	
			50	30.5 ± 0.5				
			40	16.9 ± 0.1				
		DMF	60	30.2 ± 0.2	7.7	59 ± 3	86 ± 11	
			50	16.2 ± 0.1				
			40	7.2 ± 0.1				
	NM	60	25.5 ± 0.5	6.0	61 ± 2	80 ± 5		
		50	12.6 ± 0.1					
		40	5.6 ± 0.1					
	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CN	NB	50	2.72 ± 0.04	1.35			
		DMF	50	2.05 ± 0.05				
		NM	50	1.71 ± 0.03				
	PhCN	NB	50	0.91 ± 0.03	0.43			
		DMF	50	0.88 ± 0.06				
		NM	50	0.85 ± 0.05				
MeCN	AN	50	0.65 ± 0.03	0.31				
	NM	50	0.15 ± 0.01					
[NiL <sup>2</sup> N <sub>3</sub> ]	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CN	NB	60	49 ± 1	11.4	56 ± 2	92 ± 4	
			50	23.7 ± 0.3				
			40	11.1 ± 0.1				
[NiL <sup>3</sup> N <sub>3</sub> ]	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CN	NB	60	13.4 ± 0.1	3.03	64 ± 2	77 ± 3	
			50	6.35 ± 0.05				
			40	2.80 ± 0.05				
[L <sup>1</sup> Ni(N <sub>3</sub> )NiL <sup>1</sup> ](ClO <sub>4</sub> )	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CN	NB	60	51.0 ± 0.5	12.0	58 ± 2	83 ± 6	
			50	24.6 ± 0.2				
			40	12.3 ± 0.1				
	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CN	NB	50	4.5 ± 0.1	2.16			
			NM	50				3.1 ± 0.1
			NM	50				1.23 ± 0.03
	PhCN	NB	50	1.37 ± 0.03	0.66			
			NM	50				0.56 ± 0.03
[NiL <sup>2</sup> N <sub>3</sub> ]	MeO <sub>2</sub> CC≡CCO <sub>2</sub> Me	NB	50	352 ± 16	171	40 ± 2	117 ± 6	
			40	202 ± 5				
			30	122 ± 6				
	Ph(CO)C≡C(CO)Ph	NB	30	881 ± 15	1130 <sup>c</sup>	37 ± 1	111 ± 5	
			20	528 ± 9				
			10	287 ± 3				
[NiL <sup>3</sup> N <sub>3</sub> ]	MeO <sub>2</sub> CC≡CCO <sub>2</sub> Me	NB	50	87 ± 2	42	49 ± 2	102 ± 8	
			40	50.5 ± 0.5				
			30	24.5 ± 0.5				
	Ph(CO)C≡C(CO)Ph	NB	30	99 ± 2	147 <sup>c</sup>	43 ± 2	110 ± 5	
			20	53.6 ± 1.4				
			10	28.0 ± 0.5				

<sup>a</sup> NB = nitrobenzene; DMF = dimethylformamide; NM = nitromethane; AN = acetonitrile. <sup>b</sup> Obtained as the ratio  $k_{\text{obsd}}/[\text{complex}]$ . <sup>c</sup> Estimated value obtained by interpolation.

**5. Reaction with Carbon Monoxide.** Azido complexes are known to react with CO to produce isocyanato complexes<sup>8,15,41</sup> via atom-transfer redox reactions. Reactions with binuclear azido complexes<sup>8,14,16</sup> give bridged isocyanato products under relatively mild condition for palladium(II), platinum(II), rhodium(I), and gold(I) reactants and forcing conditions for cobalt(III).<sup>18</sup> We found that neither [NiL(N<sub>3</sub>)] nor [L<sup>1</sup>Ni(N<sub>3</sub>)NiL<sup>1</sup>](ClO<sub>4</sub>) reacted with CO at ambient temperature and pressure over long time periods.

**Spectrochemical Series.** The precursor azido complexes and their cycloaddition products have square-planar geometries according to their spectra. Consideration of only the d-d bands observed in these compounds (Table II) and similar spectral features exhibited by other [NiLX] (X = Cl, Br, I, NCS) complexes<sup>30</sup> suggests the following spectrochemical series for the fourth coordination site:



**II. Kinetics and Mechanism of Cycloaddition.** The kinetics of cycloaddition reactions of [NiL(N<sub>3</sub>)] (L = L<sup>1</sup>-L<sup>3</sup>) and [L<sup>1</sup>Ni(N<sub>3</sub>)NiL<sup>1</sup>](ClO<sub>4</sub>) complexes with nitriles (MeCN, PhCN, *p*-ClC<sub>6</sub>H<sub>4</sub>CN, *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN) and alkynes (PhCOC≡CCOPh, MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me) were investigated as a function of temperature and solvent (NO<sub>2</sub>Me, NO<sub>2</sub>Ph, DMF).

Preliminary studies showed that the reaction rate of *trans*-MeO<sub>2</sub>CCH=CHCO<sub>2</sub>Me with [NiL<sup>1</sup>(N<sub>3</sub>)] is slow below 40 °C but that

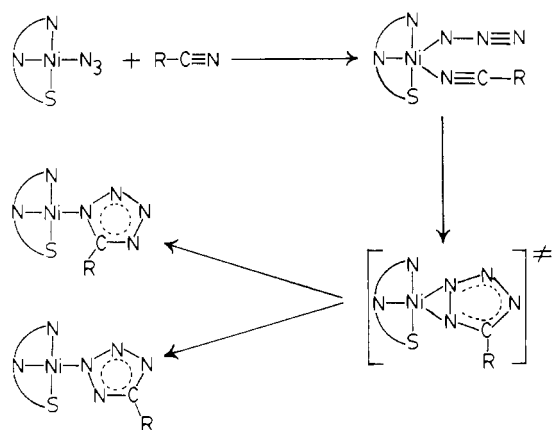
at least partial decomposition of the cycloaddition product takes place above 60 °C. For this reason the kinetics of reactions with alkenes were not investigated in detail. However, it is noted that MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me reacts much more rapidly with [NiL<sup>1</sup>(N<sub>3</sub>)] than does *trans*-MeO<sub>2</sub>CCH=CHCO<sub>2</sub>Me at room temperature.

The rate constants ( $k_{\text{obsd}}$ ) obtained under pseudo-first-order conditions for all the systems are given in Table IV, which also includes estimates of ΔH<sup>‡</sup> and ΔS<sup>‡</sup> for each system. The results show a strong dependence of  $k_{\text{obsd}}$  on the polarizing characteristics of the dipolarophiles. Linear plots were obtained when log  $k_{\text{obsd}}$  values were plotted vs.  $\sigma_p$  values for the substituents in aromatic nitriles. The order of reactivity of the nitriles, *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN > *p*-ClC<sub>6</sub>H<sub>4</sub>CN > PhCN > MeCN, is consistent with the decreasing electron-withdrawing power of the substituents in this same order.

We have already noted that both N(1)- and N(2)-bound tetrazolate products are formed, their relative abundances depending on the nitrile reactant. A mixture of N(1) and N(2) isomers is obtained with MeCN, EtCN, and PhCN, but only the N(2) isomer is obtained with *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN. Resonance structure 3 of metal azides suggests that regioselective attack by nitrile is unlikely since it is not possible to identify unequivocally the nucleophilic center of the 1,3-dipole. The formation of a three-centered activated complex<sup>19</sup> (shown in Scheme II) can be invoked to explain the type of isomer(s) formed. The breaking of Ni-N(1) or Ni-N(2) bonds in the activated state is affected by the substituent R. When R is strongly electron-withdrawing, the Ni-N(1) bond breaks because this nitrogen is electron-poor, whereas with an electron releasing R, both Ni(2)- and Ni-N(1) bonds can break; the product of the latter process will be more stable with a strongly electron-releasing

(41) Collman, J. P.; Kubota, M.; Hoshing, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 4809.

Scheme III



R. The  $^1\text{H}$  NMR results are in agreement with these expectations.

The kinetics of cycloaddition reactions of  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  and  $\text{PhCOC}\equiv\text{CCOPh}$  with complexes II and III were investigated. Complex I was not studied because its reaction with  $\text{PhCOC}\equiv\text{CCOPh}$  is complicated (section I). The rate data in Table IV show considerably faster reactions with alkynes than with nitriles (especially the electron-rich ones). The higher reactivity of  $\text{PhCOC}\equiv\text{CCOPh}$  compared to  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  is due to the greater polarizing ability of the former. Although the addition of an alkyne to coordinated azide is expected to produce the N(1)-bound triazole, the N(2) isomer is actually obtained. Spontaneous conversion of the N(1) to the N(2) isomer (Scheme 1) observed in the present study and other reported studies<sup>18</sup> appears to be electronically and sterically promoted.

An important question about these reactions is whether they are concerted or stepwise. An answer was sought by investigating the effects of temperature and solvent on reaction rates for the following reason. Unlike two-center reactions, multicenter or concerted reactions require<sup>2</sup> a high degree of order in the transition state so that the reactants are precisely aligned. For a concerted process we anticipate a large negative entropy of activation ( $\Delta S^\ddagger$ ), but only a moderate enthalpy of activation ( $\Delta H^\ddagger$ ). The measured  $\Delta H^\ddagger$  ( $52 \pm 12 \text{ kJ mol}^{-1}$ ) and  $-\Delta S^\ddagger$  ( $100 \pm 20 \text{ J mol}^{-1} \text{ K}^{-1}$ ) values in Table IV support a concerted reaction mechanism.

Concerning the solvent effect, it is generally held<sup>2</sup> that the rates of polar cycloaddition reactions do not significantly increase with increasing solvent polarity. The dielectric constants of the three solvents used, viz.  $\text{PhNO}_2$  (34.8),  $\text{MeNO}_2$  (35.9), and DMF (36.7), are nearly same; how-

ever, the rate constants in these media are different. Such irregularities have also been observed in organic cycloaddition reactions and are thought to be due to variations in charge separation in the activated state.<sup>2</sup>

Variation of electron-donor ability of the principal ligand (L) significantly affect reaction rates. Thus, reactivities of  $[\text{NiL}(\text{N}_3)]$  toward a given dipolarophile decrease in the order  $[\text{NiL}^1(\text{N}_3)] > [\text{NiL}^2(\text{N}_3)] > [\text{NiL}^3(\text{N}_3)]$ . That is, replacement of the terminal  $\text{NH}_2$  group of L<sup>1</sup> by *N,N*-dialkyl groups decreases reaction rates, presumably because augmentation of electron density at the metal center leads to depletion of charge separation in the azide.

The effect of different metal centers on the rates of cycloaddition reactions remains unexplored. Preliminary kinetic data with  $[\text{PdL}(\text{N}_3)]$  complexes<sup>42</sup> indicate slower reactions than with nickel under identical conditions.

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**Registry No.** 4a, 107681-54-9; 4b, 107681-51-6; 4c, 107681-55-0; 5a, 108616-81-5; 5b, 109530-72-5; 5c, 109552-38-7; VII (isomer 1), 109530-62-3; VII (isomer 2), 109211-88-3; VIII (isomer 1), 109530-63-4; VIII (isomer 2), 109211-89-4; IX (isomer 1), 109530-64-5; IX (isomer 2), 109211-90-7; X, 109211-91-8; XI, 109530-65-6; XII (isomer 1), 109530-66-7; XII (isomer 2), 109212-00-2; XIII (isomer 1), 109530-67-8; XIII (isomer 2), 109212-01-3; XIV, 109211-74-7; XV, 109583-60-0; XVI, 109583-61-1; XVII, 109583-62-2; XVIII, 109583-63-3; XIX, 108616-88-2; XX, 108616-86-0; XXI, 108616-96-2; XXII, 109583-64-4; XXIII, 109583-65-5; XXIV, 109212-06-8; XXV, 109211-68-9; XXVI, 109212-05-7; XXVII, 109211-69-0; XXVIII, 109583-66-6; XXIX, 109530-70-3; XXX, 108638-35-3; XXXI, 108638-41-1; XXXII, 109583-67-7; XXXIII, 108638-37-5; XXXIV, 109530-68-9;  $[\text{NiL}^1(\text{NCMe})](\text{ClO}_4)$ , 93402-28-9;  $[\text{NiL}^2(\text{NCMe})](\text{ClO}_4)$ , 107680-92-2;  $[\text{NiL}^3(\text{NCMe})](\text{ClO}_4)$ , 107680-94-4;  $\text{N}_3^-$ , 14343-69-2; EtCN, 107-12-0; MeCN, 75-05-8; PhCN, 100-47-0; *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{CN}$ , 619-72-7; *p*- $\text{ClC}_6\text{H}_4\text{CN}$ , 623-03-0;  $\text{CH}_2=\text{CHCN}$ , 107-13-1;  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ , 762-42-5;  $\text{PhCOC}\equiv\text{CCOPh}$ , 1087-09-8; PhNCS, 103-72-0;  $\text{CS}_2$ , 75-15-0; dimethyl fumarate, 624-49-7.

**Supplementary Material Available:** The analytical data for representative complexes (Table I) and the  $^1\text{H}$  NMR spectra of complexes VII and X (Figures 1 and 2) (4 pages). Ordering information is given on any current masthead page.

(42) Paul, P.; Chakladar, S.; Nag, K., unpublished work.