

steric constraint in VII.

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**Registry No.** [Pt(CH<sub>2</sub>CH=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>, 36484-05-6; [Pt(CH<sub>2</sub>CH=CHMe)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>, 56994-03-7; [Pt-(CH<sub>2</sub>CMe=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>, 37036-84-3; IVa, 55031-61-3; IVb, 56930-27-9; IVc, 55031-63-5; IVd, 56930-29-1; V, 56930-31-5; VI, 55031-65-7; [PtH(PPh<sub>3</sub>)<sub>2</sub>CO]ClO<sub>4</sub>, 55057-91-5; [PtH(PPh<sub>3</sub>)<sub>3</sub>]ClO<sub>4</sub>, 19568-66-2; [PtH(PPh<sub>3</sub>)<sub>2</sub>(AsPh<sub>3</sub>)]ClO<sub>4</sub>, 55031-67-9; Vd, 56930-33-7; *trans*-PtDCI(PPh<sub>3</sub>)<sub>2</sub>, 22899-18-9; III, 32109-29-8; II, 37383-70-3; CH<sub>2</sub>=CHCH<sub>2</sub>NH<sub>2</sub>, 107-11-9; CH<sub>2</sub>=CHCH<sub>2</sub>NHEt, 2424-02-4; CH<sub>2</sub>=CHCH<sub>2</sub>NEt<sub>2</sub>, 5666-17-1; *trans*-MeCH=CHCH<sub>2</sub>NH<sub>2</sub>, 56930-04-2; CH<sub>2</sub>=CMeCH<sub>2</sub>NH<sub>2</sub>, 2878-14-0; CH<sub>2</sub>=CHCHMeNH<sub>2</sub>, 34375-90-1; CH<sub>2</sub>=CHCH<sub>2</sub>NHCOMe, 692-33-1.

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## Reactions of (4,9-Dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)copper(II), (Cu(baen)) with Isocyanates<sup>1</sup>

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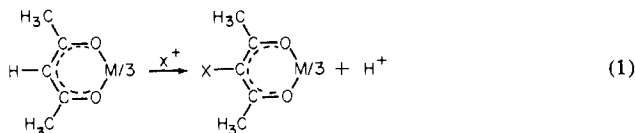
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The complex (4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione)copper(II), Cu(baen), reacts quickly and quantitatively in dry benzene solution at the methine position with isocyanates, RN=C=O, where R = 1-naphthyl, C<sub>6</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, and *t*-C<sub>4</sub>H<sub>9</sub>, in a stepwise manner to yield mono- and diamides of Cu(baen). The rates of these reactions have been qualitatively determined and found to be dependent upon the R group in the order: 1-naphthyl > C<sub>6</sub>H<sub>5</sub> > CH<sub>3</sub> > C<sub>2</sub>H<sub>5</sub> > *i*-C<sub>3</sub>H<sub>7</sub> > *t*-C<sub>4</sub>H<sub>9</sub>. They are also metal dependent with Cu(baen) reacting much faster than Ni(baen). The complexes have been characterized by elemental analyses, melting points, and electronic and infrared spectra. The ligands have been displaced intact from the complexes with H<sub>2</sub>S in benzene or chloroform and characterized by elemental analyses, melting points, and infrared, nuclear magnetic resonance, and mass spectrometry. Sulfuric acid degradation of the complexes in methanol produces N-substituted acetoacetamides. These have been characterized by melting points, infrared, nuclear magnetic resonance, and mass spectrometry and in some cases by their 2,4-dinitrophenylhydrazone derivatives. It is concluded from the data presented that these reactions are essentially electrophilic aromatic substitution reactions.

## Introduction

Reactions of coordinated ligands<sup>3,4</sup> have been shown to be potentially very useful, not only for their synthetic applications<sup>5</sup> to organic chemistry and homogeneous catalysis,<sup>6</sup> but also for their relations to life processes. Numerous  $\beta$ -diketone complexes have been studied, and it has been noted that these complexes undergo reactions characteristic of aromatic systems.<sup>7</sup> The methine hydrogen on these chelate rings can be replaced by several groups under electrophilic conditions as illustrated in reaction 1.



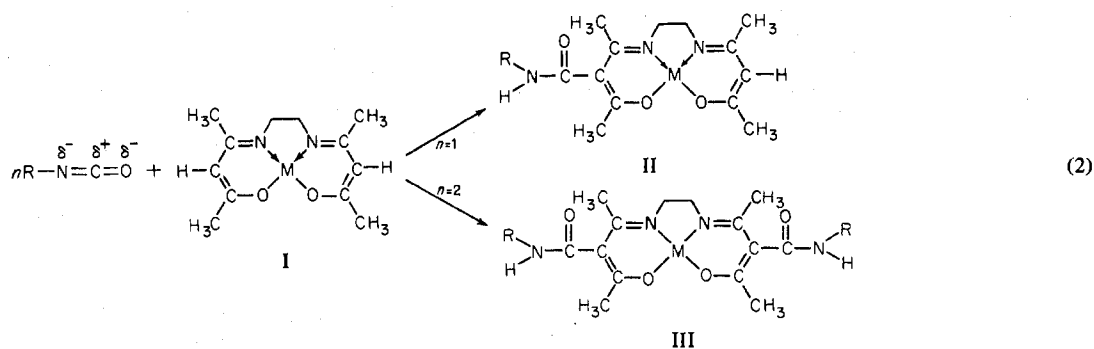
M = Co, Rh, Cr; X = I, Br, Cl, SCN, SA, SA, NO<sub>2</sub>, CH<sub>2</sub>Cl, CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>, COR, CHO

Due to the acid lability of these complexes, selective reagents must be employed in order to minimize degradation of the chelate rings.<sup>7</sup> Complexes of Schiff base condensation products of 2,4-pentanedione and diamines such as I, abbreviated M(baen), are even more susceptible to acid hydrolysis.<sup>8</sup> It is probably for this reason that similar reactions of these complexes have not been as extensively investigated. Prior to our initial report<sup>9</sup> few reactions of complexes such as I had been reported.<sup>10-16</sup>

During the course of our studies with compounds I we discovered<sup>9</sup> that these complexes react quickly and quantitatively (reaction 2) with isocyanates to form compounds II and III. These reactions are described in detail herein.

## Experimental Section

The starting ligands and their complexes were synthesized according to published procedures,<sup>8</sup> recrystallized from dry benzene-cyclohexane, and dried under vacuum at 60°C. Benzene was distilled, purified by azeotropic distillation, and finally dried over Linde 3Å molecular

Table I. Elemental Analyses for the Compounds<sup>a</sup> I

R <sub>1</sub>	R <sub>2</sub>	Mp, °C	% yield	% C		% H		% N		% Cu	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
CONHPh	H	210-212	96.6	56.38	56.45	5.68	5.76	10.38	9.74	15.70	15.31
CONHPh	CONHPh	203-203.5	89.8	59.62	59.47	5.35	5.35	10.69	10.73	12.13	12.16
CONHEt	H	173-173.5	72	50.50	50.30	6.45	6.84	11.78	11.71	17.83	17.97
CONHEt	CONHEt	182-185.5	75	50.60	50.90	6.55	6.85	13.10	12.86	14.83	14.70
CONHMe	H	175-177	85	49.07	49.26	6.13	5.90	12.26	12.25	18.54	18.74
CONHMe	CONHMe	211-212	98	48.08	48.20	6.00	5.88	14.01	13.99	15.90	16.09
CONH- <i>i</i> -Pr	H	173-175	91	51.84	51.91	6.74	6.67	11.33	11.60	17.14	16.99
CONH- <i>i</i> -Pr	CONH- <i>i</i> -Pr	196.5-197	55	52.71	52.48	7.02	7.28	12.29	12.22	13.94	13.87
CONH- <i>t</i> -Bu	H	155-156.5	95	53.08	52.78	7.02	6.72	10.92	11.01	16.51	17.19
CONH- <i>t</i> -Bu	CONH- <i>t</i> -Bu	177-178	56.8	54.62	54.36	7.44	7.25	11.58	11.46	13.13	13.47
CONH(1-naphth)	H	213-214	96.4	65.42	65.43	5.17	4.86	8.98	9.00	10.18	10.15

<sup>a</sup> All complexes are mauve or light purple.

Table II. Elemental Analyses for the Displaced Ligands

R <sub>1</sub>	R <sub>2</sub>	Mp, °C	% yield	% C		% H		% N	
				Calcd	Found	Calcd	Found	Calcd	Found
CONHPh	H	129-131	72	66.45	66.57	7.34	7.36	12.24	12.07
CONHPh	CONHPh	183-186	16 <sup>a</sup>	67.51	67.13	6.54	6.71	12.11	11.87
CONHEt	H	134-136	75	60.99	60.77	8.53	8.65	14.23	14.09
CONHEt	CONHEt	181.5-183.5	78	59.00	59.35	8.20	8.60	15.30	14.87
CONHMe	H	131-132.5	65	59.80	59.84	8.19	8.51	14.90	14.42
CONHMe	CONHMe	215-217	94	56.83	55.68	7.69	7.40	16.56	16.23
CONH- <i>i</i> -Pr	H	177.5-179.5	72	62.10	61.89	8.73	8.74	13.60	13.51
CONH- <i>i</i> -Pr <sup>b</sup>	CONH- <i>i</i> -Pr	202-203.5	75	58.27	57.78	8.73	8.60	13.58	13.20
CONH- <i>t</i> -Bu	H	138-139.5	79	63.18	62.78	8.97	8.79	13.00	13.08

<sup>a</sup> Yield for displacement reaction in benzene; when run in chloroform the yield was 90%. <sup>b</sup> Monohydrate, confirmed by ir and NMR.

sieves. All products were vacuum dried at 60°C prior to analysis.

Nuclear magnetic resonance spectra were recorded for deuteriochloroform solutions using either a Varian A-60 or a Jeolco 4-H 100 nuclear magnetic resonance spectrometer with chemical shifts relative to internal TMS. Infrared spectra were recorded on Beckman IR-8 and Perkin-Elmer 621 and 137 spectrometers as Nujol mulls between NaCl plates and were calibrated with polystyrene. Electronic spectra were recorded on chloroform solutions with a Cary 14 spectrophotometer. Mass spectra were obtained with a Jeolco JMS-07 mass spectrometer at 75 eV ionization potential. Melting points were determined on Fischer-Johns and Meltemp melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. and are listed in Tables I and II.

The reactions were all run in a similar manner in oven dried glassware. The following are exemplary.

**I. Isocyanate Reactions (Caution! Isocyanates Are Extremely Lacrimatory).**

(A) **Cu(baen)·2PhNCO.** To a solution containing 5.710 g ( $2 \times 10^{-2}$  mol) of purified and vacuum dried Cu(baen) in 50 ml of dry benzene was added 4.35 ml (4.76 g;  $4 \times 10^{-2}$  mol) of phenyl isocyanate. The reaction was topped with a calcium chloride drying tube and

stirred magnetically. After about 5 min a purple precipitate began to appear in the deep purple solution. After stirring at room temperature for 16 hr, the solution was filtered and the precipitate washed with 50 ml of chloroform, 50 ml of dry benzene, and 50 ml of hexane, in that order. The product was then dried overnight under high vacuum at 60°C to yield 9.40 g (89.8%) of light purple crystals, mp 203-203.5°C.

(B) **Cu(baen)·PhNCO.** To a solution containing 5.2570 g ( $1.84 \times 10^{-2}$  mol) of purified and vacuum dried Cu(baen) in 50 ml of dry benzene was added 2 ml (2.19 g;  $1.84 \times 10^{-2}$  mol) of phenyl isocyanate. The reaction was topped with a calcium chloride drying tube and stirred magnetically for 4 days. After about 5 min a purple precipitate began to appear in the deep purple solution. The precipitate was filtered, washed with 50 ml of dry benzene and 100 ml of hexane, and vacuum dried overnight at 60°C to yield 7.1982 g (96.6%) of light purple crystals, mp 210-212°C. The elemental analyses for the complexes are given in Table I.

**II. Ligand Displacements. (A) H<sub>2</sub>S in Benzene or Chloroform.** Gaseous hydrogen sulfide was passed through a suspension of 1.44 g (3.56 mmol) of Cu(baen)·PhNCO in 50 ml of dry benzene for 30 min with stirring. The suspension changed color from purple to

chocolate brown. This brown suspension was filtered and the precipitate washed with 15 ml of dry benzene. The combined filtrate and wash were heated with activated charcoal and filtered to yield a faint yellow solution. This solution was concentrated on a rotary evaporator at 60°C to about 15 ml, cooled to room temperature, and about 30 ml of hexane added. After standing at 0°C for about 3 hr, the white crystals which had formed were filtered and washed with three 10-ml portions of hexane and vacuum dried to yield 0.8684 g (2.56 mmol, 72%) of *baen*-PhNCO, mp 129–131°C. The rest of the ligands were similarly liberated from the copper except *baen*-2MeNCO which was done in the same manner using chloroform as the solvent. The elemental analyses for the displaced ligands appear in Table II.

**(B) Sulfuric Acid in Methanol.** To a suspension of 2.3610 g (4.50 mmol) of *Cu*(*baen*)-2PhNCO in 25 ml of methanol was added 0.5 ml of concentrated H<sub>2</sub>SO<sub>4</sub> (9 mmol). Addition of the acid caused an immediate color change of the solution from purple to deep blue together with dissolution of all material in the flask. The solution was reduced to dryness on a rotary evaporator at 60°C and the residue was extracted with three 10-ml portions of hot benzene. The extracts were filtered, clarified with activated charcoal, and filtered again. The volume of benzene was reduced to 10 ml on a rotary evaporator and 25 ml of hexane was added to yield 0.62 g (3.50 mmol, 78%) of acetoacetanilide, mp 84–85°C. The NMR, infrared, and mass spectra were identical with those of an authentic sample. Similar treatment of *Ni*(*baen*)-PhNCO likewise produced acetoacetanilide.

The complexes *Cu*(*baen*)-2MeNCO and *Cu*(*baen*)-2EtNCO were treated similarly to produce in 60 and 50% yields respectively *N*-methylacetoacetamide<sup>17</sup> and *N*-ethylacetoacetamide,<sup>17</sup> mp's 47 and 30°C, respectively.<sup>14</sup>

The 2,4-dinitrophenylhydrazones of these were prepared and their melting points agreed with the literature.<sup>17</sup> The NMR, infrared, and mass spectra support the structures.

## Results and Discussion

Reaction of *Cu*(*baen*) with isocyanates in dry benzene affords *Cu*[*baen*-CONH(R)] (II) and *Cu*[*baen*-2CONH(R)] (III). Selective production of these compounds may be affected by precise regulation of stoichiometry and reaction time. For example, a 1:1 molar ratio of RNCO to *Cu*(*baen*) produces the monoamides while ratios between 1:1 and 2:1 produce mixtures of mono- and diamides; precise 2:1 ratios produce diamides if the reaction is allowed to proceed to completion. Separation of the mono- and diamide complexes is very difficult since neither species is very soluble in any of the solvents attempted. *Cu*(*baen*)-2PhNCO can, however, be recrystallized from dimethylformamide by the addition of water, but the mono- and diamides could not be separated from one another in this way. It is possible to separate them for the isopropyl pair as the monoamide is somewhat more soluble than the diamide complex in chloroform and can be extracted therefrom. Even though no special effort has been made to maximize the yields of these reactions, they are very high (55 to 98%). Since the filtrate contains no ir detectable isocyanate, the reactions are apparently quantitative.

The structures of the complexes were assigned in the following manner. Each of the products of the isocyanate reactions with *Cu*(*baen*) possess strong infrared absorptions in the regions 1600–1660 cm<sup>-1</sup> and 3210–3420 cm<sup>-1</sup> (Table III) which are not present in the infrared spectrum of *Cu*(*baen*). These are assigned to  $\nu_{C=O}$ (amide) and  $\nu_{NH}$ (amide), respectively. In addition, the disubstituted complexes do not possess the infrared absorption at ~1140 cm<sup>-1</sup> which has been assigned to the methine C–H in-plane bending mode.<sup>11</sup>

Further structural confirmation derives from data obtained on the displaced ligands. Ligand displacement was achieved by passing gaseous H<sub>2</sub>S through either a chloroform or benzene suspension of the complex. Elemental analyses (Table II), infrared spectra (Table III), and <sup>1</sup>H NMR spectra (Table IV) as well as mass spectral data indicate that the ligands were displaced intact by this process. Each of the displaced ligands displays  $\nu_{C=O}$  and  $\nu_{N-H}$  in their infrared spectra at frequencies characteristic of amides.<sup>18</sup> The infrared spectra, while

**Table III.** Infrared Data for the Complexes and Displaced Ligands<sup>a</sup>

Complexes		$\nu_{C-H}$ in-plane bend	$\nu_{C=O}$	$\nu_{C=O}$ (amide)	$\nu_{C=N}$	$\nu_{N-H}$
R <sub>1</sub>	R <sub>2</sub>					
H	H	1115	1590		1515	
CONHPh	H	1180	1590	1645	1515	3210
CONHPh	CONHPh		1575	1630	1505	3210
CONHEt	H	1150	1590	1650	1515	3305
		1160		1620		3222
CONHEt	CONHEt		1579	1618	1519	3140
CONHMe	H	1150	1588	1620	1535	3245
		1160		1650	1515	3225
CONHMe	CONHMe		1580	1615	1515	3235
CONH- <i>i</i> -Pr	H	1170	1580	1615	1505	3250
				1635		3230
CONH- <i>i</i> -Pr	CONH- <i>i</i> -Pr		1574	1617	1517	3224
CONH- <i>t</i> -Bu	H	1160	1578	1635	1505	3315
CONH- <i>t</i> -Bu	CONH- <i>t</i> -Bu		1577	1640	1512	3310
Ligands						
H	H	1140	1600		1520	
			1580			
CONHPh	H	1140	1570	1655	1515	3245 br
			1595			
CONHPh	CONHPh		1590	1625	1515	3160 br
CONHEt	H	1150	1570	1600	1535	3280
					1515	
CONHEt	CONHEt		1560	1610	1510	3240
					1535	
CONHMe	H	1160	1595	1605	1570	3280
					1550	
CONHMe	CONHMe		1595	1620	1515	3235
					1540	
CONH- <i>i</i> -Pr	H	1165	1600	1610	1520	3240
					1560	
CONH- <i>i</i> -Pr <sup>b</sup>	CONH- <i>i</i> -Pr		1575	1615	1530	3215
				1600		
CONH- <i>t</i> -Bu	H	1145 w	1570	1660	1513	3420
CONH- <i>t</i> -Bu	CONH- <i>t</i> -Bu		1572	1660	1510	3410
			1612			

<sup>a</sup> Assignments are consistent with K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955), data for Nujol mulls. <sup>b</sup> Hydrate;  $\nu_{OH}$ , 3400 cm<sup>-1</sup> br.

confirming that all the products are amides, do not allow a distinction to be readily made between the mono- and diamide ligands. The only apparent difference is the presence (monoamides) or absence (diamides) of the weak C–H in-plane bending frequency at about 1140 cm<sup>-1</sup>. Since other absorptions appear in this region, assignments based upon this alone are not conclusive.

The distinction is readily apparent, however, in the NMR data (Table IV). Each of the monosubstituted ligands show three or four methyl resonances whereas the disubstituted ligands show only two. The difference is a consequence of the fact that the monosubstituted ligands do not possess a plane or rotational axis of symmetry relating the methyl groups whereas the disubstituted ligands do. In addition the monosubstituted ligands show a vinyl hydrogen resonance at  $\delta$  5.03 ± 0.01 which is not present in the NMR spectra of the disubstituted ligands. These ligands are further characterized by N–H resonances which appear as broad low-field doublets characteristic of the hindered rotation of amides.<sup>19</sup> The hindered rotation is also evidenced in the doubling of the N–CH<sub>3</sub> resonances of (*baen*-CO-NHCH<sub>3</sub>) and *baen*-2CO-NHCH<sub>3</sub> but not observed in the N–R resonances of the other ligands. There is nothing unusual about the chemical shifts or coupling constants as they are all relatively constant, appearing in the anticipated regions with normal coupling constants. The NMR data suggest that all of these ligands exist in chloroform solution as the ene-ol tautomer (IV) and not as the ketone tautomer (V) contrary to what is found for the parent molecule *baen* which exists as an equilibrium

Table IV. Proton NMR data for the Displaced Ligands<sup>a</sup>

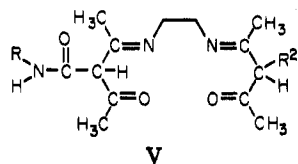
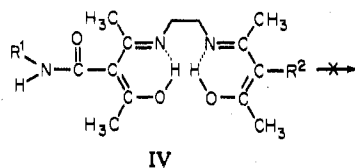
R <sub>1</sub>	R <sub>2</sub>	δCH <sub>3</sub>	δNH	δC=CH	δCH <sub>2</sub>	δOH	δN sub
CONHPh	H	1.93 s, 2.01 s, 2.08 s, 2.23 s	11.26 d (58)	5.03 s	3.45 m	9.19	7.48 (AB q)
CONHPh	CONHPh	2.03 s, 2.21 s	11.29 d (42)		3.52 m	8.67	7.43 (AB q)
CONHEt	H	1.93 s, 1.98 s, 2.13 s	11.22 d (53)	5.02 s	3.43 m	7.08	1.19 t (7) 3.3 q (7) 1.19 t (7)
CONHEt	CONHEt	1.88 s, 2.13 s	9.85 d (280)		3.50 m	7.07	3.34 q (7)
CONHMe	H	1.93 s, 1.94 s, 2.00 s, 2.16 s	11.30 d (25)	5.04 s	3.44 m	7.38	2.88 d (5)
CONHMe	CONHMe	1.71 s, 2.13 s	11.60		3.49 m	6.99	2.90 d (5)
CONH <i>i</i> -Pr	H	1.93 s, 2.03 s, 2.17 s	11.25 d (52)	5.03 s	3.63 m	6.68	1.23 d (7) 4.88 dq (7)
CONH <i>i</i> -Pr <sup>b</sup>	CONH <i>i</i> -Pr	1.89 s, 2.14 s	11.63 d (49)		3.49 m	7.35 <sup>b</sup>	1.22 d (7) 4.18 dq (7)
CONH <i>i</i> -Bu	H	1.93 s, 1.98 s, 2.03 s, 2.15 s	11.07 d (49)	5.03 s	3.46 m	6.32	1.43 s
H	H	1.93 s, 2.02 s		5.04	3.46 m	10.97	

<sup>a</sup> Assignments are consistent with G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961). Data presented as chemical shift (δ) multiplicity, d = doublet, t = triplet, m = multiplet, q = quartet, dq = doublet of quartets (coupling constant or separation); chloroform-*d* solutions, δ relative to internal TMS. <sup>b</sup> Hydrate, δH<sub>2</sub>O, 7.35.

Table V. Electronic Spectral Data for the Complexes<sup>a</sup> Given as ν (kK) (ε, l. mol<sup>-1</sup> cm<sup>-1</sup> × 10<sup>-3</sup>)

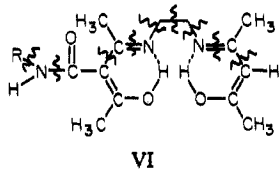
R <sub>1</sub>	R <sub>2</sub>	ν <sub>1</sub>	ν <sub>2</sub>	ν <sub>3</sub>	ν <sub>4</sub>	ν <sub>5</sub>
H	H <sup>b</sup>	18.52 (0.18)	29.85 (5.9)	32.68 (23.3)	36.36 (11.0)	43.67 (17.5)
CONHPh	H	18.35 (0.12)		32.26 (31.90)	36.36 (32.22)	
CONHPh	CONHPh	18.45 (0.50)		31.95 (21.69)	36.36 (27.40)	38.91 sh
CONHEt	H	18.45 (0.37)		32.26 (21.05)	34.72 (18.01)	
CONHEt	CONHEt	18.21 (0.14)		31.85 (26.23)	37.04 (27.21)	
CONHMe	H	18.42 (0.36)		30.96 (21.11)	33.90 (18.35)	
CONHMe	CONHMe	18.38 (0.43)		31.85 (35.51)	34.84 (26.17)	
CONH <i>i</i> -Pr	H	18.45 (0.37)		31.95 (18.35)	35.21 (15.60)	
CONH <i>i</i> -Pr	CONH <i>i</i> -Pr <sup>i</sup>	18.45 (0.42)		31.95 (21.43)	35.59 (14.73)	

<sup>a</sup> Data were obtained on 10<sup>-3</sup>, 10<sup>-4</sup>, and 10<sup>-5</sup> M solutions in chloroform. <sup>b</sup> Data taken from K. Ueno and A. E. Martell, *J. Phys. Chem.*, **61**, 257 (1957).



mixture of the two tautomers.<sup>20</sup> This is probably the result of the stabilizing influence of the cross conjugation and hydrogen bonding present in IV which is not present in V.

The ligands were further characterized by mass spectrometry. The mass spectrum of each ligand possesses a parent ion and an *M* + 1 ion which occur at *m/e* in accord with the calculated molecular weights. Further, each spectrum demonstrates the consequences of the McLafferty rearrangement.<sup>21</sup> Major fragmentations resulting at each of the bonds depicted by wavy lines in VI were noted in each mass spectrum.

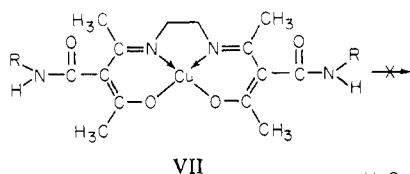


When the complexes were treated with H<sub>2</sub>SO<sub>4</sub> in methanol,

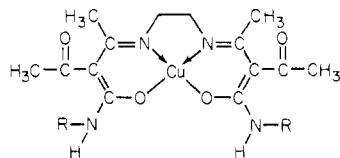
(2:1 mol ratio H<sub>2</sub>SO<sub>4</sub>-complex), ring cleavage of the Schiff base occurred producing *N*-alkylacetoacetamides in high yield. These compounds were characterized by infrared, <sup>1</sup>H NMR, and mass spectra and in some cases as their 2,4-dinitrophenylhydrazone derivatives.<sup>17</sup> This represents an alternative synthesis of *N*-alkylacetoacetamides which avoids the preparation and handling of diketene.<sup>17</sup> The fate of the rest of the molecule and the mechanism of this reaction have not been determined but are under investigation.

The only precedents for the addition of isocyanates to active methylene compounds that we could locate by a rather extensive literature search were those to diethyl oxalacetate<sup>22</sup> and ethyl cyanoacetate.<sup>23</sup> These reactions were catalyzed by the Lewis base triethylamine and are formally analogous to the reactions reported herein.

As anticipated, the electronic spectral data presented in Table V for the amide complexes are very similar to that of Cu(baen) itself.<sup>24</sup> They differ only in extinction coefficients, in a lowering in energy of the third transition ν<sub>3</sub>, and in an increase in energy of the fourth transition ν<sub>4</sub> as well as the absence of ν<sub>2</sub>. Since ν<sub>3</sub> and ν<sub>4</sub> are likely intraligand transitions,<sup>24</sup> cross conjugation of the amide with the pseudoaromatic ring of the molecule should affect these. The fact that ν<sub>1</sub>, the d-d transition, is essentially unaffected indicates that linkage isomerization as depicted in VII and VIII is not occurring. This type of linkage isomerism has been found to occur for [3,3'-(ethylenebis(nitrilomethylidene)]di-2,4-pentanedionato(2-))nickel<sup>25</sup> a diacetyl analogue of Cu(baen-2CONH(R)). Since amides do not enolize as readily as ketones, this is not too surprising. This conclusion is consistent with the <sup>1</sup>H NMR results on the free ligands which



VII



VIII

supported structure IV.

Qualitative measures of the rates of these reactions were obtained by noting the time required for the commencement of precipitation of the sparingly soluble products II from benzene solutions that were 0.5 *M* in I and 1.0 *M* in isocyanate, R<sup>3</sup>NCO.

As these reactions proceed, the initially purple homogeneous solutions become a mass of precipitate almost immediately after precipitation commences. The products isolated at this point are found to be the monoamides. Since all these complexes are only very sparingly soluble in benzene ( $\leq 10^{-3}$  *M*) and since complete precipitation is almost instantaneous, the time of incipient precipitation is a reasonable measure of the relative reaction rates. Attempts at determining the quantitative rates of these reactions by following the rate of disappearance of RNCO by infrared spectroscopy were unsuccessful as the products precipitated in the ir solution cells. Gas chromatographic analysis was equally unsuccessful; efforts to obtain quantitative reaction rates are in progress.

The qualitative rates are influenced both by the metal ion and by the nature of the isocyanate substituent R<sup>3</sup>. For Cu(baen) the incipient precipitation times were R<sup>3</sup> = 1-naphthyl (5 min) < Ph (7 min) < CH<sub>3</sub> (15 min) < C<sub>2</sub>H<sub>5</sub> (30 min) < *i*-C<sub>3</sub>H<sub>7</sub> (60 min) < *t*-C<sub>4</sub>H<sub>9</sub> (65 Hr). Copper complexes react at a much faster rate than nickel complexes. Only phenyl and 1-naphthyl isocyanates reacted with Ni(baen) to produce monoamides. All other isocyanates failed to react with Ni(baen) within two weeks as shown by infrared and <sup>1</sup>H NMR spectra of the recovered material, Ni(baen). Reactions proceed similarly<sup>27</sup> with Cu(bapn) and Ni(bapn) where bapn is the bis(2,4-pentanedione)-1,2-diaminopropane Schiff base analogue of baen.

Although the nickel complexes cannot in general be prepared by the reaction of Ni(baen) with isocyanates, they can be prepared by reaction of the free ligand (obtained from the copper complex) with nickel acetate in 95% ethanol. In this manner, the complex Ni[baen-CONH(Et)] was isolated as red crystals: dec pt 189–191°C; ir (Nujol mull) 1150 and 1169 (CH in plane bend), 1575 (C=O), 1625, 1650 (C=O, amide), 1515 (C=N), 3250 cm<sup>-1</sup> (NH); NMR (CDCl<sub>3</sub>)  $\delta$  6.29 (s, 1, NH), 4.91 (s, 1, CH), 3.26 (q, 2, *J* = 7 Hz, CH<sub>2</sub>N), 3.14 (s, 4, CH<sub>2</sub>), 2.01, 1.98, 1.88, 1.81, (s's, 12, CH<sub>3</sub>), 1.18 (t, 3, *J* = 7 Hz, CH<sub>3</sub>CH<sub>2</sub>N).

Reactions of this type at the methine position of 2,--pentanedione complexes are thought to be electrophilic.<sup>5,7</sup> The base-catalyzed methine proton exchange in [Co(baen)X<sub>2</sub>]<sup>28</sup> suggests similar behavior for baen complexes. Elfring and Rose<sup>29</sup> and Martin and Cummings<sup>30</sup> have found that the p*K*<sub>a</sub>'s for the active methine hydrogens of 13- and 14-membered tetraazamacrocyclic complexes of nickel are 3 p*K*<sub>a</sub> units less than those of the corresponding copper complexes. Thus, replacement of nickel(II) by copper(II) in both the 13- and 14-membered systems results in a 100-fold decrease in acidity. Therefore, if these reactions are in fact electrophilic, it is not too surprising that the copper compounds react faster than the

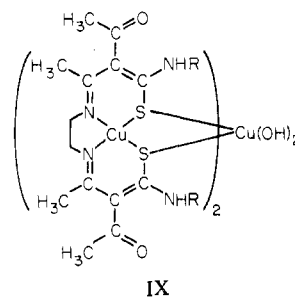
nickel compounds.

At this point it seems reasonable to assume that the methine carbon in these complexes is an electron-rich center that can be attacked by electrophiles and that the C=C double bond in the ring offers a directing influence by interacting with the  $\pi$  system of the isocyanates. This is in turn polarized by the metal and thereby somewhat explains the metal influence upon the rates. The more electron rich the metal, the more easily it can  $\pi$  back bond into the ring and thereby enhance the electron density at the methine carbon. In keeping with this explanation, complexes of high valent metals, with few d electrons, do not react,<sup>9</sup> whereas when reaction does occur Cu(II), d<sup>9</sup>, reacts faster than Ni(II), d<sup>8</sup>.

If the qualitative rates of the reactions are compared with the p*K*<sub>b</sub>'s of the amines<sup>29</sup> RNH<sub>2</sub> (R, p*K*<sub>b</sub>, time of reaction: 1-naphthyl, 10.18, 5 min; Ph, 9.38, 7 min; CH<sub>3</sub>, 3.34, 15 min; C<sub>2</sub>H<sub>5</sub>, 3.30, 30 min; *i*-C<sub>3</sub>H<sub>7</sub>, 3.37, 60 min; *t*-C<sub>4</sub>H<sub>9</sub>, 3.32, 3900 min), it is apparent that for the first three the reaction times parallel the p*K*<sub>b</sub>'s. For the last three the p*K*<sub>b</sub>'s are very similar but the reaction times are very different. This seems to indicate that substituent electronic effects are more important than substituent steric effects in controlling the rate of the reaction. This seems especially true since the difference in the steric effects of the naphthyl and methyl groups is large and the more bulky group gives rise to the faster reaction. When electronic effects are similar, as is the case for the three substituents Et, *i*-Pr, and *t*-Bu, steric effects control the rate. These concepts are consistent with the supposition that these reactions are electrophilic substitution reactions.

Similar reactions have been conducted with I and hexamethylene diisocyanate, OCN(CH<sub>2</sub>)<sub>6</sub>NCO, in a 1:1 mol ratio in refluxing benzene and a compound has been isolated which appears from reduced viscosity measurements<sup>31</sup> to have a molecular weight in the vicinity of  $2 \times 10^5$ . This compound analyzes correctly,<sup>32</sup> has infrared and electronic spectra which support its proposed structure, and melts at 177–180°C. Thus although data are incomplete, at present it appears that high polymers with reasonable thermal stability may be prepared in this way. Further work in this area is in progress.

Similar reactions also occur with isothiocyanates but the reactions are not straightforward. Satisfactory elemental analyses were not obtained. Typical analyses are exemplified by those for the product of reaction of Cu[baen] and PhNCS which are: C, 51.48; H, 4.88; N, 9.24; Cu, 15.71; S, 10.64. These satisfy the molecular formula C<sub>52</sub>H<sub>58</sub>N<sub>8</sub>O<sub>6</sub>Cu<sub>3</sub>S<sub>4</sub> for which the calculated analytical results are: C, 51.62; H, 4.83; N, 9.26; S, 10.60; Cu, 15.76. This compound is olive green in color, melts at 184.5–185.5°C, and shows  $\nu_{\text{NH}}$  at 3279 cm<sup>-1</sup>,  $\nu_{\text{C=S}}$  at 1582 cm<sup>-1</sup>, and the absence of the methine  $\nu_{\text{CH}}$  at 1140 cm<sup>-1</sup>. Thus, it appears that two phenyl isothiocyanate molecules react with each Cu(baen) but other reactions are also occurring. These reactions were not pursued further. These compounds likely possess the structure depicted in IX which is consistent with the analytical and spectroscopic data and for which there is reasonable precedence.<sup>33</sup>



IX

**Acknowledgment.** The financial support of the University of Nevada Research Advisory Board and the donors of the

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**Registry No.** Cu(baen-CONH(Ph)), 50520-15-5; Cu(baen-2CONH(Ph)), 50520-21-3; Cu(baen-CONH(Et)), 50520-16-6; Cu(baen-2CONH(Et)), 50495-29-9; Cu(baen-CONH(Me)), 50520-17-7; Cu(baen-2CONH(Me)), 50520-22-4; Cu(baen-CONH(*i*-Pr)), 50520-18-8; Cu(baen-2CONH(*i*-Pr)), 50520-23-5; Cu(baen-CONH(*t*-Bu)), 50520-19-9; Cu(baen-2CONH(*t*-Bu)), 50520-24-6; Cu(baen-CONH(1-naphth)), 50520-14-4; baen, 6310-76-5; baen-CONHPh, 50564-45-9; baen-2CONHPh, 50564-39-1; baen-CONHEt, 50564-46-0; baen-2CONHEt, 50564-40-4; baen-CONHMe, 50564-47-1; baen-2CONHMe, 50564-41-5; baen-CONH-*i*-Pr, 50564-48-2; baen-2CONH-*i*-Pr, 50564-42-6; baen-CONH-*t*-Bu, 50479-45-3; baen-2CONH-*t*-Bu, 50564-43-7; EtNCO, 109-90-0; MeNCO, 624-83-9; *i*-PrNCO, 1795-48-8; *t*-BuNCO, 1609-86-5; 1-naphthNCO, 86-84-0; PhNCO, 103-71-9; Ni(baen-CONH(Et)), 50520-07-5; PhNCS, 103-72-0; IX (R = Ph), 57091-05-1; Cu(baen), 36885-37-7; Ni(baen)·2naphthNCO, 50495-20-0; Ni(baen)·PhNCO, 50495-23-3; Cu(bapn)·2naphthNCO, 57108-97-1; Cu(baen)·NCO(CH<sub>2</sub>)<sub>6</sub>NCO, 57108-96-0; Ni(baen), 36802-27-4; acetoacetanilide, 102-01-2; *N*-methylacetoacetamide, 20306-75-6; *N*-ethylacetoacetamide, 10138-46-2.

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- Anal. Calcd for Cu(bapn)·2naphth NCO, C<sub>35</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>Cu: C, 65.87; H, 5.37; N, 8.78; Cu, 9.96. Found: C, 65.86; H, 5.27; N, 8.14; Cu, 9.31; dec pt 177-179°C.
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- Anal. Calcd for Cu(baen)·NCO(CH<sub>2</sub>)<sub>6</sub>NCO, C<sub>20</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>Cu: C, 53.00; H, 6.61; N, 12.6; Cu, 14.00. Found: C, 52.99; H, 6.77; N, 12.07; Cu, 14.53. The infrared spectrum shows  $\nu_{NH}$  (3210 cm<sup>-1</sup>) and  $\nu_{C=O}$  (1615 cm<sup>-1</sup>) and the absence of the methine  $\nu_{CH}$  (~1140) and  $\nu_{NCO}$  suggesting that the polymer terminates with the complex and not with NCO groups. This material is flammable with difficulty in an open flame and burns with a copper green flame.
- We thank a referee for this suggestion: L. F. Lindoy and W. E. Moody, *J. Am. Chem. Soc.*, **97**, 2276 (1975).

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## Manganese and Zinc Complexes Incorporating an Unsaturated Cyclic Schiff Base Ligand

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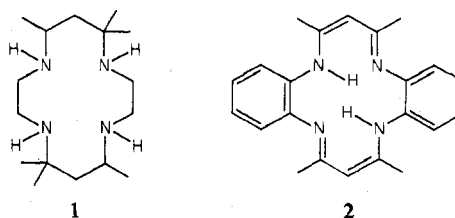
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A number of manganese(II) and -(III) as well as two zinc(II) complexes with the conjugated cyclic Schiff base, H<sub>2</sub>[14]12eneN<sub>4</sub>, have been synthesized and fully characterized. The high-spin Mn(III) complexes have the stoichiometry Mn(III)[14]12eneN<sub>4</sub>X, where X is Cl<sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup>, and N<sub>3</sub><sup>-</sup>. The compounds are intensely colored and exhibit a number of electronic transitions which appear to be associated with the ligand framework. The reduced magnetic moment of the azide derivative suggests that for this complex the Mn(III) ions are linked via an azide bridge in the solid state. Manganese(II) and zinc(II) form five-coordinate complexes with H<sub>2</sub>[14]12eneN<sub>4</sub> having stoichiometry M(II)[14]12eneN<sub>4</sub>(amine), where amine is triethyl- or tri-*n*-propylamine. NMR studies on the diamagnetic zinc(II) complexes indicate that the sterically hindered tertiary amine is axially coordinated to the metal ion. The distorted five-coordinate geometry is attributed to the mismatch between the relatively large high-spin d<sup>5</sup> and d<sup>10</sup> metal ions and the hole provided by the macrocyclic ligand. The chemical reactivity of the complexes is also discussed.

### Introduction

Although a considerable effort has been expended on the study of manganese-porphyrin complexes,<sup>1</sup> examples of synthetic macrocyclic ligands complexed to manganese are rare. The facile variation of ring size, charge, and unsaturation of cyclic Schiff bases and their analogues<sup>2,3</sup> permit the exploration of structure-function relationships which cannot be readily examined in metalloporphyrin chemistry. In an effort to explore the properties of manganese complexes containing synthetic macrocyclic ligands, we reported the synthesis and characterization of a number of complexes with the saturated

uncharged tetraazo macrocyclic ligand *meso*-[14]aneN<sub>4</sub> (1).<sup>4,5</sup>



This report deals with the synthesis and properties of man-