

Discussion

Interest in the structural behavior of organometallics has persisted for several years. A number of fluxional compounds have been examined in order to probe the structural basis for fluxional behavior. This paper presents elements leading toward a rationale for such behavior. In addition to defining the scope of the migrating group, it summarizes the argument that the rearrangement pathway is governed by the HOMO of the organic group in the activated complex.

Table II shows the agreement between the predicted and observed fluxional shifts associated with compounds described in recent years. The chloromercurial derivative ($h^1-C_9H_7$)HgCl has been reported to be non-fluxional at 33°, in conflict with the present predictions. Note, however, that the temperature of nmr line broadening for ($h^1-C_5H_5$)₂Hg (-70°) is over 100° below that for its chloromercury analog, ($h^1-C_5H_5$)HgCl (+33°). Since the broadening temperature for the bisindenyl

derivative, ($h^1-C_9H_7$)₂Hg, is reported as -3°, it is not unreasonable to suppose that temperatures well above 33° are necessary for fluxional behavior in its chloromercury counterpart. Further work, at higher temperatures, would be of interest here.

The rearrangement of some compounds reported by Fritz and Kreiter¹² is consistent with the present treatment. However, more certain identification of the rearrangement pathway appears to be desirable.

Note that all compounds in Table II feature indenyl and cyclopentadienyl groups. Further study of fluxional compounds derived from additional organic systems, to corroborate the present treatment, is obviously desirable.

Acknowledgements. The author wishes to thank Professors E. S. Gould and D. F. T. Tuan for their encouragement and valuable discussion.

(12) H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.*, **4**, (313) (1965).

Cyclopentadienylcopper(I)-Isocyanide Complex. A New Preparative Method and Catalyst Activity

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Abstract: (*pentahapto*-Cyclopentadienyl)(*tert*-butyl isocyanide)copper(I) (**1**) and (indenyl)tris(*tert*-butyl isocyanide)copper(I) (**2**) were readily prepared by the reactions of cyclopentadiene and indene, respectively, with the Cu₂O-*tert*-BuNC system. These organocopper(I) complexes catalyzed the reactions of cyclopentadiene homologs with carbonyl compounds, producing the corresponding fulvene derivatives **3**. The catalytic activity of **1** was much increased by the addition of an equimolar amount of *tert*-BuNC. For catalysis of these reactions, it was not necessary to isolate an organocopper complex; *i.e.*, these reactions were effectively catalyzed by the Cu₂O-*tert*-BuNC system. In addition, the Cu₂O-*tert*-BuNC system catalyzed the reactions of active hydrogen compounds such as malonate with aldehyde affording the corresponding alkylidene malonate derivatives.

The present paper is concerned with organocopper(I)-isocyanide complexes derived from cyclopentadiene homologs, Cu₂O, and isocyanide. In recent years, much attention has been paid to the usefulness of organocopper reagents in organic syntheses¹ as well as the characterization of organocopper compounds.² For several years, we have devoted ourselves to studies of catalytic activity of Cu(I)-alkyl isocyanide complexes.³ Characteristic catalytic activity of the Cu(I)-isocyanide system has been demonstrated in reactions

involving so-called active hydrogen compounds, such as the dimerization of α,β -unsaturated carbonyl and nitrile compounds^{4a,b} (eq 1), Michael-type addition reactions,^{4c} and cycloaddition of benzyl and carboalkoxy-methyl isocyanides^{4d} (eq 3 and 4). In these reactions, we assumed a reaction scheme with an organocopper(I)-isocyanide complex as active intermediate.

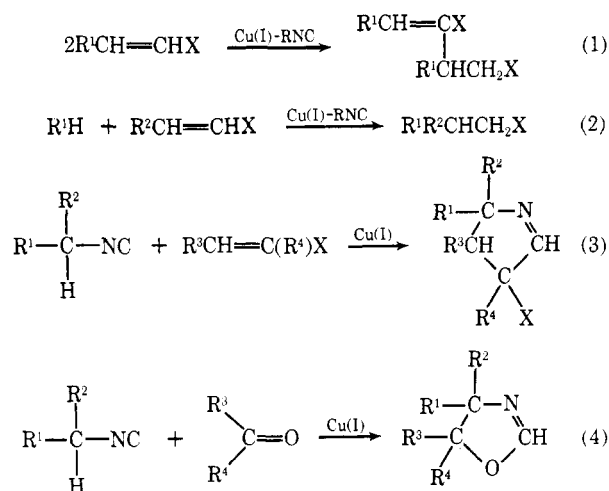
The present paper reports the preparation of (*pentahapto*-cyclopentadienyl)(*tert*-butyl isocyanide)copper(I) (**1**) and (indenyl)tris(*tert*-butyl isocyanide)copper(I) (**2**) by the reactions of cyclopentadiene and indene, respectively, with the Cu₂O-*tert*-BuNC system. These organocopper complexes were found to be key intermediates in reactions of cyclopentadiene homologs with carbonyl compounds, catalyzed by the Cu₂O-isocyanide system. In addition, complex **1** was found to catalyze reactions 1 and 2.

(1) (a) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); (b) E. J. Corey and G. H. Posner, *ibid.*, **90**, 5615 (1968); (c) E. J. Corey and J. A. Katzenellenbogen, *ibid.*, **91**, 1851 (1969); (d) J. B. Siddall, M. Biskup, and J. H. Fried, *ibid.*, **91**, 1853 (1969); (e) E. J. Corey and I. Kuwagima, *ibid.*, **92**, 395 (1970); (f) R. J. Anderson, C. A. Henrick, and J. B. Siddall, *ibid.*, **92**, 735 (1970).

(2) (a) F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7281 (1969); (b) F. A. Cotton and J. Takats, *ibid.*, **92**, 2353 (1970); (c) G. M. Whitesides and J. S. Fleming, *ibid.*, **89**, 2855 (1967); (d) F. A. Cotton and T. J. Marks, *ibid.*, **92**, 5114 (1970).

(3) (a) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota and H. Yoshioka, *Bull. Chem. Soc. Jap.*, **42**, 3310 (1969); (b) T. Saegusa, Y. Ito, S. Kobayashi, J. Hirota, and N. Takeda, *Can. J. Chem.*, **47**, 1217 (1969); (c) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *J. Amer. Chem. Soc.*, **89**, 2240 (1967).

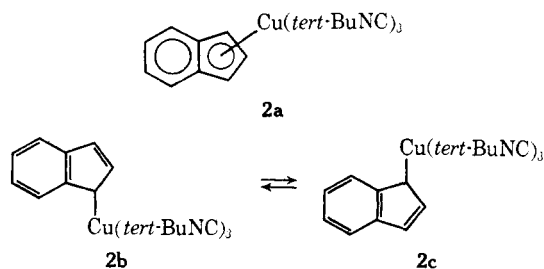
(4) (a) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *J. Org. Chem.*, **35**, 670 (1970); (b) T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, *Bull. Chem. Soc. Jap.*, **43**, 877 (1970); (c) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *ibid.*, in press; (d) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *J. Org. Chem.*, in press.



Results and Discussion

Preparation of 1 and 2. When a mixture of Cu_2O , cyclopentadiene, and *tert*-BuNC was warmed to 50° , an exothermic reaction occurred and Cu_2O went into solution. From the reaction mixture, (*pentahapto*-cyclopentadienyl)(*tert*-butyl isocyanide)copper(I), $h^5-C_5H_5-Cu(tert-BuNC)$ (**1**), was isolated by recrystallization as a white crystalline solid. The structure of **1** was established by ir and nmr spectra and elemental analysis as well as by the results of treatment of **1** with $FeCl_2$ giving ferrocene. The *pentahapto* structure of **1** is supported by a singlet ir absorption ν_{C-H} of the cyclopentadienyl ring, at 3084 cm^{-1} ^{2d} and by singlet nmr absorption at τ 3.76 ($r_i = 5$) of the cyclopentadienyl ring. The presence of a cyclopentadienyl-copper bond has been substantiated by the fact that ferrocene was produced in a quantitative yield when **1** was treated with $FeCl_2$. As to the cyclopentadienylcopper-isocyanide complex, Cotton, *et al.*,^{2d} prepared $h^5-C_5H_5Cu(CH_3CN)$ (**4**) for the first time by reaction of $Tl(C_5H_5)$ with $Cu(CH_3CN)_n$. The present study provides a new preparative procedure of **1** from Cu_2O , cyclopentadiene, and isocyanide. It is interesting that **1** is more stable than **4**. Cotton, *et al.*,^{2d} reported that **4** decomposes in several minutes at room temperature, whereas **1** of the present study remained unchanged for at least 1 month at room temperature under nitrogen.

From a mixture of indene, Cu_2O , and *tert*-BuNC, an indenylcopper(I) complex, **2**, $C_9H_7Cu(tert-BuNC)_3$, was isolated. Unlike **1**, **2** contains three molecules of isocyanide ligand. As to the indene ring-copper bond of **2**, *pentahapto* (**2a**) and *monohapto* (**2b** \rightleftharpoons **2c**) structures



are possible from nmr spectral evidence. The *monohapto* structures **2b** and **2c** are chemically equivalent. The nmr spectrum of **2** (in C_6D_6) is shown in Figure 1. The numbering of the indenyl group is shown below.

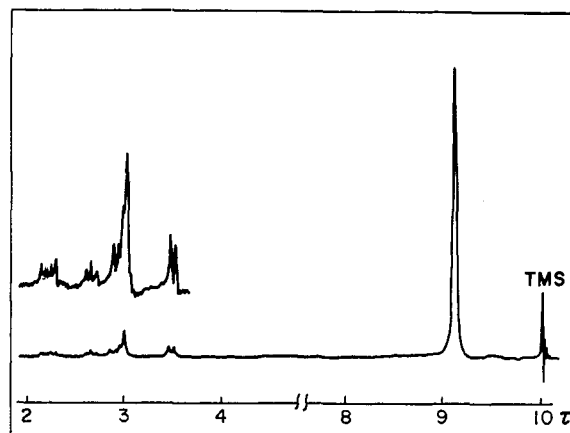
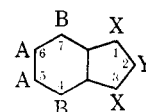


Figure 1. Nmr spectrum of **2** in C_6D_6 at room temperature.

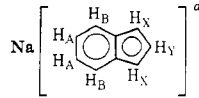

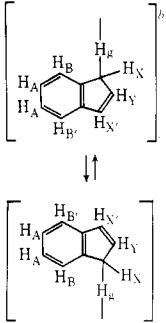
In the nmr spectrum of **2** in C_6D_6 , a broad singlet at τ 9.10 is assigned to the *tert*-butyl protons ($r_i = 27$) of *tert*-butyl isocyanide. The doublet at τ 3.50 ($r_i = 2$) is assigned to the C-1 and C-3 protons (H_X) of the indenyl



group and the triplet at τ 2.65 ($r_i = 1$) corresponds to the indenyl C-2 proton (H_Y). The coupling constants J_{H-H} (3 Hz) of these two absorptions are identical. These absorptions are well explained by an X_2Y pattern. The quartet at τ 2.22 is assigned to the C-4 and C-7 protons (H_B) of the benzene ring. The sharp singlet at τ 3.03 is due to an impurity of benzene in C_6D_6 , which has also been observed in the spectrum of the C_6D_6 solvent. The absorptions near the singlet of the benzene impurity may be assumed to be a part of a quartet having its center at τ 3.0, which is assigned to the C-5 and C-6 protons (H_A) of the benzene ring on the basis of an A_2B_2 pattern. Full analysis of the C-5 and C-6 protons' quartet has not been made because **2** is quite unstable and decomposes in other solvents such as acetonitrile, dioxane, tetrahydrofuran, methylene chloride, carbon disulfide, and chloroform. Thus, the nmr spectrum of **2** is explained by an $A_2B_2X_2Y$ pattern for the indenyl group.

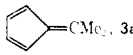
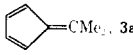
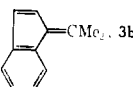
The $A_2B_2X_2Y$ nmr pattern of the indenyl protons of **2** suggests to us two possible structures. One is the *pentahapto* structure **2a**. The other is the *monohapto* structure **2b,c**, in which a rapid interconversion of the copper-carbon bond between the C-1 and C-3 carbon atoms takes place (**2b** \rightleftharpoons **2c**). Although the structure of **2** has not been conclusively established, the *monohapto* structure may be preferred on the basis of the nmr chemical shift of the indenyl protons of **2**. Table I summarizes the nmr spectral data and characterizations of indenyl-metal bonds of several indenyl-metal compounds in the literature. From the data of Table I it is generally seen that in *pentahapto* indenyl compounds, the τ value of H_X at C-1 and C-3 is lower than that of H_Y at C-2, whereas in the *monohapto* compound, in which a rapid interconversion of the carbon-metal bond between C-1 and C-3 has been also assumed, the τ value of H_X is higher than that of H_Y at C-2. On the basis of this criterion, **2** may be assumed to have a

Table I. Proton Nmr Data for Indenylmetal Derivatives

Compound	Character of compound	$\tau(\text{H}_X)$	$\tau(\text{H}_Y)$	$\tau(\text{H}_A)$	$\tau(\text{H}_B)$	J_{X-Y} , Hz	Solvent
 $\text{Na} \left[\begin{array}{c} \text{H}_B \text{ H}_X \\ \text{H}_A \text{ H}_Y \\ \text{H}_A \text{ H}_B \\ \text{H}_X \text{ H}_Y \end{array} \right]^a$	Ionic	4.17 (d)	6.80 (t)	2.75	3.62	2.5	THF- d_8
$\text{Fe} \left[\right]_2^a$	h^5	5.39 (d)	5.95 (t)	3.09	3.09	2.5	THF- d_8
$\text{Ru} \left[\right]_2^a$	h^5	5.11 (d)	5.41 (t)	3.34	3.39	2.5	THF- d_8
 $\left[\text{Indene} \right] \text{Fe}^-]^a$	h^5	5.25 (d)	6.11 (t)	2.59	3.22	2.5	THF- d_8
Complex 2	h^1	3.50 (d)	2.65 (t)	2.22	3.0	3	Benzene- d_6
	h^1	4.68 (\approx d)	3.3 (t)	\sim 2.7	\sim 2.4	3.5	CDCl_3

^a M. Tsutsui and H. J. Gysling, *J. Amer. Chem. Soc.*, **91**, 3175 (1969). Nmr spectra were obtained at room temperature. ^b F. A. Cotton and T. J. Marks, *ibid.*, **91**, 3178 (1969). Nmr spectrum were obtained at 68°. At this temperature, the indicated rapid interconversion has been assumed. τ values are expressed for protons H_X (or $\text{H}_{X'}$), H_A (or $\text{H}_{A'}$), and H_B (or $\text{H}_{B'}$).

Table II. Reaction of Cyclopentadiene and Indene with Acetone Catalyzed by **1** and **2**^a

Reactants (mmol)		Catalyst (mmol)	Product	Yield, %
C_5H_6 (30)	Me_2CO (50)	1 (0.50)	 CMe_2 , 3a	7.2
C_5H_6 (30)	Me_2CO (50)	1 (0.46) + <i>tert</i> -BuNC (0.40)	 CMe_2 , 3a	80
C_9H_8 (10)	Me_2CO (30)	2 (0.134)	 CMe_2 , 3b	75

^a The reaction was carried out at room temperature for 24 hr under nitrogen.

monohapto structure, *i.e.*, the τ value of the H_X doublet is higher than that of the H_Y triplet in **2**.

As for evidence regarding the carbon-copper bond of **2**, the following results were obtained. The decomposition of **2** with acidic water regenerates indene. In addition, only the C-1 and C-3 protons of the indenyl group were quantitatively deuterated when the reaction mixture of indene, Cu_2O , and *tert*-BuNC was treated with D_2O at room temperature.

Catalysis Behavior of 1 and 2. Complexes **1** and **2** were examined for catalytic activity toward the reactions of cyclopentadiene and indene, respectively, with acetone. Table II shows the interesting finding that the catalytic activity of **1** is not high, that of **2** is quite high, and the activity of **1** is much increased by the addition of an equimolar amount of *tert*-BuNC. As will be discussed later, cyclopentadienylcopper and indenylcopper species, respectively, act as key intermediates in these two reactions, which are consumed by reaction with carbonyl compounds and reproduced in the subsequent step of a single reaction cycle. In most reactions hitherto reported, an organocopper complex is employed as a reaction component, and the organocopper species is consumed and not reproduced. The

behavior of **1** and **2** "as the catalyst" in the present study is to be noted.

For synthetic purposes, the isolation of an organocopper complex as the catalyst in reactions of cyclopentadiene with carbonyl compounds is not necessary. These reactions are effectively catalyzed by the Cu_2O -isocyanide system. The reactions are illustrated by the general equation (5). The results are summarized in

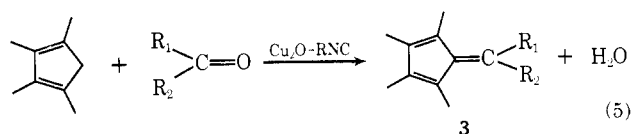
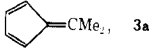
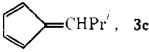
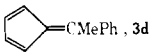
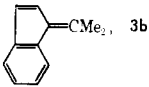
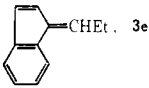
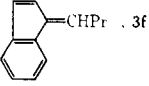
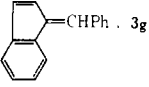
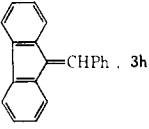


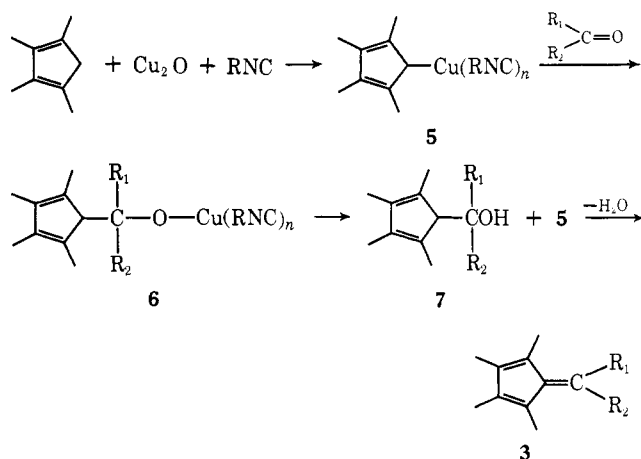
Table III. Cyclopentadiene, indene, and fluorene react successfully with ketones and aldehydes. The combination of Cu_2O and isocyanide is essential for catalytic activity. A single component of the catalyst system, Cu_2O or isocyanide alone, did not induce the reaction. In addition, an active hydrogen compound such as diethyl malonate also reacts with aldehyde in the presence of the Cu_2O -isocyanide system under more severe conditions.

Table III. Reactions of Cyclopentadiene Homologs with Carbonyl Compounds Catalyzed by the Cu_2O -*tert*-BuNC System^a

Cyclopentadiene homolog (mmol)	Carbonyl compound (mmol)	Catalyst, mmol, $\text{Cu}_2\text{O}:\textit{tert}$ -BuNC	Time, hr	Solvent (ml)	Product	Yield, %
C_5H_6^b (50)	Me_2CO (50)	0.2/10	24		 3a	95
C_5H_6 (60)	<i>i</i> -PrCHO (50)	0.3/10	4		 3c	43
C_5H_6 (25)	PhC(=O)Me (30)	0.2/10	5		 3d	66
C_9H_8^c (20)	Me_2CO (30)	0.3/10	24		 3b	50
C_9H_8 (30)	EtCHO (40)	0.2/20	3	Et ₂ O (5)	 3e	56
C_9H_8 (30)	<i>i</i> -PrCHO (30)	0.2/10	3	Et ₂ O (5)	 3f	55
C_9H_8 (20)	PhCHO (30)	0.3/10	1		 3g	80
$\text{C}_{13}\text{H}_{10}^d$ (20)	PhCHO (30)	0.5/20	24	C_6H_6 (5)	 3h	60

^a The reaction was carried out at room temperature. ^b C_5H_6 = cyclopentadiene. ^c C_9H_8 = indene. ^d $\text{C}_{13}\text{H}_{10}$ = fluorene.

On the basis of the isolation of **1** and **2** as well as their catalytic behavior, Scheme I is presented for the reac-

Scheme 1

tion of eq 5. Organocopper complex **5** is first formed from Cu_2O , a cyclopentadiene homolog, and an isocyanide; **5** in turn reacts with a carbonyl compound to afford a copper alkoxide species **6**. In the hydrogen abstraction of **6** from the second molecule of the cyclopentadiene homolog, a carbinol **7** is produced and **5** is reproduced. The dehydration of **7** gives rise to the fulvene-type product. Isocyanide functions as an essential ligand in a series of copper complexes. From the results of Table II, the presence of **2** or more than 2 mol of isocyanide ligand seems to be required for high catalyst activity.

Dimerization of Crotononitrile and a Michael-Type Reaction Catalyzed by 1. It has been found by us that the dimerization of crotononitrile (eq 1) and the Michael-type addition reaction **2** are catalyzed by the Cu_2O -isocyanide system.^{4a-c} In the schemes of these reactions, it has been assumed that an organocopper-isocyanide complex is formed from an active hydrogen compound (crotononitrile or the hydrogen donor of the Michael-type addition reaction), Cu_2O , and an isocyanide, which behaves as the key intermediate in these reactions. The organocopper-isocyanide complex **1** of the present study was examined for catalytic activity in these reactions on the basis of the assumption that the reaction of **1** with an active hydrogen compound would afford a key intermediate of the corresponding organocopper-isocyanide complex. The catalytic activity of **1** in these two reactions is shown in Table IV. Increase of the catalytic activity by the addition of an equimolar amount of isocyanide is also interestingly demonstrated here.

Experimental Section

Reagents. Cu_2O was a commercial reagent and was used without further purification. *tert*-Butyl isocyanide was prepared by Ugi's procedure.⁵ All the other reagents and solvents were purified by usual methods and distilled under nitrogen prior to use.

Spectroscopic Measurements. Proton nuclear magnetic resonance spectra were recorded on a Japan Electric Optics Laboratory 60-MHz spectrometer or a Varian Associates T-60 spectrometer in a sealed nmr tube under nitrogen.

Preparation of 1. A mixture of 5.0 g (35 mmol) of Cu_2O , 5.0 g (60 mmol) of *tert*-BuNC, and 16.5 g (250 mmol) of cyclopentadiene

(5) I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).

Table IV. Dimerization of Crotonitrile and Some Michael Reactions Catalyzed by 1^a

Reactants (mmol)	Catalyst (mmol)	Product	Yield, %
Dimerization CH ₃ CH=CHCN (20)	1 (0.40)	CH ₃ CH=C—CN CH ₃ CHCH ₂ CN	16
CH ₃ CH=CHCN (20)	1 (0.40) + <i>tert</i> -BuNC (0.40)		42
Michael-type reaction Indene (30) + CH ₂ =CHCO ₂ Me (20)	1 (0.40)	C ₉ H ₇ CH ₂ CH ₂ CO ₂ Me	29
CH ₃ CH(OMe) ₂ (20) ^b + CH ₂ =CHCN (15)	1 (1.00)	(MeCO) ₂ C(Me)CH ₂ CH ₂ CN	83
CH ₂ (CO ₂ Et) ₂ (30) + CH ₃ CH=CHCO ₂ Me (20)	1 (0.40) 1 (0.40) + <i>tert</i> -BuNC (0.40)	(EtO ₂ C) ₂ CHCH(Me)CH ₂ CO ₂ Me	17 32

^a All reactions were carried out at 80° for 5 hr unless otherwise noted. ^b Carried out at room temperature for 6 hr.

Table V. Identification Data of Products from Cyclopentadiene Homologs and Carbonyl Compounds

Products	Analysis, %		Bp or mp, °C	Principal ir bands, cm ⁻¹	Nmr τ (CCl ₄)	
	C	H				
3a	Calcd	90.50	9.50	Bp 60 (25 mm)	1632 (s), 1360 (s), 760 (s) ^c	7.85 (s, -CH ₃ , 6 H), 3.68 (s, vinyl H, 4 H)
	Found	90.46	9.51			
3b	Calcd	92.26	7.74	Bp 83–84 (0.5 mm)	1630 (s), 786 (s), 745 (s), 716 (s) ^c	7.82, 7.72 (2 s, -CH ₃), 2.30–3.36 (m, vinyl H, 6 H)
	Found	92.20	8.03			
3c	Calcd	89.94	10.06	Bp 50 (13 mm)	1630 (s), 1455 (s), 822 (s), 760 (s) ^c	8.85 (d, -CH ₃), 7.00 (m, >CH), 4.0–3.5 (m, vinyl H, 6 H)
	Found	90.12	10.24			
3d	Calcd	92.81	7.19	Bp 83 (2.5 mm)	1625 (s), 775 (s), 703 (s) ^c	7.23 (s, -CH ₃), 3.66–3.06 (m, vinyl H, 7 H), 2.35 (s, Ph, 5 H)
	Found	92.42	7.31			
3e	Calcd	92.26	7.74	Bp 77 (0.8 mm)	1640 (s), 1600 (w), 1445 (s), 734 (s) ^c	8.65 (t, -CH ₃), 7.29 (q, -CH ₂ CH ₃) 3.7–2.4 (m, vinyl H, 7 H)
	Found	92.18	7.85			
3f	Calcd	91.91	8.56	Bp 85–87 (0.9 mm)	1650 (m), 1610 (w), 1450 (s), 760 (s) ^c	8.80 (d, -Cw ₃), 7.30–6.52 (m, >CH), 3.75–2.40 (m, vinyl H, 7 H)
	Found	91.71	8.29			
3g	Calcd	94.08	5.92	Mp 87–88 ^a	1628 (w), 800 (s), 755 (s), 700 (s) ^d	3.05–2.30 (m, vinyl H)
	Found	94.18	6.08	(lit. 90 ^a)		
3h	Calcd	94.45	5.57	Mp 74 ^b	1600 (m), 1440 (s), 780 (s), 750 (s), 734 (s), 702 (s) ^d	3.30–2.35 (m, vinyl H)
	Found	94.11	5.55	(lit. 76 ^b)		

^a Recorded, 90°: G. Krensze, H. G. Henkel, and H. Goetz, *Justus Liebigs Ann. Chem.*, **674**, 18 (1964). ^b Recorded, 76°: H. Lettre, H. Barnbeck, and W. Lege, *Chem. Ber.*, **69**, 1154 (1936). ^c Neat. ^d KBr pellet.

was heated at 50° for 20 min under nitrogen. An exothermic reaction occurred, and Cu₂O dissolved to give a slurry. The reaction mixture was heated for an additional 30 min at 50°. Then 50 ml of ether was added to the reaction mixture and the mixture was filtered to remove unreacted Cu₂O. *n*-Pentane (30 ml) was added to the filtrate and the mixture was allowed to stand at room temperature. A white crystalline solid began to precipitate slowly. Sometimes, the filtrate was cooled to 0° in order to ensure the crystallization. The crystalline substance was washed with *n*-pentane and dried *in vacuo* at room temperature for 8 hr. A white crystalline solid, 6.9 g (55% based on *tert*-BuNC), was obtained, which was shown to be *h*⁵-C₅H₅Cu(*tert*-BuNC) (1) by the following analytical data: nmr (C₆D₆) τ 9.36 (t, *tert*-Bu r_i = 9), 3.76 (s, cyclopentadiene, r_i = 5); principal ir bands (KBr pellet) 3084 (singlet, m, ν_{C-H}), 2170 (s, ν_{C=N}), 1625 (w, ν_{C=C}), 770 (s), 755 (s) (δ_{C=C-H}) cm⁻¹. The singlet absorption at 3084 cm⁻¹ indicates the *h*⁵-C₅H₅Cu structure.

Analysis of Cu Content. 1 (0.5259 g, 2.48 mmol) was decomposed by 5 ml of concentrated HNO₃. The Cu content was determined by iodometry⁶ with 0.1 N sodium thiosulfate under nitrogen. *Anal.* Calcd for C₁₀H₁₄NCu: Cu, 30.0. Found: Cu, 29.7.

Reaction of 1 with FeCl₂ was carried out as follows. In 7 ml of tetrahydrofuran, 0.4490 g of 1 was treated with 0.25 g (2 mmol) of FeCl₂ at 60° for 1 hr. By glpc analysis the amount of ferrocene produced was 0.186 g, which was 99.5% of the calculated value (0.187 g).

Preparation of 2. All the reagents were carefully dried and distilled under nitrogen. A small amount of air greatly decreased the yield of 2. A mixture of 1.43 g (10 mmol) of Cu₂O, 8.3 g (100

mmol) of *tert*-BuNC, 11.6 g (100 mmol) of indene, and 10 ml of benzene was stirred at room temperature for 2 hr. An exothermic reaction occurred and part of the Cu₂O dissolved to give a slurry. The reaction mixture was diluted with 60 ml of benzene and was filtered to remove unreacted Cu₂O. When 60 ml of ether was added to the filtrate, a light yellow crystalline solid separated out. The crystalline substance was washed with ether repeatedly and dried *in vacuo* at room temperature. A light greenish yellow solid, 2.6 g (30% based on Cu₂O), was obtained. This solid was quite vulnerable to air and heat. Even in the process of drying *in vacuo*, the color of the crystals changed gradually from light yellow to light greenish yellow. Prolonged drying seemed unfavorable owing to the thermal instability and air sensitivity of the product. When complex 2 is exposed to air in solid form and in solution, it turns black immediately. As compared with the high stability of 1, the peculiar instability of 2 is notable. 2 was stored under nitrogen without noticeable decomposition at least for a week at room temperature, but it decomposed slowly, emitting the odor of isocyanide over a longer period. An attempt at repeated recrystallization was unsuccessful owing to decomposition. The structure was examined by ir and nmr spectra as well as by a D₂O-quenching experiment. The nmr spectrum is shown in Figure 1. From the relative intensities of the *tert*-butyl and indenyl protons in the nmr spectrum of 2, the structure of 2 was revealed to be C₉H₇Cu(*tert*-BuNC)₂. Principal ir bands (in Nujol under nitrogen) were observed at 2170 (s, ν_{C=N}), 730 (s), and 695 (s) cm⁻¹ (based on Ph ring). A monohapto structure may be assumed on the basis of the nmr spectrum (see the Results and Discussion section).

D₂O Quenching. A mixture of 3.48 g (30 mmol) of indene, 0.7 g (5 mmol) of Cu₂O, and 2.5 g (30 mmol) of *tert*-BuNC was allowed to react for 3 hr at 50° until the reaction system became homogeneous. D₂O (6 g, 33 mmol) was added to the reaction mixture and the mixture was stirred for 12 hr at room temperature, then

(6) W. T. Elwell and J. R. Scholes, "Analysis of Copper and its Alloys," Pergamon Press, London, 1967, p 19.

poured slowly into 30 ml of petroleum ether (30–60°) with stirring. Deuterated indene was recovered by extraction with petroleum ether followed by distillation. The nmr spectrum of the recovered indene revealed that only the C-1 and C-3 protons were deuterated, to an equal extent of 89%. This fact is rationalized by the rapid interconversion of the carbon-copper bond between C-1 and C-3 atoms, and it is quite compatible with nmr spectrum of 2.

Reactions of Cyclopentadiene and Indene with Acetone Catalyzed by 1 and 2. A mixture of cyclopentadiene (or indene), 1 (or 2), and acetone was stirred at room temperature for 24 hr. In one experiment, *tert*-BuNC (equimolar to 1) was also added in the reaction mixture. As the reaction proceeded, an aqueous layer separated out. The organic layer was subjected to fractional distillation under reduced pressure. 6,6-Dimethylfulvene (3a), bp 60° (25 mm), was obtained from cyclopentadiene and acetone, and 1-isopropylideneindene (3b), bp 83–84° (0.5 mm), was formed from indene and acetone. The yields of 3a and 3b were determined by glpc using the peak area method to ensure accuracy. Identification of 3a and 3b was by ir and nmr spectra as well as elemental analysis. The identification data are summarized in Table V.

Reaction of Cyclopentadiene with Carbonyl Compounds Catalyzed by the Cu₂O-*tert*-BuNC System. A mixture of cyclopentadiene, carbonyl compound, Cu₂O, and isocyanide was stirred at room temperature for an indicated time (Table III). In some cases, the reaction was carried out in the presence of a solvent. The reaction mixture was worked up by a similar procedure to the reaction with 1 as catalyst, and the products were isolated by fractional distillation. The identification data are shown in Table V.

Reaction of Indene (or Fluorene) with Carbonyl Compounds Catalyzed by the Cu₂O-*tert*-BuNC System. An example follows.

A mixture of 2.3 g (20 mmol) of indene, 48 mg (0.3 mmol) of Cu₂O, and 0.83 g (10 mmol) of *tert*-BuNC was heated at 60° for 1 hr with stirring under nitrogen. Cu₂O dissolved in the liquid reaction mixture to give a reddish purple solution. To this solution, 1.74 g (30 mmol) of acetone was added slowly. The reaction mixture was stirred at room temperature for 24 hr, and then was worked up by a procedure similar to that of the reaction with 2 as catalyst. The identification data of the products from several carbonyl compounds are summarized in Table V. Product 3g of the table was purified by recrystallization from EtOH-benzene and 3h was purified from EtOH.

Reaction of Diethyl Malonate with Isobutyraldehyde Catalyzed by the Cu₂O-*tert*-BuNC System. A mixture of reaction components was heated in a sealed test tube at 80° for 24 hr. Then the reaction mixture was distilled, and a fraction boiling at 70–80° (0.5 mm) was collected. By preparative glpc, the main product was isolated, which was identified as diethyl isobutylidene malonate: yield 47%; nmr (in CCl₄) τ 8.90 (d, (CH₃)₂CH-, r_i = 6), 8.70 (t, CH₂CH₂-, r_i = 6), 7.60–7.10 (m, >CH-, r_i = 1), 5.78 (q, CH₂CH₂-, r_i = 4), and 3.38 (d, -CH=, r_i = 1). *Anal.* Calcd for C₁₁H₁₈O₄: C, 61.66; H, 8.47. Found: C, 61.51, H, 8.73.

Dimerization of Crotonitrile and a Michael-Type Reaction Catalyzed by 1. A mixture of 1.34 g (20 mmol) of crotonitrile and 0.4 ml (0.4 mmol) of a 1 M solution of 1 in benzene was heated at 80° for 5 hr under nitrogen. The yield of dimer was determined by glpc analysis using an authentic sample.^{4a} The yield of dimer was increased by the addition of an equimolar amount of *tert*-BuNC (see Table IV). The Michael-type addition reaction was carried out similarly and the reaction mixture was worked up according to the procedure of our previous study.^{4c}

Electron Transfer through Organic Structural Units. IX. Reductions of Carboxylatopentaamminecobalt(III) Complexes with Copper(I)^{1a}

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Abstract: Specific rates for reductions of carboxylatopentaamminecobalt(III) complexes with Cu(I) are only 10⁻⁷–10⁻² times as great as the corresponding rates for reduction with Cr(II), which is more strongly reducing by 0.56 V. Reductions, with Cu⁺, of benzoate and ordinary aliphatic derivatives are so slow ($k < 0.01 M^{-1} sec^{-1}$) that precipitation of copper metal from solution generally prevents quantitative measurements; for these, it is impossible to say whether reduction occurs by an inner- or outer-sphere mechanism. Neighboring hydroxyl groups are without apparent effect on rates, but reductions are enhanced by neighboring -SR. No evidence for Cu⁺ reduction *via* remote attack is obtained with the aldehydobenzoate, nitrobenzoate, pyruvate, maleate, or 4-pyridinecarboxylate complexes, all of which are reduced rapidly by Cr²⁺. Rapid reductions are observed with pyridine and pyrazine complexes in which -COOC^{III} lies α to a basic nitrogen; these almost certainly are inner-sphere reactions, proceeding through chelated transition states, for they no longer occur if the nitrogen is protonated or methylated. A first-order acid dependence for reduction of the pyrazine derivatives indicates that the tripositive forms of these complexes, in which the 4 nitrogen is protonated, are reduced somewhat more rapidly than the nonprotonated form. The 4-cinnolinecarboxylate complex V is the only complex in this series rapidly reduced by Cu⁺ for which chelation is structurally excluded, and thus appears to be the sole example of reduction by remote attack. It is suggested that, because of the low reducing potential of Cu⁺, remote attack requires a more basic lead-in atom and a more reducible mediating path than is the case for Cr²⁺ reductions.

Studies of bridging action by organic ligands in redox reactions have dealt principally with reductions by Cr^{II}.² This direction of emphasis has been advan-

(1) (a) From the Ph.D. Thesis of E. R. Dockal, Kent State University, 1971. This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, under Grant No. 2878-A3; (b) NSF Trainee, 1969–1971.

(2) (a) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969); see, however, (b) R. T. M. Fraser, *J. Amer. Chem. Soc.*, **84**, 3436 (1962); (c) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

tageous in that the substitution-inert character of the resulting Cr(III) complexes has often provided critical information about reaction mechanism; however, the question remains as to whether the various effects observed require the presence of chromium or whether they are properties principally of the organic ligands.

The impetus for the present work was a report by Parker and Espenson,³ who studied the rates of reduc-