Inorganica Chimica Acta, *149* (1988) 45–56

Stoichiometry, Products and Kinetics of Transmetalation of Dimeric Copper(II) Complexes $L_2Cu_2X_2Y$ (L is an *N,N,N′,N′*-Tetraalkyldiamine; X is Cl or Br; Y is O or CO_3) by $M(NS)_2$ Reagents*

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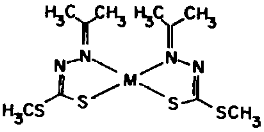
(Received December 21, 1987)

Abstract

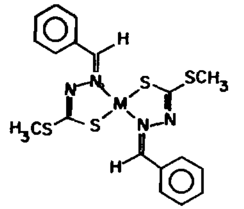
This paper reports the stoichiometry and kinetics of seventeen monotransmetalations of dimeric copper(II) targets $L_2Cu_2X_2O$ (**E**) and $L_2Cu_2X_2CO_3$ (**F**) by neutral $M(NS)_2$ transmetalators in nitrobenzene. Here, L is an *N,N,N′,N′*-tetraalkyldiamine, X is Cl or Br, M is Co, Ni or Zn and NS is monoanionic *S*-methylisopropylidenehydrazinecarbodithioate or *S*-methylbenzylidenehydrazinecarbodithioate in $M(NS)_2$ transmetalators **C** and **D**, respectively. All these monotransmetalations proceed with rate = k[transmetalator][target]^n, where n is 0, 1 or 2. Reaction order n is generally smaller than for monotransmetalations of $(\mu_4\text{-O})N_4Cu_4X_6$ targets by **C** because terminal X in **E** and **F** lead to more stable transmetalation precursors even with X = Cl. Based on derived activation entropies, the formation of discrete transmetalation products is the rate-determining step when n is 1 or 2, but metal exchange is rate-determining in systems involving especially stable precursors when n is zero. The results demonstrate the effects of L, X, NS and M on transmetalation rates and rate laws and suggest selective transmetalation of five-coordinate copper(II) in asymmetrical targets $\mathbf{F}_{II}$.

Introduction

Copper(II) complexes $(\mu_4\text{-O})N_4Cu_4X_6$ (**A**) [2], and copper(I) complexes $L_2Cu_2X_2$ (**B**) [3, 4], where N is a monodentate pyridine and L is an *N,N,N′,N′*-tetraalkyldiamine, contain μ-halo bridges, X, Fig. 1. This common feature led us to compare the rate laws and kinetic parameters for rapid reactions of excess **A** and **B** with bis(*S*-methylhydrazinecarbodithioate Schiff base)metal(II) complexes **C** or **D** because M–X bond formation is a likely requirement for metal exchange via $\overline{\text{Cu–X–M–S}}$ rings in monotransmetalation reactions (1) and (2) [5].



C



D

$$(\mu_4\text{-O})N_4Cu_4X_6 + M(NS)_2 \longrightarrow (\mu_4\text{-O})[N_3Cu_3M]X_6 + Cu(NS)_2 \qquad (1)$$

$$L_2Cu_2X_2 + M(NS)_2 \longrightarrow LCuM(NS)X_2 + Cu(NS)(s) + L \qquad (2)$$

Reactions (1) and (2) differ in several important respects. (i) Because reactant $M(NS)_2$ and coproduct $Cu(NS)_2$ have the same stoichiometry, there are no NS ligands in the polynuclear products of eqn. (1) [6–9], whereas this is the case for eqn. (2) and related copper(I) systems [10–12]. (ii) Formation of discrete coproduct $Cu(NS)_2$ is the rate-determining step in the majority of reactions (1): exceptions include slower metal exchange in particularly stable $\overline{\text{Cu–Br–Co(Zn)–S}}$ rings or with especially stable reactant **D** (M = Ni) [9]. By contrast, formation of discrete Cu(NS)(s) coproducts is slow in eqn. (2) [5]. (iii) The rates and rate laws of irreversible monotransmetalation reactions (1) seem to depend more on the inherent thermodynamic stabilities of $M(NS)_2$ complexes **C** and **D** and the nucleophilicity of their carbothioate sulfur atoms than on their different molecular geometries

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*Taken in part from ref. 1.

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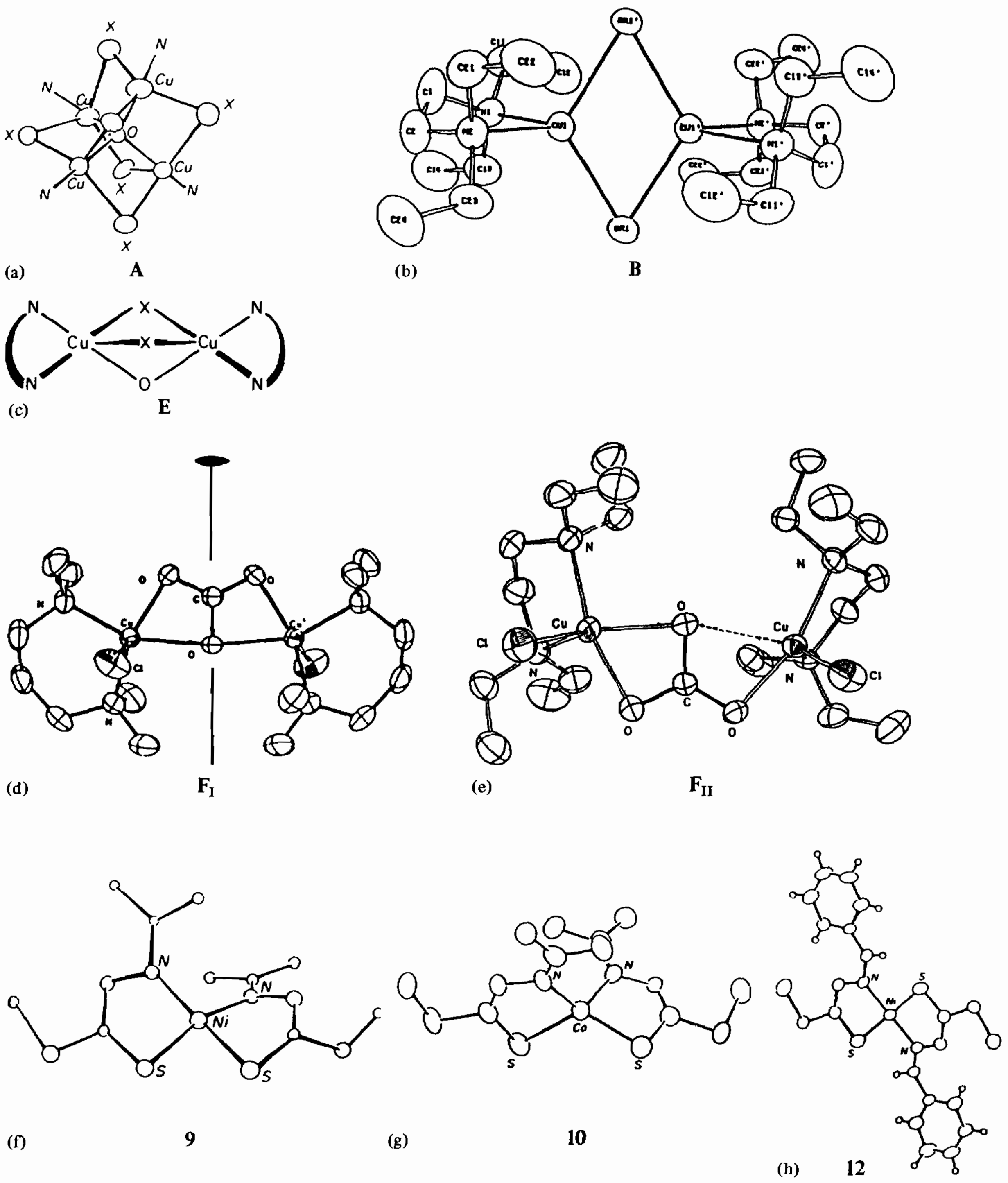


Fig. 1. Structures of (a) $(\mu_4\text{-O})N_4Cu_4X_6$ (A, [2]); (b) $(TEED)_2Cu_2Br_2$ (B, [3]); (c) $L_2Cu_2X_2O$ (E, tentatively proposed in ref. 14); (d) $(TMPD)_2Cu_2Cl_2(CO_3)$ (F_I, [17, 19]); (e) $(TEED)_2Cu_2Cl_2(CO_3)$ (F_{II}, [18, 19]); (f) *bis*-(*S*-methylisopropylidenehydrazinecarbodithioate)nickel(II) [28]; (g) bis-(*S*-methylisopropylidenehydrazinecarbodithioate(cobalt(II) [13]; (h) bis-(*S*-methylbenzylidenehydrazinecarbodithioate)nickel(II) [29]. Note: structures are not on the same scale.

(structure **10** [13]), whereas there is evidence for steric factors in reactions (2), especially with M = Co; indeed, some of the earliest steps in reactions (2) are reversible and interfere with irreversible metal exchange required for transmetalation [5].

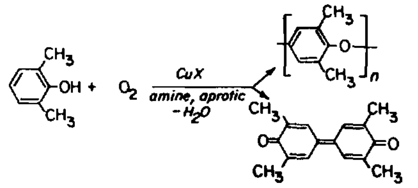
Copper(I) complexes **B** are rapidly oxidized to dimeric oxocopper(II) complexes **E** by dioxygen in aprotic solvents, eqn. (3) [3, 14, 15]. The spectra

$$\underset{\mathbf{B}}{2L_2Cu_2X_2} + O_2 \longrightarrow \underset{\mathbf{E}}{2L_2Cu_2X_2O} \qquad (3)$$

of **E** suggest five-coordinate copper(II) centers in a triply-bridged (X,O,X) constitution, Fig. 1 [3, 14, 15]. Products **E** undergo irreversible polymerization and ligand degradation in the absence and presence of excess dioxygen, respectively, but these processes are too slow to interfere with kinetic measurements of eqn. (3) or with primary product characterization [3, 14, 16]. Products **E** are greatly stabilized by rapid reactions (4), which give μ-carbonatodicopper(II) products $L_2Cu_2X_2CO_3$ (**F**) [17–19]. All **F**

$$\underset{\mathbf{E}}{2L_2Cu_2X_2O} + CO_2 \longrightarrow \underset{\mathbf{F}}{2L_2Cu_2X_2CO_3} \qquad (4)$$

contain bridging carbonate and terminal X. Structural studies show that **F** either contain symmetrical μ-carbonato bridges and *trans*-terminal X (EPR-silent, type F_I) [17] or asymmetrical μ-carbonato bridges and *cis*-terminal X (EPR-active, type F_{II}) [18], Fig. 1. These structural types also can be chemically distinguished by different stoichiometries of reaction with 2,4,6-trichlorophenol [19]. Type F_I seems to be restricted to ligand L = *N,N,N',N'*-tetramethyl-1,3-propanediamine, TMPD [17–19]. Complexes **E** and both types of stable complexes **F** are of considerable interest as initiators for copper-catalyzed oxidative coupling reactions of phenols, eqn. (5) [17–21]; complexes **E** are the likely catalysts in such processes [22].



(5a)

(5b)

We have reported that μ-carbonato complexes **F** can be partially and completely transmetalated with reagents **C** and **D** (M = Ni), eqns. (6) and (7) [23].

$$L_2Cu_2X_2CO_3 + Ni(NS)_2 \longrightarrow L_2CuNiX_2CO_3 + Cu(NS)_2 \qquad (6)$$

$$L_2Cu_2X_2CO_3 + 2Ni(NS)_2 \longrightarrow L_2Ni_2X_2CO_3 + 2Cu(NS)_2 \qquad (7)$$

This paper reports the stoichiometries, products and kinetics of reactions of **E** (L = *N,N,N',N'*-tetraethylethylenediamine, TEED, and TMPD; X = Cl or Br) and their derivatives **F** from eqn. (4) (L = TEED, TMPD and *N,N,N',N'*-tetramethylethylenediamine, TMED) with **C** and **D** (M = Co, Ni, Zn). Direct monotransmetalations with different rate laws and rate-determining steps are observed with excess **E** and **F**. Particular attention is paid to the roles of (i) μ-O [3, 14] and terminal X [17, 19] ligands; (ii) the relative thermodynamic stability [12], S-nucleophilicity [24, 25] and geometry [13] of $M(NS)_2$; and (iii) the possibility that monotransmetalation is site-selective in asymmetrical reactants **E** and **F** in formulating mechanisms for these reactions.

Experimental

Most of the procedures and measurement techniques of this work have been described previously [2, 3, 5, 9, 14, 17–19, 23]. Ligands TMED, TEED and TMPD (Alfa or Aldrich) were vacuum-distilled immediately before use in the synthesis of dimeric copper(II) reactants **E** [3, 4] and **F** [17–19]. It was confirmed that the primary products **E** of oxidation of $(TMED)_2Cu_2X_2$ [4] with dioxygen, eqn. (3), polymerize too rapidly under dinitrogen at 5–30 °C in methylene chloride or nitrobenzene to allow their use as reactants for reproducible kinetic measurements of transmetalation; it also was confirmed that polymerization is prevented by oxidizing $(TMED)_2Cu_2X_2$ in the presence of excess carbon dioxide, which gives stable dimers (asym-μ-CO_3)*cis*-dihalo-bis-(*N,N,N',N'*-tetramethylethylenediamine)dicopper(II) as the products, eqn. (4) [14, 19]. The properties of each reactant used in this study were found to be in excellent agreement with literature data [2, 3, 5, 13, 14]. Each is labelled in Table I.

Stoichiometry and Products of Transmetalation of E and F with C and D

We have reported the stoichiometry and products of reactions of μ-carbonato complexes **4** and **6** with $Ni(NS)_2$ reagents **9** and **12** in aprotic solvents, eqns. (6) and (7) [23]. The same procedures were used in the title reactions. Our previous work demonstrates that products $(\mu\text{-}CO_3)L_2Cu_{2-x}Ni_xX_2$ (x = 1 or 2) have a marked tendency to lose their coordinated ligands L by reaction with water [23], and so stringent precautions were taken to prevent hydrolysis of primary products of transmetalation of **E** and **F** by $M(NS)_2$ transmetalators with either reagent in excess.

Kinetic Measurements

All of the kinetic measurements of this study were made with our stopped-flow apparatus, which has an all glass-quartz flow system and is interfaced with a Digital Equipment PRO-350 computer. The experimental arrangement and methods of data analysis have been described previously [5].

TABLE I. Labels for Targets and Transmetalators

Binuclear copper(II) targets E and F

Label	L	X	Y	Type[a]	Reference
1	TEED	Cl	O	E	14
2	TEED	Br	O	E	13
3	TMPD	Cl	O	E	14
4	TEED	Cl	CO_3	F_{II}	18, 19
5	TEED	Br	CO_3	F_{II}	18, 19
6	TMPD	Cl	CO_3	F_I	17–19
7	TMPD	Br	CO_3	F_I	17–19
8	TMED	Cl	CO_3	F_{II}	18, 19

Mononuclear $M(NS)_2$ transmetalators[b]

Label	NS	M	Geometry[c]
9	C	Ni	*cis*-sp.
10	C	Co	tet.
11	C	Zn	tet.
12	D	Ni	*trans*-sp.

[a] Type F_I are symmetrical, *trans*-X-dicopper(II) entities containing only five-coordinate copper(II); type F_{II} are unsymmetrical, *cis*-X-dicopper(II) entities containing four- and five-coordinate copper(II). See Fig. 1. [b] See refs. 13, 31, 32 for pertinent structural details. [c] Abbreviations: *cis*-sp is (essentially) *cis*-square planar; tet is tetrahedral; *trans*-sp is *trans*-square planar.

All kinetic measurements were conducted with a sufficient excess of the copper(II) reactant to ensure pseudo-first-order systems: experimental conditions are detailed in 'Results and Discussion'. Each system was studied under dinitrogen to eliminate alkyl substituent oxidation in **E** [3, 14, 16] and oxidation of **10** [10] by dioxygen. Solutions of **E** were freshly prepared *in situ* in nitrobenzene immediately before use to avoid the known, slow polymerization of **E** [3, 14]. This precaution gave time-independent, reproducible rate constants for transmetalation of **E** under fixed experimental conditions. Since the structures of polymerized forms of **E** are unknown, we made no attempt to measure the kinetic properties of deliberately aged solutions of **E***.

All of the reactions resulted in absorbance increases at 500–750 nm due to the formation of coproducts $Cu(NS)_2$, eqns. (6) and (7).

Results and Discussion

We have demonstrated that transmetalation of polynuclear metal complexes with $M(NS)_n$ reagents is an excellent means of obtaining families of heteropolynuclear molecules which cannot be obtained by other means [8, 12, 21]. Transmetalation products include molecules containing up to four different metals [27]. One of the results of complete transmetalation of oxo- [2] and carbonatocopper(II) [23] complexes with $Ni(NS)_2$ reagents is inhibition of initiation and catalysis of reaction (5).

The impetus for the present work was twofold. First, we wanted to partially (eqn. (6)) and completely (eqn. (7)) transmetalate dimeric copper(II) complexes **E** and **F** with $M(NS)_2$ and determine the properties of the CuM- and M_2-containing products, as we already have done for the reactions of **F** with **9** and **12** [23]. Second, we wished to compare the rate laws for monotransmetalation of copper(II) complexes **E** and **F** by $M(NS)_2$ reagents with those for **A** [9] and **B** [5] and to deduce likely reaction mechanisms.

Stoichiometry and Products of Transmetalation and Demetalation of Targets 1–8 with Transmetalators 9–12 and HNS

Figure 1 of ref. 23 shows the results of separate spectrophotometric titrations of **6** with **9** and HNS at 575 nm in methylene chloride. The results correspond to eqns. (7) and (8), respectively, and demonstrate that the driving force for transmetalation and demetalation of **6** is the formation of **C** (M = Cu), which is the principal absorber at 575 nm. The stoichiometries of eqns. (7) and (8) were observed in all the title reactions.

$$\mathbf{6} + 4\mathrm{HNS} \longrightarrow 2\mathbf{C}\,(\mathrm{M} = \mathrm{Cu}) + 2\mathrm{HCl} + \mathrm{H_2CO_3} + 2\mathrm{TMPD} \qquad (8)$$

Although neither experiment provided direct spectrophotometric evidence for eqn. (6) or partial

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*Polymerization of E results in precipitation that precludes accurate kinetic measurement like those in ref. 26.

demetalation of **1**–**8** by HNS, we demonstrated that total transmetalation of **4** and **6** by **9** and **12** proceeds via eqn. (6) and isolated products with CuNi and Ni_2 metal stoichiometries [23].

Difficulties encountered in the previous work [23] included low yields of pure, desired binuclear products from gel permeation chromatography or selective precipitation and a marked tendency for new nickel centers to lose their coordinated ligands L by reaction with water. These difficulties were even more pronounced for CuM- and M_2-containing products (M = Co, Zn) from the title reactions, so that pure products of the analogues of eqns. (6) and (7) could not be isolated even under the most rigorously anhydrous conditions. The difficulties are solely due to the necessity of removal of coproducts **C** and **D** (M = Cu), whose presence prevents cryoscopic measurements on the desired transmetalation products. Nevertheless, (i) the clean spectrophotometric results for eqns. (7) and (8); (ii) the fact that coproduct $Cu(NS)_2$ formation is the major driving force in all transmetalations of copper(II) targets; and (iii) very reproducible kinetic results under monotransmetalation conditions indicate that the primary products of the title transmetalation reactions are L_2CuMX_2Y and $L_2M_2X_2Y$, respectively.

Kinetics of Monotransmetalation of E and F by $M(NS)_2$ Reagents. Experimental Conditions

The kinetics of seventeen of the thirty-two possible monotransmetalation reactions of targets **1**–**8** with transmetalators **9**–**12** were studied spectrophotometrically in nitrobenzene under pseudo-first-order conditions with excess **1**–**8** ([**1**–**8**] = $(2.5–7.5) \times 10^{-3}$ M and [**9**–**12**] = 2.0×10^{-4} M) to ensure monotransmetalations of **1**–**8**. Absorbances were monitored between 505 and 625 nm and temperature was controlled to ±0.05 °C in the range 10.0–54.0 °C. Plots of $\ln(A_\infty - A_t)$ *versus* time, where A_t is the absorbance at fixed wavelength and time t, were linear to at least 4 half-lives in all systems, indicating a first-order dependence of monotransmetalation rates on [**9**–**12**].

Third-order Rate Laws for Monotransmetalation of Excess 1, 4 and 5 by 9

Plots of the observed pseudo-first-order rate constants for the reactions of **1**, **4** and **5** (Table I) with **9** at constant temperature, k_{obs}, *versus* $[Cu_2^{II}]_T^2$ were linear and passed through the origin (Fig. 2) indicating irreversible third-order rate law (9). This same high reaction order was previously observed in the reactions of oxo-copper(II) complexes **A** [9] and of dimeric copper(I) complexes **B** [5] with **9** and is indicative of reactant preassociation.

$$\text{rate} = k_9[\text{transmetalator}][\text{target}]^2 \qquad (9)$$

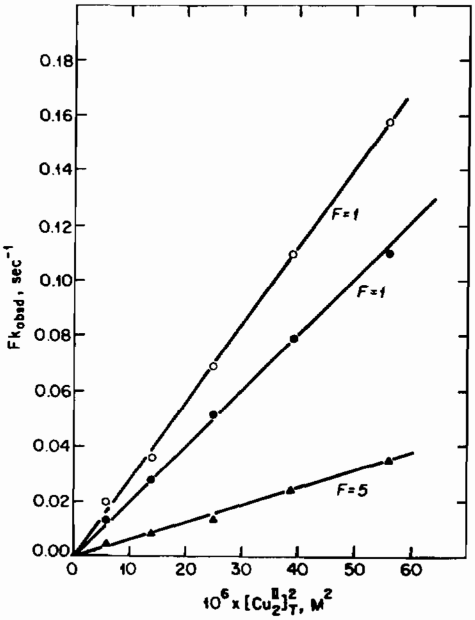


Fig. 2. Plots of F k_{obs} (s^{-1}) *vs.* $[Cu_2^{II}]_T^2$ for the following systems in nitrobenzene (rate law (9)): **1** with **9** at 24.5 °C, ▲; **4** with **9** at 30.3 °C, ●; **5** with **9** at 30.3 °C, ○.

Third-order rate constants k_9 and their associated activation parameters are collected in Table II. Plots of log k_9 *versus* $1/T$ were accurately linear in each system, showing that eqn. (9) is obeyed under all experimental conditions: thus, there is no evidence for changes in copper(II) target or reaction precursor molecularity in any of the systems investigated. Excess copper(II)/**9** systems which do not obey rate law (9) under the same experimental conditions are considered in a later section.

Features of the Kinetic Data for Third-order Rate Law (9)

Transmetalation of **1**, **4** and **5** by nickel reagent **9** is third-order (eqn. (9)). Changing the bidentate ligand, L, from TEED to TMPD in **E** or **F** or M from Ni to Co in **C** or X from Cl to Br in **E** causes a change in the rate law. This restricts observation of third-order rate law (9) to reactions of **1**, **4** or **5** with **9**. The presence of Cl or Br in the reaction of **F** (L = TEED) with **9** has a very small effect on k_9. The data in Table II also indicate that the reactions of **F** with **9** are faster than those of **E**. $\Delta H^{\ddagger}_9$ ranges from 11.1 to 14.5 kcal/mol; the smallest is for the reaction of carbonato complex **4** with **9** and the largest is for the reaction of oxocopper complex **1** with **9**. Reaction of **1** with CO_2 thus facilitates its transmetalation by **9**. $\Delta S^{\ddagger}_9$ is in the narrow range 0 to 7 cal deg^{-1} mol^{-1} for these monotransmetalation reactions.

TABLE II. Kinetic Data for Transmetalation of Targets E and F by $M(NS)_2$ Reagents in Nitrobenzene (eqns. (9)–(11))

Reactants^a				$\Delta S^{\ddagger}_{rds}$^{d}
Rate law (9)	k_9^{b}	$\Delta H^{\ddagger}_9$^{c}	$\Delta S^{\ddagger}_9$^{d}	
1, **9**	85	14.5 ± 0.4	0 ± 3	60 ± 3
4, **9**	1100	11.1 ± 0.4	−7 ± 3	53 ± 3
5, **9**	1400	11.8 ± 0.4	−4 ± 3	56 ± 3
Rate law (10)	k_{10}^{e}	$\Delta H^{\ddagger}_{10}$^{c}	$\Delta S^{\ddagger}_{10}$^{d}	
2, **9**	5.2	9.2 ± 0.3	−24 ± 4	21 ± 4
3, **9**	1.1	15.0 ± 0.3	−8 ± 3	37 ± 3
3, **10**	18.0	12.7 ± 0.3	−10 ± 3	35 ± 3
5, **10**	4.5	8.8 ± 0.3	−26 ± 3	19 ± 4
6, **9**	0.95	8.8 ± 0.3	0 ± 3	45 ± 3
7, **9**	0.63	13.2 ± 0.4	−15 ± 4	30 ± 4
8, **9**	2.41	15.3 ± 0.4	−5 ± 3	40 ± 3
8, **12**	0.063	17.7 ± 0.4	−4 ± 3	41 ± 3
Rate law (11)	k_{11}^{f}	$\Delta H^{\ddagger}_{11}$^{c}	$\Delta S^{\ddagger}_{11}$^{d}	
1, **10d**	0.027	20.4 ± 0.4	3 ± 3	
2, **10**	0.16	10.6 ± 0.4	−26 ± 4	
4, **10**	0.0039	25.6 ± 0.4	17 ± 3	
4, **11**	0.023	17.7 ± 0.3	−6 ± 3	
6, **10**	0.0046	17.1 ± 0.4	−11 ± 3	
7, **10**	0.0040	9.4 ± 0.3	−38 ± 4	

^{a}See Table I for identification. Reactants **1**–**8** always in large excess. ^{b}Units are M^{-2} s^{-1} at 21 °C (typical error is ±5%). ^{c}Units are kcal mol^{-1} (error shown is 1 standard deviation). ^{d}Units are cal deg^{-1} mol^{-1} at 25 °C (error shown is 1 standard deviation). ^{e}Units are M^{-1} s^{-1} at 21 °C (typical error is ±5%). ^{f}Units are s^{-1} at 21 °C (typical error is ±5%).

Second-order Rate Laws for Monotransmetalation of E and F by 9, 10 and 12

Plots of the observed pseudo-first-order rate constant for particular title reactions at fixed temperature, k_{obs}, *versus* $[Cu_2^{II}]_T$ were linear and passed through the origin, Fig. 3, indicating second-order rate law (10). Second-order rate constants

$$\text{rate} = k_{10}[\text{transmetalator}][\text{target}] \qquad (10)$$

k_{10} and their associated activation parameters are collected in Table II. Plots of $\log k_{10}$ *versus* $1/T$ were accurately linear in each system; there is thus no evidence for changes in copper(II) reactant molecularity in any of the systems investigated.

Features of the Kinetic Data for Second-order Rate Law (10)

All previously investigated monotransmetalations of copper(II) complexes by reagents **D** are irreversible processes with second-order rate laws. By contrast, third-order rate law (9) is observed for the majority of reactions with **C** under similar experimental conditions [9]. We now report that the reaction of **4** with **12** also obeys an irreversible second-order rate law (10), which thus appears to be characteristic of transmetalator **12**.

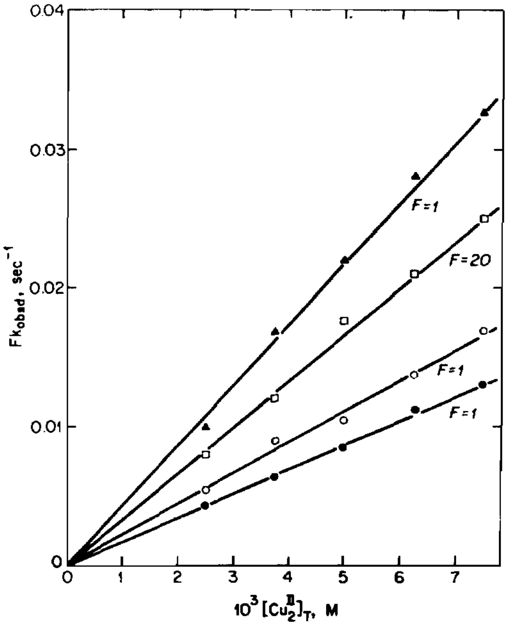


Fig. 3. Plots of F k_{obs} (s^{-1}) *vs.* $[Cu_2^{II}]_T$ for the following systems in nitrobenzene (rate law (10)): **6** with **9** at 30.3 °C, ○; **7** with **9** at 35.4 °C, ●; **8** with **9** at 28.0 °C, ▲; **4** with **12** at 31.0 °C, □.

The data in Table II indicate that having L = TMPD or TMED ligands in **E** or **F** never leads to third-order rate law (9) even with transmetalator **9**: methyl substituents in L evidently do not favor reactant preassociation. $\Delta H^{\ddagger}_{10}$ covers the large range from 8.8 to 17.7 kcal/mol. The largest $\Delta H^{\ddagger}_{10}$ is for the reaction of carbonato complex **4** with **12**, which is also the slowest reaction at 21 °C. The smallest $\Delta H^{\ddagger}_{10}$ is for the reaction of **5** with **10**, which also has the smallest $\Delta S^{\ddagger}_{10}$ (−26 cal deg^{-1} mol^{-1}). Comparison of the data for **3** with those for its carbonato derivative **6** both reacting with **9** shows that there is no large effect of the carbonate bridge but that both $\Delta H^{\ddagger}_{10}$ and $\Delta S^{\ddagger}_{10}$ are slightly increased by changing from **E** to $\mathbf{F_I}$. Having Cl or Br in the reactions of **6** and **7** with **9** also has little effect on k_{10} but $\Delta H^{\ddagger}_{10}$ and $\Delta S^{\ddagger}_{10}$ are higher with X = Br. Reactions of excess **3** with **10** are 17 times faster than those with **9** because $\Delta H^{\ddagger}_{10}$ and $\Delta S^{\ddagger}_{10}$ are both considerably lower.

First-order Rate Laws for Transmetalation of E and F by 10 and 11

The observed pseudo-first-order rate constants, k_{obs}, for the reactions of excess **1**, **2**, **4**, **6** and **7** with transmetalators **10** and **11** at constant temperature were found to be independent of $[Cu_2^{II}]_T$

indicating first-order rate law (11). First-order rate constants k_{11} and their associated activation parameters are collected in Table II.

$$\text{rate} = k_{11}[\text{transmetalator}][\text{target}]^0 \qquad (11)$$

Features of the Kinetic Data for First-order Rate Law (11)

Rate law (11) appears only in the reactions of **10** and **11** with excess **E** and **F** and never appears in reactions of nickel reagents **9** or **12**. This form of rate law was observed previously in the reactions of excess **A** (X = Br, not Cl), with **10** and **11** [9]. It was concluded that particularly nucleophilic X and S atoms and accessible target metal centers can lead to strong interactions via $\overline{\text{Cu–X–M–S}}$ rings. The result is that there is no free **10** or **11** in the presence of excess copper(II). The data in Table II show that $\Delta H^{\ddagger}_{11}$ ranges from 9.4 to 25.6 kcal mol^{-1}, with the largest value for the reaction of carbonato complex **4** with **10**, which also exhibits the largest $\Delta S^{\ddagger}_{11}$ (17 cal deg^{-1} mol^{-1}). The smallest $\Delta H^{\ddagger}_{11}$ is for the reaction of carbonato complex **7** with **10**, which also has the smallest $\Delta S^{\ddagger}_{11}$ (−38 cal deg^{-1} mol^{-1}). Changing from X = Cl to X = Br in the reaction of **E** (L = TEED) with **10** causes an increase in k_{11} by a factor of 6 and a large, compensated decrease in $\Delta H^{\ddagger}_{11}$ and $\Delta S^{\ddagger}_{11}$. Changing from X = Cl to X = Br in the reaction of **E** (L = TMPD) with **10** has little effect on k_{11} but both $\Delta H^{\ddagger}_{11}$ and $\Delta S^{\ddagger}_{11}$ again sharply decrease. Changing the metal from Co to Zn in **C** in its reaction with excess **4** causes an increase in k_{11} by a factor of 6 and sharp, compensated decreases in $\Delta H^{\ddagger}_{11}$ and $\Delta S^{\ddagger}_{11}$.

Interpretation of the Kinetic Data. General Observations

Even monotransmetalations of polynuclear copper(I) and copper(II) complexes by $M(NS)_2$ reagents are multistep processes, but there is generally only one observable step [5,9]. What is important is that different rate laws are observed for this step and that rate law differences seem to be related to known reactant structures and properties. For example, an irreversible third-order rate law of type (9) is most often observed for reactions of polynuclear copper complexes with nickel transmetalator **9**. It seems to arise from the ability of this nearly flat transmetalator [28] to coordinate a total of two copper(II) reactants above and below its N_2S_2 ligand plane. However, a simple third-order rate law (9) indicates that these **9**·(copper)$_2$ precursors are weak, which has two important implications: (i) that a complete four-membered Cu–X–Ni–S ring is required for irreversible metal exchange leading to transmetalation; but (ii) that the carbothioate sulfur atoms of **9** are not sufficiently nucleophilic to allow formation of especially stable four-membered rings that (a) lead to complete coordination of **9** by excess copper; (b) rate saturation leading to rate law (11); and (c) rate-determining metal exchange, as would be indicated by near-zero activation entropies [9].

In earlier work [5,9], we reduced third- and second-order rate laws for copper transmetalation to the same, first-order dependence by accounting for the effects of reactant preassociation on measured entropies of activation. The magnitudes of the derived activation entropies $\Delta S^{\ddagger}_{\text{rds}}$ for rate-determining first-order processes were used to assign metal exchange or discrete product formation as the slowest step in each system [5,9].

A few copper(I) systems are governed by reversible rate laws that do not refer to transmetalation [5]. All of the other systems investigated [5,9] are governed by one of three irreversible rate laws of the form of eqn. (12), where n is 2, 1 or 0 in eqns. (9), (10) or (11), respectively.

$$\text{rate} \propto [\text{transmetalator}][\text{target}]^n \qquad (12)$$

The extreme and most useful case is where the rate law is independent of copper concentration (n = 0), for then the observed rate constants and activation parameters can be directly used to assign the rate-determining step without the need for any assumptions concerning the thermodynamics of weak reactant preassociation [9].

Another observation is that enthalpies and entropies of activation for related reactions of fixed reaction order are often correlated. One way to demonstrate and analyze such correlations is to take advantage of eqn. (13) and see if plots of $\Delta H^{\ddagger}$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (13)$$

versus $\Delta S^{\ddagger}$ are linear [10]. Linearity will, of course, be automatic if $\Delta G^{\ddagger}$ varies over only a small range for a reaction series, but the approach does allow the identification of systems with the same basic mechanistic requirements. Of particular value is plots of $\Delta H^{\ddagger}$ *versus* $\Delta S^{\ddagger}$ for systems involving the transmetalation of copper(I) and copper(II) complexes with common rate laws.

Activation Parameter Correlations. Third-order Rate Laws

Respective $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the third-order rate law (9) for monotransmetalation of **A** by **C** [9] and particular systems in Table II appear to be correlated: respective plots gave two parallel straight lines, Fig. 4, for all third-order nickel data in ref. 9 and Table II. The slopes of these lines, Table III, are larger than the slope of the line representing $\Delta H^{\ddagger}$ *versus* $\Delta S^{\ddagger}$ for third-order monotransmetalation of $L_2Cu_2X_2$ complexes by **9** [5], Fig. 4. This indicates that third-order rates of transmetalation

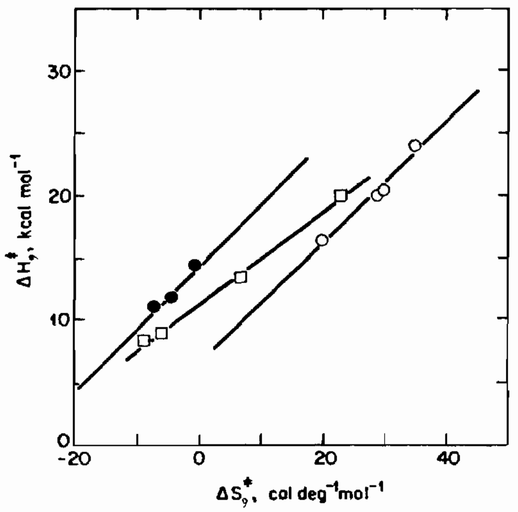


Fig. 4. Plots of $\Delta H^{\ddagger}_{9}$ (kcal mol^{-1}) *vs.* $\Delta S^{\ddagger}_{9}$ (cal deg^{-1} mol^{-1}) for the following third-order rate systems: **A** with **9** [9], ○; **B** with **9** [5], □; **E** and **F** with **9** (Table II), ●.

TABLE III. Slopes for Plots of $\Delta H^{\ddagger}_{9}$ *vs.* $\Delta S^{\ddagger}_{9}$ for Third-order Rate Law (9) for Monotransmetalation of Copper(II) and Copper(I) Complexes by **9** (Fig. 4)

Target	Slope (K)	Reference
A	480 ± 15	9
E, F	520 ± 20	this work
B	370 ± 20	5

of copper(II) complexes by **9** have a characteristic slope in plots of $\Delta H^{\ddagger}$ *versus* $\Delta S^{\ddagger}$. The straight line correlating $\Delta H^{\ddagger}_{9}$ and $\Delta S^{\ddagger}_{9}$ for **E** and **F** is displaced to the left of the line correlating $\Delta H^{\ddagger}_{9}$ and $\Delta S^{\ddagger}_{9}$ for reactions of **A**. At fixed $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ for **E** and **F** is smaller than $\Delta S^{\ddagger}$ for **A** by about 16 cal deg^{-1} mol^{-1}. Since the $\Delta H^{\ddagger}$ *versus* $\Delta S^{\ddagger}$ correlation includes all data for reactions of **E** and **F** with **9**, and because **F** have known structures with terminal halogens [17–19], we conclude that $L_2Cu_2X_2O$ complexes **E** must contain at least one terminal halogen. The target and transmetalator would be expected to associate through this more nucleophilic halogen in preference to any other bridging atom in **E** or **F**.

All other things being equal, interaction of nickel in **9** with a terminal halogen X in **E** or **F** would be expected to be stronger than if X were bridging and would thus lead to a larger decrease in entropy on forming two Ni ← X–Cu bonds in a transmetalation precursor **9**·(**E** or **F**)$_2$.

It is known that **F** (L = TEED) has an asymmetrical bridging carbonato group with stereochemically inequivalent copper atoms, Fig. 1e; we suggest that transmetalations preferentially take place at the five-coordinate copper(II) centers in these $\mathbf{F}_{II}$ targets. Reactant preassociation through terminal halogens and the presence of bidentate ligands, L, evidently make the activated complexes more compact than those for $(\mu_4\text{-O})N_4Cu_4X_6$ complexes **A**, which have monodentate ligands and bridging halogens; this is consistent with the more negative $\Delta S^{\ddagger}$ for **E** and **F** systems. The formation of more stable precursors would result from lower enthalpies of formation, but the enthalpies of activation for transmetalations of **E** and **F** are higher than for $(\mu_4\text{-O})N_4Cu_4X_6$ complexes **A** at fixed, common $\Delta S^{\ddagger}$, so the enthalpy differences seem to have a kinetic origin.

First-order Rate Laws

A first-order rate law was previously observed for reactions of excess **A** (X = Br, not Cl) [9] with **10** or **11**, but not **9**, eqn. (11), and we see it here again in the reactions of excess **E** or **F** (X = Cl or Br) with **10** or **11**, but not with **9**, Table II; this indicates that having M = Co or Zn in **C** is the major factor leading to a first-order rate law for copper(II) transmetalation. Structural differences between **9** and **10** (Fig. 1) or **11** are the obvious reason for their different behavior. Plots of $\Delta H^{\ddagger}_{11}$ *versus* $\Delta S^{\ddagger}_{11}$ also gave two parallel straight lines (slope ≃340 K), Fig. 5, for all first-order data in ref. 9 and Table II. We observe that for a given $\Delta H^{\ddagger}$ value, $\Delta S^{\ddagger}_{11}$ is more negative for **E** and **F** than for **A** by about 8 cal deg^{-1} mol^{-1}. This plot includes all data for **E** and **F** (with L = TEED or TMPD) and suggests (i) similar structural-mechanistic features and (ii) again that **E** contain terminal halogens like **F** [17–19]. It is known that **F** (L = TMPD) has a symmetrical bridging carbonato group with stereochemically equivalent copper atoms, each of which is five-

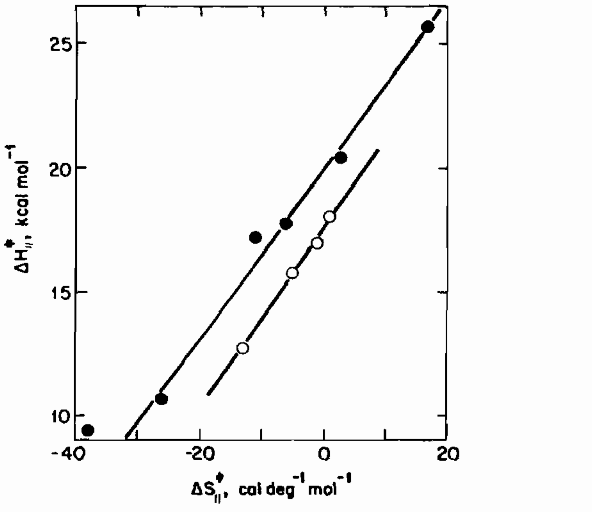


Fig. 5. Plots of $\Delta H^{\ddagger}_{11}$ (kcal mol^{-1}) *vs.* $\Delta S^{\ddagger}_{11}$ (cal deg^{-1} mol^{-1}) for the following first-order rate systems: **A** with **10** and **11** [9], ○; **E** and **F** with **10** and **11** (Table II), ●.

coordinate [17–19], (Fig. 1). This means that monotransmetalation can take place at either site. Since similar structural features were suggested for **E** and **F** (L = TEED or TMPD), we can again suggest that transmetalation preferentially takes place at five-coordinate copper atoms in both **E** and **F** (L = TEED). The reason for more negative values of $\Delta S^{\ddagger}_{11}$ with targets **E** and **F** is the higher stability of the precursors formed by reactant association through terminal halogens.

Second-order Rate Laws

A second-order rate law was previously observed only in the transmetalation of excess **A** by **D** (M = Ni or Zn), eqn. (10) [9]. In this study of transmetalation of excess **E** and **F** by $M(NS)_2$ we find that a second-order rate law is observed with either **C** or **D** as transmetalator, eqn. (10), but only with particular combinations of L and X in **E** or **F** and M in **C** or **D**.

Plots of $\Delta H^{\ddagger}_{10}$ *versus* $\Delta S^{\ddagger}_{10}$ for **A** and **E** or **F** systems gave two straight lines which are not parallel, Fig. 6. This is probably because the data for rate law (10) (reactants **A**) are for transmetalators **D** reacting with excess $(\mu_4\text{-O})N_4Cu_4X_6$ complexes **A**, while the other data are all for transmetalators **C** (except one labeled **D** in Fig. 6) reacting with complexes **E** or **F**. This demonstrates the kinetic effect of changing the NS ligand in $M(NS)_2$ reagents. The line correlating $\Delta H^{\ddagger}_{10}$ and $\Delta S^{\ddagger}_{10}$ has slope 340K, which is equal to the slope of the line which correlates the first-order parameters $\Delta H^{\ddagger}_{11}$ and $\Delta S^{\ddagger}_{11}$ (Fig. 5). This similarity of slope strongly suggests that first-order rate law (11) actually is the result of a saturated second-order system, eqn. (14), where $B[\text{copper(II)}] \gg 1$ and the observed first-order rate constant is equal to A/B. This very important conclusion enables us to recognize the requirements for first-order transmetalation of excess copper complexes.

$$\text{rate} = \frac{A\,[\text{copper(II)}]\,[\text{transmetalator}]}{1 + B\,[\text{copper(II)}]} \qquad (14)$$

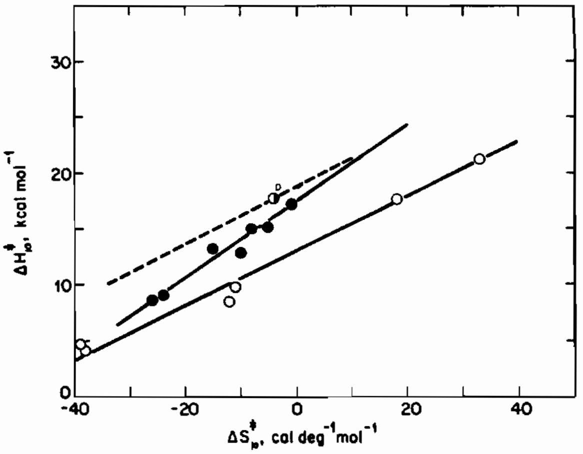
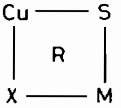


Fig. 6. Plots of $\Delta H^{\ddagger}_{10}$ (kcal mol^{-1}) *vs.* $\Delta S^{\ddagger}_{10}$ (cal deg^{-1} mol^{-1}) for the following second-order rate systems: **A** with **D** (M = Ni, Zn) [9], ○; **E** and **F** with **9**, **10** (Table II), ●; **E** with **12** (◑) (labeled **D**), (Table II).

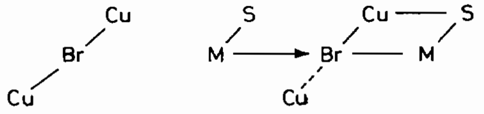
Requirements for First-order Transmetalation of Excess Copper Complexes

It appears from all the kinetic observations that have been made [5, 9, this work] that the monotransmetalation of excess copper complexes by $M(NS)_2$ reagents with a first-order rate law arises from the formation of complete, and therefore especially stable, four-membered rings R. It also appears that the requirements for each component involved in formation of these complete, four-membered rings are as follows.



1. Copper. The copper component must be copper(II), because first-order behavior is never observed for transmetalation of copper(I) centers in $L_2Cu_2X_2$ molecules **B** containing the same ligands L and X as in complexes **E** and **F**. Copper(I) evidently has a reluctance to increase its coordination number from 4 to 5 or to release extant ligands; also, its effective nuclear charge is lower than that of copper(II), which disfavors four-membered ring formation by coordination of S by copper(I).

2. Halide. The halide component must be nucleophilic and preferably terminal. Rate saturation does not occur in $L_2Cu_2X_2$ transmetalation systems even with transmetalators containing metals M = Co and Zn that favor strong ring formation with copper(II) centers [9, this work]. This implies that the bridging halogens in $L_2Cu_2X_2$ complexes cannot be broken for the purpose of constructing four-membered transmetalation rings. On the other hand, it could be that the bridging bonds to X in $(\mu_4\text{-O})N_4Cu_4X_6$ reactants **A** can be broken for this purpose, but only when X = Br, since rate saturation is not observed with X = Cl [9]. The broken bond shown at the right below is reasonable because



(15)

the essential structural 'anchor' in $(\mu_4\text{-O})N_4Cu_4X_6$ complexes **A** is the central μ_4-oxo group: under these circumstances, breaking of one of the six outer halogen bridges could be tolerated without loss of the tetranuclear integrity of the copper(II) reactant. This does not necessarily imply that halogen bridging is weakest in bromo complexes **A**, but it does suggest that transmetalators **10** and **11** have a higher affinity for Br than for Cl.

3. Sulfur. The sulfur component must be nucleophilic. As pointed out previously [9], the most likely sulfur atom for formation of a complete, four-membered ring R is the carbothioate sulfur atom of M(NS)$_2$ complexes, which is derived from the enol form of the ligand. If this is the case we would not expect an increase of transmetalation rate law order (indicating weaker precursor formation) on replacing the S-methyl groups of **C** (M = Co and Zn) with non-coordinating groups like amines under otherwise favorable circumstances.

4. M(NS)$_2$ Reagent Geometry. Ni(NS)$_2$ complexes **9** and **12** are essentially flat molecules with *cis*-(structure **9** [28]) and *trans*-carbothioate sulfur (structure **12** [29]) atoms, respectively. This geometry seems to have two effects. First, it reduces the nucleophilicity of sulfur, but second it allows **9** to form **9**·(Cu)$_2$ reaction precursors, although they are weak. The result is a third-order rate law for transmetalation of polynuclear copper(I) and copper(II) complexes. The nucleophilicity of S in **12** must be lower than in **9** because **12** never transmetalates with a third-order rate law (second-order behavior is always observed) [5, 9], despite the fact that it is planar [29].

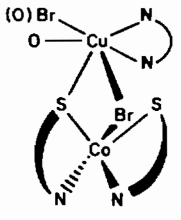
Transmetalators **C** and **D** (M = Co or Zn) are tetrahedral [13], but **D** neither transmetalates excess copper complexes with a third-order rate law nor exhibits first-order kinetic behavior. This is a further indication that the carbothioate sulfur in **D** is always less nucleophilic than in **C**.

It thus appears that the geometries of C (M = Co, Zn) and the nucleophilicities of their S-donor atoms are correlated, with the result that, under the right circumstances, they can form strong transmetalation rings R with excess copper(II) reactants. The result is first-order rate law (11). The similarity of slopes in Figs. 5 and 6 suggests that the slopes have a kinetic origin and that first-order behavior actually is the result of second-order systems that become saturated because of the existence of especially stable precursors with copper(II) reactants **E** and **F** that contain terminal halogen ligands.

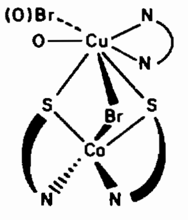
5. Other Ligands on Copper. Because no assumptions have to be made concerning the thermodynamics of precursor complex formation, it is relatively easy to decide whether metal exchange in rings R or discrete product formation is the rate-determining step [9]. In first-order monotransmetalation of (μ_4-O)N$_4$Cu$_4$Br$_6$ by **10** or **11** the measured entropies of activation are all near zero [9], which would not be consistent with slow formation of products. This conclusion is further supported by strong indications that first-order behavior is due to strong interactions in 1:1 precursors, eqn. (14); metal exchange in R involves no loss of extant ligands.

On the other hand, the wide range of first-order rate constants k_{11} and their activation parameters in Table II indicates that a variety of effects occurs on changing ligands L or X, or from oxo to carbonate in reactions of **E** and **F** with **10** or **11**. Three of the six data sets in Table II have $\Delta S^{\ddagger}$ between -11 and $+17$ cal deg^{-1} mol^{-1} for X = Cl, which we take to indicate rate-determining metal exchange [9]. The parallelism of the lines in Fig. 5 indicates that metal exchange in stable **E**·**C** and **F**·**C** precursors has an activation enthalpy that is, on average, 2.5 kcal mol^{-1} more positive than these for metal exchange in (μ_4-O)N$_4$Cu$_4$Br$_6$·**C** precursors [9]; it is also evident that, when L = TEED and X = Cl, a change from –O– to –(CO$_3$)– bridging causes increases in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. All of these effects are consistent with the much more extensive bridging structure of **F**, which would slow metal exchange.

The very negative $\Delta S^{\ddagger}$ for transmetalation of **2** and **7** by **10** deserve special comment. These systems both contain terminal bromide, but it does not seem to matter whether the copper targets are oxo or carbonato complexes. We suggest that the activated complexes for rate-determining metal exchange in these particular systems contain two, four-membered rings, as indicated below.



Precursor



activated complex

Breaking the dotted bond to bridging O (from carbonate) or Br on formation of the second four-membered ring would explain similar $\Delta S^{\ddagger}$ for transmetalation of **E** (oxo) or **F** (carbonato) complexes and would limit the coordination number at copper to six (seven-coordination seems very unlikely). It would also explain similar $\Delta H^{\ddagger}$, because only one Cu–O bridging bond would have to be broken for metal exchange. The fact that $\Delta H^{\ddagger}$ for metal exchange is roughly doubled by changing X = Br to X = Cl (Table II) suggests that only one four-membered ring is present in the activated complex when X = Cl and, therefore, that the dotted bond is unbroken prior to rate-determining metal exchange.

An alternative description of the activated complex with X = Br in **E** and **F** is one in which a second four-membered ring is formed with the other copper(II) center of each dimer. This also would lead to especially negative entropies of activation. The difference is that either copper center of the dimer could then be exchanged for M.

These suggestions are all consistent with the tendency of X = Br towards strong precursor formation, the tetrahedral geometry of **C** (M = Co or Zn) and the relatively high nucleophilicity of their carbothioate sulfur atoms [9, 13].

Interpretation of the Data for Third-order Transmetalation

Third-order rate law (9) is only observed for transmetalation of **E** and **F** by the *cis*-square planar transmetalator **9**. We feel that the relatively negative entropies of activation $\Delta S^{\ddagger}_9$ for **E** and **F** are due to the presence of terminal halide in the copper reactants, which leads to precursors with inherently low entropies.

As in previous work [5, 9], precursor formation needs to be accounted for in assigning the first-order rate determining step for transmetalation*. We assign $\Delta S_{16} = -60$ cal deg^{-1} mol^{-1} for precursor formation (16) leading to third-order rate law (9)

$$2(\mathbf{E} \text{ or } \mathbf{F}) + \mathbf{9} \rightleftharpoons \mathbf{9}\cdot(\mathbf{E} \text{ or } \mathbf{F})_2 \qquad (16)$$

(Table II). This estimate comes from the literature data [30] for formation of $\mathbf{C}\cdot py_2$ precursors (−44 cal deg^{-1} mol^{-1}, used previously in analysis of the data for transmetalation of $L_2Cu_2X_2$ [5] and $(\mu_4\text{-}O)N_4Cu_4X_6$ [9] complexes by **C**, in which there is no evidence for terminal halide), to which has been added the −16 cal deg^{-1} mol^{-1} required to move the left outer line of Fig. 4 to make it coincident with the right outer line. In other words, the entropies of formation of $\mathbf{E}_2\cdot\mathbf{C}$ and $\mathbf{F}_2\cdot\mathbf{C}$ precursors are $-44 + (-16) = -60$ cal deg^{-1} mol^{-1}, the adjustment reflecting the availability of terminal halide for precursor formation.

If this suggested adjustment is applied to $\Delta S^{\ddagger}_9$ of Table II, the resulting $\Delta S^{\ddagger}_{rds} = \Delta S^{\ddagger}_9 + 60$ are all markedly positive, which suggests formation of discrete products, rather than metal exchange, as the rate-determining step for transmetalation of **E** and **F** by **9**. Discrete transmetalation product formation also was suggested as the rate-determining step for transmetalation of $L_2Cu_2X_2$ [5] and $(\mu_4\text{-}O)N_4Cu_4Cl_6$ [9] by **9**.

Interpretation of the Data for Second-order Transmetalation

As noted previously, a variety of changes in the reactants leads to transmetalation governed by second-order rate law (10). Extensive previous work [5, 9] indicates that the rate law for irreversible transmetalation of both copper(I) and copper(II) centers by **D** is characteristically second-order. Figure 6 indicates that the slopes of $\Delta H^{\ddagger}$ *versus* $\Delta S^{\ddagger}$ plots of the data in refs. 5 and 9 and Table II for transmetalation of **A** by **D** and of **E** and **F** by **C** are different. Assumption of the same slope for transmetalation of **E** and **F** by **D** in rate law (10) as for transmetalation of **A** by **D** [9] leads to the dotted line in Fig. 6. This predicts that the enthalpies of activation for transmetalation of **E** and **F** by **D** are about 5 kcal mol^{-1} more positive than those for transmetalation of **A** in second-order rate law (10).

We suggest that the entropies of formation of **E·C**, **E·D**, **F·C** and **F·D** precursors are about 20 cal deg^{-1} mol^{-1} more negative than those for **A·D** precursors because of the availability of terminal halide in **E** and **F**. This leads to the addition of 25 + 20 = 45 cal deg^{-1} mol^{-1} to the measured entropies of activation in Table II to give $\Delta S^{\ddagger}_{rds} = \Delta S^{\ddagger}_{10} + 45$ [9] suggesting that the first-order rate-determining step in all of these systems is discrete product formation. This slowest process was indicated as the rate-determining step for transmetalation of **A** (X = Br) by **D** (M = Zn) [9]. On the other hand, metal exchange was suggested as the rate determining step for transmetalation of $(\mu_4\text{-}O)N_4Cu_4Cl_6$ by **12**; when M = Zn in **D** the entropies were on the borderline of discrimination [9].

Summary and Conclusions

The guiding principles in assigning the rate-determining steps for transmetalation of excess copper reactants by transmetalators **C** and **D** are the experimental or derived entropies of activation in rate laws of fixed order. This work shows that precursor bridging by terminal halide favors the formation of stable reaction precursors even with X = Cl and leads to first-order rate laws (11). Metal exchange is the slowest transmetalation step under these circumstances. Metal exchange requires breaking of one or two bridging bonds to copper(II). On the basis of the first-order data in Fig. 5, these bonds are stronger in **E** and **F** than in $(\mu_4\text{-}O)N_4Cu_4X_6$ complexes **A**; also, bonds to bridging halide or O (from oxo and carbonate) are of approximately the same strength in **E** and **F**.

The data for second-order rate law (10) in Table II indicate that changes in the ligands attached to copper(II) can have two effects. First, they can

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*See ref. 9 for a detailed derivation of the relationship between measured $\Delta S^{\ddagger}$ and $\Delta S^{\ddagger}_{rds}$ for rate laws (9) and (10).

interfere with **9**·(E or F)$_2$ precursor construction so that the observed rate law is not third-order eqn. (9). Second, they can impede the construction of stable transmetalation rings R even when the transmetalator is tetrahedral complex **10** and the copper(II) reactant contains terminal halide. The difficulty in understanding second-order transmetalation systems is that we have no independent information on the total conformation of transmetalation rings R. Nevertheless, the data in Fig. 6 indicate that the mechanisms of all known second-order copper(II) transmetalation systems are related.

Acknowledgements

This work was supported financially by Grant RR07143 from the Department of Health and Human Services and Grant INT-8512210 from the National Science Foundation. M.A.E.-S. and A.E.-T. thank Alexandria University for study leave.

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