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Rate Law Variations in the Specific Monotransmetalation of $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_{4-x}\text{M}_x\text{X}_6$ Complexes with Zn(NS)_2 in Nitrobenzene

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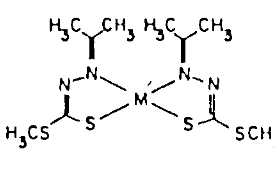
The copper(II) centers of the heteropolymetallic target family $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_{4-x}\text{M}_x\text{X}_6$ are specifically replaced with M′ from $\text{M}'(\text{NS})_n$ transmetalators by monotransmetalation in nitrobenzene. Here, N is *N*,*N*-diethylnicotinamide, py is pyridine, $x = 1\text{–}3$, M is Co or $\text{Ni(H}_2\text{O)}$, X is Cl or Br, M′ is Co, Ni, or Zn, NS is monoanionic *S*-methyl isopropropylidenehydrazinecarbodithioate, and n = 2 ($n = 3$ only for M′ = Co). The rate laws for reaction of $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_4\text{Cl}_6$ (A) with Co(NS)_2 (B_1), Ni(NS)_2 (B_2), and Zn(NS)_2 (B_3) are first-order in [B] and second-order in [A] (i.e., third-order overall). Although the monotransmetalation of $(\mu_4\text{-O})\text{N}_4\text{Cu(Ni(H}_2\text{O)}_3\text{Cl}_6$ (NCuNi_3Cl) with B_2 also is third-order, its reactions with B_1 and B_3 are governed by rate = $k_4\beta_1[\text{NCuNi}_3\text{Cl}][\text{B}_1 \text{ or } \text{B}_3]/(1 + \beta_1[\text{NCuNi}_3\text{Cl}])$, which demonstrates the involvement of "sticky" 1:1 reaction precursors with determinable stability constants β_1. The rate laws for specific monotransmetalation of other members of the family $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_{4-x}\text{M}_x\text{X}_6$ (D) by B_3 have been investigated as a function of ligand N or py, M = Co or $\text{Ni(H}_2\text{O)}$, X = Cl or Br, and *x*. Interactions between heteropolymetallic targets D and B_3 are "stickier" than are those with homometallic targets A. Pronounced stickiness is ascribed to the presence of Ni–X–Cu edges and CuNi_2 faces in $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_{4-x}(\text{Ni(H}_2\text{O))}_x\text{X}_6$ targets.

Introduction

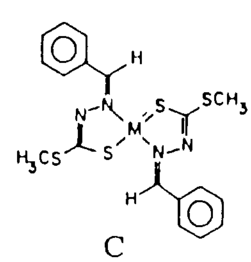
We are investigating the products, rates, and mechanisms of transmetalation reactions[1] in aprotic solvents.[2-10] The targets (T) are neutral, polymetallic molecules and the transmetalators (TM′) are neutral, monomeric $\text{M}'(\text{NS})_n$ complexes. An example is eq 1, where the amine ligand is pyridine (py) or monodentate

$$\underset{\text{A}}{(\mu_4\text{-O})(\text{py,N})_4\text{Cu}_4\text{X}_6} + \underset{\text{B or C}}{x\text{M}'(\text{NS})_2} \rightarrow \underset{\text{D}}{(\mu_4\text{-O})(\text{py,N})_4\text{Cu}_{4-x}\text{M}'_x\text{X}_6} + \underset{\text{B or C}}{x\text{Cu(NS)}_2} \quad (1)$$

N,*N*-diethylnicotinamide (N), X is Cl or Br, $x = 1\text{–}4$, M′ is Co,[4] Ni,[3] or Zn,[4] and NS is a monoanionic *S*-methyl hydrazinecarbodithoate ligand in complexes B and C. The driving force of rapid[5,6] reactions 1 is the formation of especially stable coproducts Cu(NS)_2.[2]



B



C

Our previous work discusses the rates of monotransmetalation of structurally characterized homopolymetallic copper(I) and copper(II) targets A,[2a,5,6] $\text{L}_2\text{Cu}_2\text{X}_2$,[7] and $\text{L}_2\text{Cu}_2\text{X}_2\text{Y}$,[8] where L is an *N*,*N*,*N*′*N*′-tetraalkyldiamine and Y is O or CO_3, with reagents B and C. We found three different rate laws (eqs 2–4), the

$$\text{rate} = k_2[\text{TM}'][\text{T}]^2 \quad (2)$$

$$\text{rate} = k_3[\text{TM}'][\text{T}] \quad (3)$$

$$\text{rate} = k_4[\text{TM}'] \quad (4)$$

$$\text{TM}' + n\text{A} \rightleftarrows \text{TM}'\cdot\text{T}_n \quad \beta_n \quad (5)$$

appropriateness of which depends on X, L, N, py, and Y in the target and on M′ and NS in the transmetalator. Second-order rate law 3 appears to be characteristic of transmetalators C,[6,8] while first-order rate law 4 has never been observed with copper(I) targets.[7] These observations and the forms of eqs 2 and 4 indicate that *precursors* of different stoichiometry and stability (eq 5) are involved in these reactions.[5-9]

Although rate law 4 appears to result from the involvement of 1:1 precursors with especially large β_1 in eq 5,[6,8,9] eqs 2–4 cannot be used to determine the actual values of equilibrium constants β_n. However, knowledge of how precursor stability varies with the reactants is necessary for a full understanding of transmetalation reactions, particularly with regard to their known specificity.[2,9,10b]

Reaction 1 can be used to generate heteropolymetallic products D containing up to four different metals.[3,4] Although products D ($x = 1\text{–}3$) cannot be crystallized without disproportionating to A, their analytical and spectral properties indicate that they have the same basic core structure as in A.[3,4] The latter contain four equivalent metal centers attached to a central oxo group, with each metal pair bridged by two-coordinate halide (Figure 1).[2a]

Recently,[9] we employed eq 1 to generate $(\mu_4\text{-O})\text{N}_4\text{Cu(Ni(H}_2\text{O))}_3\text{Cl}_6$[3,11] ($\text{NCuNi}_3\text{Cl}$),[12] which was then used as a target for monotransmetalation with B (M = Co (B_1), Ni (B_2), Zn (B_3))

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(1) Definitions are as follows. *Transmetalation* is the stoichiometric replacement of metals in a polymetallic target with different metals from reagents called transmetalators. *Direct* transmetalation reactions leave the target molecularity unchanged. *Monotransmetalation* refers to the replacement of just one of several metal centers in a target. The replacement of a particular element in a heteropolymetallic target is said to be *specific*.[2]

(2) (a) Al-Toukhy, A.; Cai, G.-Z.; Davies, G.; Gilbert, T. R.; Onan, K. D.; Veidis, M. *J. Am. Chem. Soc.* **1984**, *106*, 4596. (b) Cai, G.-Z.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Gilbert, T. R.; Henary, M.; Onan, K. D.; Veidis, M. transmetalation of Copper(II) Complexes. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J. A., Eds.; Adenine Press: Guilderland, NY, 1986; Vol. 2, p 237. (c) Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Comments Inorg. Chem.* **1989**, *8*, 203.

(3) Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.* **1986**, *25*, 2269.

(4) Direct transmetalation of A by B_1 and B_3 is limited to $x \leq 2$ in eq 1. However, the complete $(\mu_4\text{-O})\text{N}_4\text{Cu}_{4-x}\text{Co}_x\text{Cl}_6$ family can be obtained with Co(NS)_3 (E) as transmetalator: Abu-Raqabah, A.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M. *Inorg. Chem.* **1989**, *28*, 1156.

(5) Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.* **1986**, *25*, 1925.

(6) Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.* **1986**, *25*, 3899.

(7) Davies, G.; El-Kady, N.; El-Sayed, M. A.; El-Toukhy, A.; Schure, M. R. *Inorg. Chim. Acta* **1988**, *149*, 31.

(8) Davies, G.; El-Kady, N.; El-Sayed, M. A.; El-Toukhy, A.; Schure, M. R. *Inorg. Chim. Acta* **1988**, *149*, 45.

(9) Al-Shehri, A.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chem.*, preceding paper in this issue.

(10) (a) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Gilbert, T. R. *Inorg. Chem.* 1986, *25*, 2373. (b) Davies, G.; El-Sayed, M. A.; El-Toukhy, A.; Henary, M.; Kasem, T. S.; Martin, C. A. *Inorg. Chem.* **1986**, *25*, 3904.

(11) Each nickel center of primary products $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_{4-x}\text{Ni}_x\text{X}_6$ coordinates one water molecule during isolation by gel permeation chromatography. This makes each nickel center six-coordinate (see text).[3,4]

(12) Examples of target abbreviations in this paper: $\text{pyCu}_2\text{Ni}_2\text{Cl}$ denotes the target $(\mu_4\text{-O})(\text{py})_4\text{Cu}_2(\text{Ni(H}_2\text{O))}_2\text{Cl}_6$; NNi_4Cl denotes the target $(\mu_4\text{-O})\text{N}_4(\text{Ni(H}_2\text{O))}_4\text{Cl}_6$.

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Table I. Analytical and Cryoscopic Molecular Weight Data for Transmetalation Targets and Products[a]

complex	anal., % C	H	N	Cl	Cu	Ni	Zn	Co	M_r[b]
				A. Targets					
$N_4Cu_3Ni(H_2O)Cl_6O$	40.0	4.9	8.9		16.3	4.6			1240 ± 20
	(39.7)	(4.8)	(9.3)		(15.8)	(5.0)			(1208)
$N_4Cu_2(Ni(H_2O))_2Cl_6O$	36.6	4.6	8.7		11.0	10.2			1250 ± 20
	(39.4)	(4.9)	(9.2)		(10.4)	(9.6)			(1223)
$(py)_4Cu_2(Ni(H_2O))_2Cl_6O$	29.6	2.6	6.8	25.4	15.3	14.3			815 ± 20
	(29.7)	(2.9)	(6.9)	(26.0)	(15.7)	(14.6)			(823)
$N_4CuCo_3Cl_6O$	38.2	4.2	8.9	17.1	4.8			13.9	1180 ± 20
	(40.6)	(4.7)	(9.5)	(17.9)	(5.3)			(14.9)	(1181)
$N_4Cu(Ni(H_2O))_3Br_6O$	32.0	4.1	7.6		4.2	11.9			1500 ± 20
	(31.9)	(4.1)	(7.5)		(4.2)	(11.7)			(1502)
$N_4(Ni(H_2O))_4Cl_6O$	37.8	5.1	8.7			18.5			1270 ± 20
	(38.5)	(5.2)	(9.0)			(18.8)			(1249)
				B. Products[c]					
$N_4Cu_2NiZnCl_6O{\cdot}H_2O$	39.1	4.3	9.1	17.0	10.1	4.6	4.9		1220 ± 20
	(39.8)	(4.8)	(9.3)	(17.4)	(10.5)	(4.9)	(5.4)		(1207)
$N_4CuNi_2ZnCl_6O{\cdot}2H_2O$	38.8	4.7	8.9	17.0	5.0	8.9	4.9		1240 ± 20
	(39.3)	(4.9)	(9.2)	(17.2)	(5.2)	(9.6)	(5.4)		(1220)
$py_4CuNi_2ZnCl_6O{\cdot}2H_2O$	29.5	2.6	6.7	25.4	15.1	7.2	7.6		825 ± 20
	(29.6)	(2.7)	(6.9)	(25.9)	(15.6)	(7.3)	(8.1)		(811)
$N_4Ni_3ZnCl_6O{\cdot}3H_2O$	37.6	4.8	8.8	16.5		13.9	4.8		1250 ± 20
	(38.9)	(5.0)	(9.1)	(17.0)		(14.3)	(5.3)		(1240)
$N_4Ni_3ZnBr_6O{\cdot}3H_2O$	30.9	3.8	7.2			11.2	3.9		1515 ± 20
	(31.9)	(4.1)	(7.4)			(11.8)	(4.3)		(1504)
$N_4Co_3ZnCl_6O$	40.1	4.3	9.4	17.0			5.0	14.2	1170 ± 20
	(40.7)	(4.7)	(9.5)	(17.8)			(5.5)	(15.0)	(1180)

[a] Calculated values in parentheses. [b] Measured cryoscopically in nitrobenzene at the (3–5) × 10^{-2} m level. [c] All products F from eq 7 were separated by gel permeation chromatography.[2-4]

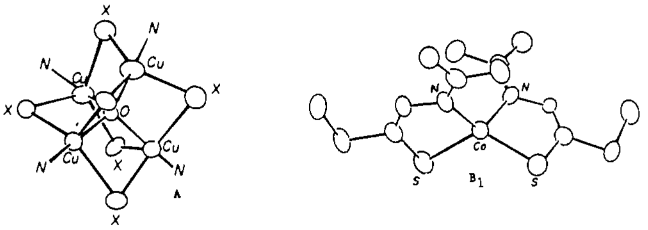

Figure 1. Core molecular structures of A[2a] and bis(*S*-methyl isopropylidenehydrazinecarbodithioato)cobalt(II)[13] (B_1). Bis(*S*-methyl isopropylidenehydrazinecarbodithioato)zinc(II) (B_3) is isomorphous with B_1.[13]

and $Co(NS)_3$ (E;[10] NS = *S*-methyl isopropylidenehydrazinecarbodithioate, as in B). The molecular structure of B_3[13] is shown in Figure 1.

Heteropolymetallic targets D contain different vertices, edges, and faces, which could be preferentially coordinated by $M'(NS)_n$ reagents in the course of transmetalation reactions. Specific replacement of either metal in D would then proceed on particular target edges or faces. For example, we know from the stability order $Cu(NS)_2 \gg B_2 \gg B_1 \gg E \gg B_3$[10b] that either Cu or Ni in $NCuNi_3Cl$ could be replaced by M′ from B_1, E, or B_3. However, we found exclusive replacement of copper by M′,[9] which points to specific interactions between $NCuNi_3Cl$, B, and E that involve the single copper site of this target. Moreover, we found that the transmetalations of $NCuNi_3Cl$ by B_1 and B_3 are governed by rate law 6, which provides access to β_1 in eq 5 and the first

$$\text{rate} = k_4\beta_1[B][D]/(1 + \beta_1[D]) \qquad (6)$$

opportunity to separate[14] thermodynamic factors (precursor formation: β_1) from kinetic factors (metal exchange or the formation of discrete products: k_4) in transmetalation reactions. Another valuable clue to the origin of metal exchange specificity was that the $NCuNi_3Cl/B_3$ reaction proceeds through different 1:1 precursors at high and low temperatures and that these precursors are converted to products in reactions with different activation parameters. We suggested that the $NCuNi_3Cl{\cdot}B_1$ and "high"-temperature $NCuNi_3Cl{\cdot}B_3$ precursors are formed by NS chelate ring opening in these relatively unstable[10b] transmetalators. Our final observation was that the first-order rate constants k_4 for formation of metal-exchanged products in $NCuNi_3Cl/B_3$ reactions decrease with increasing precursor stability constant β_1.[9]

Table II. Electronic Spectral Data for Transmetalation Targets and Products

complex	λ_{max},[a] nm (ϵ_λ, M^{-1} cm^{-1})
	A. Targets
$N_4Cu_4Cl_6O$	850 (1630), 775 (1400)
$N_4Cu_3Ni(H_2O)Cl_6O$	850 (1160), 775 (1030)
$N_4Cu_2(Ni(H_2O))_2Cl_6O$	850 (840), 775 (760)
$N_4Cu(Ni(H_2O))_3Br_6O$	850 (355), 775 (330)
$N_4(Ni(H_2O))_4Cl_6O$	*b*
$(py)_4Cu_2(NiH_2O))_2Cl_6O$	860 (650), 775 (850)
$N_4CuCo_3Cl_6O$	875 (450), 675 (1000), 650 (1200), 600 (1390), 575 (1380)
	B. Products
$N_4Cu_2NiZnCl_6O{\cdot}H_2O$	850 (820), 775 (720)
$N_4CuNi_2ZnCl_6O{\cdot}2H_2O$	850 (400), 775 (310)
$N_4Ni_3ZnCl_6O{\cdot}3H_2O$	*b*
$N_4Ni_3ZnBr_6O{\cdot}3H_2O$	850 (80), 775 (83)
$(py)_4CuNi_2ZnCl_6O{\cdot}2H_2O$	850 (230), 775 (240)
$N_4Co_3ZnCl_6O$	630 (1050), 610 (1340), 575 (1150)

[a] In nitrobenzene. [b] Negligible molar absorptivities in the region 775–860 nm.

This paper reports that the rate laws for specific monotransmetalations of the family (μ_4-O)$N_4Cu_{4-x}M_xX_6$ (D: x = 1–4; M = Co, $Ni(H_2O)$)[11,12] with zinc reagent B_3 are a very sensitive function of M, X, and x. The results suggest specific interactions between particular structural components of D with B_3 in the respective reaction precursors. Interactions involving particular edges and faces of D appear to direct specific metal exchange.

Experimental Section

Materials and Methods. Procedures for reactant synthesis, stoichiometric transmetalation of A and D with B, and isolation and characterization of the respective products have been described.[2-10] Analytical, cryoscopic, and electronic spectral data for the targets and products of

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(13) Onan, K. D.; Davies, G.; El-Sayed, M. A.; El-Toukhy, A. *Inorg. Chim. Acta* **1986**, *113*, 109.

(14) Indirect attempts previously have been made to allow for precursor formation in the interpretation of rate laws 2 and 3.[6-8]

Table IV. Kinetic Data for Second-Order Reactions of B_3 in Nitrobenzene

target	$10^{-3}k_3$[a]	ΔH_3^{*}[b]	ΔS_3^{*}[c]
$N_4Cu_3(Ni(H_2O))Cl_6O$	8.7	13.1 ± 0.3	4 ± 3
$N_4(Ni(H_2O))_4Cl_6O$	16.6	9.9 ± 0.4	6 ± 3
$N_4Co_3CuCl_6O$	6.0	12.8 ± 0.4	2 ± 4

[a] Units for k_3 are M^{-1} s^{-1} at 23 °C (typical error is ±4%). [b] Units are kcal mol^{-1}. [c] Units are cal deg^{-1} mol^{-1} at 25 °C.

this study are collected in Tables I and II.

Kinetic Measurements. All kinetic measurements were conducted in anhydrous nitrobenzene under dinitrogen with a sufficient stoichiometric excess of targets D to ensure monotransmetalation under pseudo-first-order conditions, as described previously.[5-9] Initial concentrations of D were varied in the range $10^4[D]_0 = 2.5$–25.0 M with $[B_3]_0$ fixed at 2.5×10^{-5} M. Temperature was varied from 8.0 to 40.5 °C. Monitoring wavelengths in the thermostated (±0.05 °C) Hi-Tech SFL40 stopped-flow spectrophotometer were in the range 575–650 nm, where large absorbance increases were observed in the subject monotransmetalations. All reactions were monitored for at least 10 half-lives. On-line computer-generated[7] plots of ln $(A_\infty - A_t)$, where A_t is the absorbance at time t, vs time gave the pseudo-first-order rate constant, k_{obsd}, for each set of fixed experimental conditions. Each run was repeated at least five times, and each k_{obsd} was reproducible to ±4% or better. There was no significant kinetic effects of using different samples of B_3 or D. Raw kinetic data for each system are collected in Table III.[15]

Results and Discussion

Products D (x = 1–3) from eq 1 cannot be recrystallized without disproportionating to A.[3-6] Our first task was therefore to show that isolated samples of each target D are not contaminated with coproduct $Cu(NS)_2$ or products with different x after gel permeation chromatographic isolation.[3,4]

We carefully checked the kinetic reproducibility of different samples of each D on transmetalation with different crystalline samples of B_3. The results showed that reactions 1 and subsequent gel permeation chromatographic separation[2-4] provide pure samples of D.

Monotransmetalation of Targets D with Transmetalators B and E. Properties of the Products. Spectrophotometric titrations at 600 nm, where coproduct $Cu(NS)_2$ is the principal absorber,[2-4] indicated that all targets D of this study react stoichiometrically with 1 mol of B_3. The analytical data in Table I show that the monotransmetalations of D (x = 1–3) with B_3 result in exclusive replacement of copper(II) with Zn. This result is independent of the occupancy, x, and of M in D. The observed reactions are summarized in eq 7.

$$D + Zn(NS)_2 \rightarrow \underset{F}{(\mu_4\text{-}O)(py,N)_4Cu_{3-x}M_xZnX_6} + Cu(NS)_2 \tag{7}$$

Products F of reactions 7 are unassociated tetramers in nitrobenzene (Table I). A single, sharp feature at 1630 cm^{-1} in their infrared spectra is diagnostic of products containing monodentate N.[16]

The electronic spectral data in Table II indicate that the molar absorptivities at 850 nm of D and F increase with their copper content while those at 610 nm increase with their cobalt content. Spectral data for a wide range of tetranuclear products of transmetalation of $(\mu_4\text{-}O)(N,py)_4Cu_4X_6$ complexes with different $M'(NS)_n$ reagents fit linear plots of molar absorptivity at 610 or 850 nm versus x in the formula $(\mu_4\text{-}O)N_4Cu_{4-x-y}Co_x(Ni,Zn)_yCl_6$.[3,4] Data for the new products in Table II fit the previously given plots.[17] This further supports a common core structure in the whole family of $(\mu_4\text{-}O)(N,py)_4(Cu,Co,Ni,Zn)_4X_6$ complexes.[3,4,9]

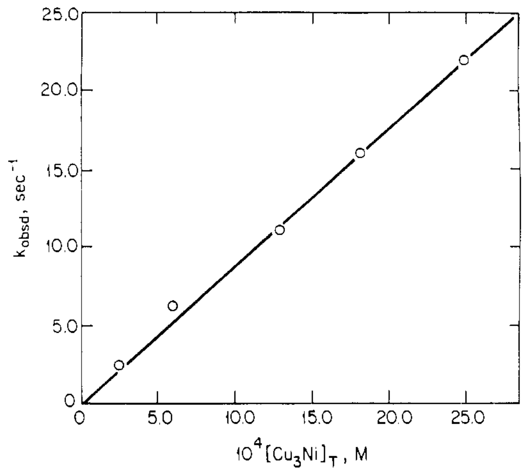
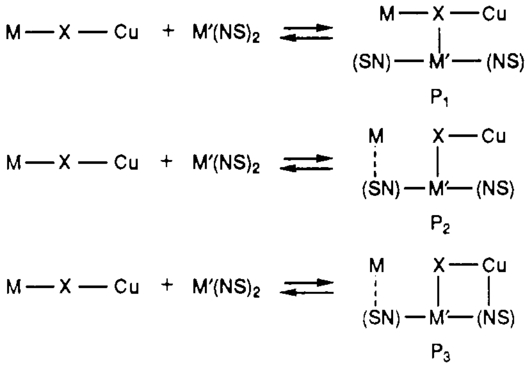


Figure 2. Plot of k_{obsd} (s^{-1}) vs $[NCu_3NiCl]$ (M) for the reaction of excess $(\mu_4\text{-}O)N_4Cu_3(Ni(H_2O))Cl_6$ with $Zn(NS)_2$ in nitrobenzene. The straight line through the origin indicates irreversible, second-order transmetalation in this system.

Kinetic Results. General Observations. Our previous work shows that the monotransmetalations of homopolynuclear halocopper(I)[7] and copper(II)[5,6,8] targets with *S*-methyl hydrazinecarbodithioate transmetalators B and C are, with very few exceptions,[7,18] governed by one or other of eqs 2–4. The basic principle behind our explanation of the observed rate law variations is that there are different kinds of interaction in precursors of forms P_1–P_3. The primary interactions employ the X atoms of T and the thiocarboate S atoms of TM′ (see Figure 1).[6,8] It is reasonable to suppose that increasing extents of reactant association in forms P_1–P_3 are responsible for a progressive change from rate law 2 (n = 2 and small β_2 in eq 5) through rate law 3 (n = 1 and small β_1) to rate law 4 (n = 1[8] and large β_1). However, this explanation is qualitative because individual values of β_n cannot be obtained from rate laws 2–4.



We have isolated members of the families $(\mu_4\text{-}O)(N,py)_4Cu_{4-x}M_xX_6$ from eqs 1 and studied the effects of M and x on their kinetic properties as transmetalation targets. Our results are discussed in the following sections.

Monotransmetalation Rate Laws. We previously reported that the monotransmetalations of A[5,6] and $NCuNi_3Cl$[9] with nickel transmetalator B_2 are governed by third-order rate law 2. This indicates that the precursors formed between these reactants are weak.[5-8] Although the rate laws for reactions of A with B_1 and B_3 are also third-order,[6] the corresponding reactions with target $NCuNi_3Cl$ are governed by rate law 6.[9] This indicates that $NCuNi_3Cl$ is a "stickier" target than A and that B_1 and B_3 are stickier transmetalators than B_2.[19] This information guided the

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[15] Table III is given as supplementary material.

[16] Davies, G.; El-Toukhy, A.; Onan, K. D.; Veidis, M. *Inorg. Chim. Acta* **1985**, *98*, 85.

[17] See, for example Figure 3 of ref 4.

[18] The exceptions are three copper(I) target complex formation systems with rate = $k_f[TM'][T] + k_r$. The equilibrium constants for such systems are given by $K_1 = k_f/k_r$.[7]

[19] Stickiness is a useful qualitative scale of precursor interaction strengths that may be gauged in any particular transmetalation system from the rate law. Marked stickiness (large β_1) is indicated by rate laws 4 and 6. Reversion of rate law 6 to rate law 4 requires $\beta_1[T] > 10$ at the lowest experimental [T], which in our systems is 2.5×10^{-4} M. This gives $\beta_1 > 4 \times 10^4$ M^{-1} at a comparison temperature of 23 °C, which is at least ten times greater than the largest known[9] value of β_1. Rate law 4 thus indicates stickier interactions than rate law 6.

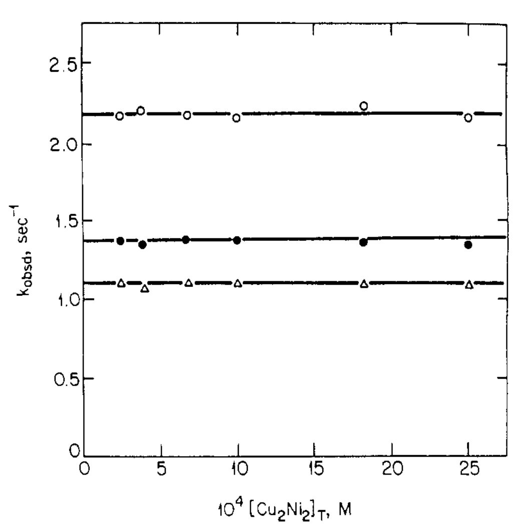

Figure 3. Plots of k_{obsd} (s^{-1}) vs $[NCu_2Ni_2Cl]$ (M) for the following transmetalation systems: $(\mu_4\text{-O})N_4Cu_2(Ni(H_2O))_2Cl_6$ with B_3 in nitrobenzene at 12 °C (△); $(\mu_4\text{-O})(py)_4Cu_2(Ni(H_2O))_2Cl_6$ with B_3 in nitrobenzene at 12 °C (●); $(\mu_4\text{-O})N_4Cu_2(Ni(H_2O))_2Cl_6$ with B_3 in nitrobenzene at 18 °C (○). These systems are governed by first-order rate law 4.

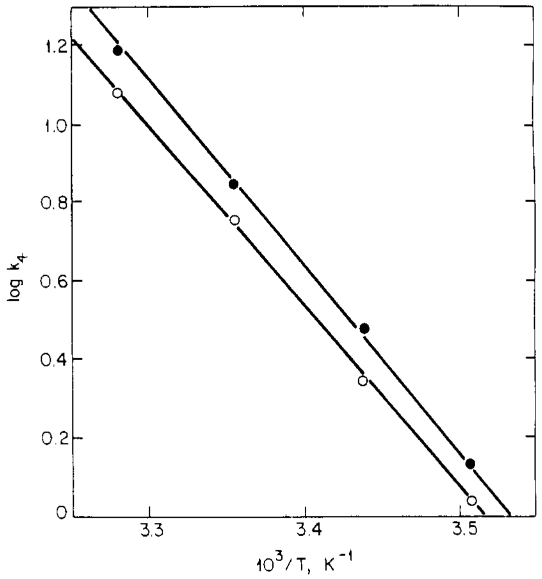

Figure 4. Plots of log k_4 (s^{-1}) vs $1/T$ (K^{-1}) for the following systems: $(\mu_4\text{-O})N_4Cu_2(Ni(H_2O))_2Cl_6$ with B_3 in nitrobenzene (○); $(\mu_4\text{-O})(py)_4Cu_2(Ni(H_2O))_2Cl_6$ with B_3 in nitrobenzene (●).

Table V. Kinetic Data for First-Order Reactions of B_3 in Nitrobenzene

target	k_4[a]	ΔH_4^{*}[b]	ΔS_4^{*}[c]
$N_4Cu_2(Ni(H_2O))_2Cl_6O$	4.0	21.1 ± 0.4	16 ± 3
$(py)_4Cu_2(Ni(H_2O))_2Cl_6O$	5.0	21.8 ± 0.4	18 ± 3
$N_4Cu(Ni(H_2O))_3Br_6O$	7.3	14.7 ± 0.4	-5 ± 3

[a] Units are s^{-1} at 23 °C (typical error is ±4%). [b] Units are kcal mol^{-1}. [c] Units are cal deg^{-1} mol^{-1} at 25 °C.

choice of systems described below.

Replacement of one copper(II) center in A with one $Ni(H_2O)$ center to give target NCu_3NiCl[12] results in a change of rate law from third-order eq 2[5] to second-order eq 3 in reactions with zinc transmetalator B_3. The data are illustrated in Figure 2 and collected in Tables III[15] and IV.

Replacement of two copper(II) centers in A with $Ni(H_2O)$ gives target NCu_2Ni_2Cl,[12] which reacts with B_3 in a one-step monotransmetalation reaction with first-order rate law 4. Target $pyCu_2Ni_2Cl$ also reacts with B_3 with first-order rate law 4. The data are illustrated in Figures 3 and 4 and collected in Tables III[15] and V. Figure 4 shows that replacement of N with py has very little effect on the kinetics of monotransmetalation of NCu_2Ni_2Cl.

Table VI. Rate Laws for Monotransmetalation of Targets $(\mu_4\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ with B_3 in Nitrobenzene

x	rate law	ref	x	rate law	ref
0	third-order (eq 2)	6	3	weak first-order (eq 6)	9
1	second-order (eq 3)	*a*	4	second-order (eq 3)	*a*
2	first-order (eq 4)	*a*			

[a] This work.

Table VII. Edges and Faces in $(\mu_4\text{-O})N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ Targets

x	edge type	no.	face type	no.
0	Cu–Cl–Cu	6	Cu_3	4
1	Cu–Cl–Cu	3	Cu_3	1
	Cu–Cl–Ni	3	Cu_2Ni	3
2	Cu–Cl–Cu	1	Cu_2Ni	2
	Cu–Cl–Ni	4	$CuNi_2$	2
	Ni–Cl–Ni	1		
3	Cu–Cl–Ni	3	$CuNi_2$	3
	Ni–Cl–Ni	3	Ni_3	1
4	Ni–Cl–Ni	6	Ni_3	4

Target $NCuNi_3Cl$[12] reacts with B_1 and B_3 with rate law 6, and its reaction with cobalt(III) transmetalator E is governed by first-order rate law 4.[9] However, we found that target $NCuNi_3Br$ reacts with B_3 with first-order rate law 4 (Tables III[15] and V) and that target $NCuCo_3Cl$[12] is transmetalated by B_3 with second-order rate law 3 (Tables III[15] and IV).

Replacement of the last copper(II) center in A with $Ni(H_2O)$ gives target NNi_4Cl,[12] which is transmetalated by reagent B_3 with second-order rate law 3. The kinetic data for this system are collected in Tables III[15] and IV.

Target and Transmetalator Stickiness. Rate laws 2,[6] 3, 4, 6,[9] and 3 for the transmetalations of $NCu_{4-x}Ni_xCl$ targets by zinc reagent B_3 at $x = 0$–4, respectively, indicate that the presence of copper(II) enhances the stickiness[19] of $(\mu_4\text{-O})(N,py)_4Cu_{4-x}M_xX_6$ targets when $x = 1$–3. We can reach the following additional conclusions from these results.

First, the stickiest members of the target family $(\mu_4\text{-O})(N,py)_4Cu_{4-x}M_xX_6$ with X = Cl are the complexes $(\mu_4\text{-O})(N,py)_4Cu_2(Ni(H_2O))_2Cl_6$. Second, target stickiness increases on substitution of X = Cl with Br, as observed previously with target A.[6] Third, transmetalator stickiness increases in the order $B_2 < B_1 \simeq B_3 < E$.[20]

We feel that complexes D are stickier targets than A because they are able to form precursors like P_2 and P_3 in their reactions with B_1,[9] B_3, and E.[9,19] The principal feature of proposed forms P_2 and P_3 is the involvement of terminal X from the target. This feature seems to associate $M'(NS)_n$ complexes much more closely with Cu than with M in the target, which would help to direct specific copper exchange. The implication is that Ni–X and Co–X bonds are weaker than Cu–X bonds in targets D and that this difference of bond strengths leads to a reduction of transmetalation rate law order on substitution of M for Cu in A. The observed rate laws with NCuCl (third-order),[6] $NCuCo_3Cl$ (second-order), and $NCuNi_3Cl$ (eq 6)[9] as targets and B_3 as transmetalator indicate that M–Cl bonds are stronger in the order $Ni(H_2O) <$ Co–Cl $<$ Cu–Cl in these targets. Each nickel center in $(\mu_4\text{-O})(N,py)_4Cu_{4-x}(Ni(H_2O))_xX_6$ is six-coordinate,[3,11] which should result in relatively weak bonds to Cl.[3]

The known transmetalator stability order is $B_2 \gg B_3 \gg E \gg B_1$,[10b] which is almost the reverse of the apparent stickiness order $E > B_1 \simeq B_3 > B_2$. This implies that a tendency toward NS chelate ring opening in $M'(NS)_n$ has something to do with transmetalator stickiness. However, a recent[9] correlation of thermodynamic data for precursor formation indicates that the majority of identifiable[21] 1:1 precursors and complexes TM′·T

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(20) Similar stickiness of B_1 and B_3 is indicated by similar β_1 values in rate law 6 for their reaction with $NCuNi_3Cl$.[9]

(21) In this context, *identifiable* means associated with measured equilibrium parameters.[9]

contain intact M′(NS) rings (see below).

Origins of Specific Target–Transmetalator Interactions. We now offer an explanation for our conclusion that $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_2(\text{Ni}(\text{H}_2\text{O}))_2\text{Cl}_6$ are the stickiest members of the $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_{4-x}(\text{Ni}(\text{H}_2\text{O}))_x\text{Cl}_6$ target family.

Table VI summarizes the rate laws for transmetalation of this family with sticky transmetalator B_3. Table VII gives the number of each kind of edge and face in $(\mu_4\text{-O})\text{N}_4\text{Cu}_{4-x}(\text{Ni}(\text{H}_2\text{O}))_x\text{Cl}_6$ complexes. The structural features that predominate through maxima with increasing x are (a) Cu–Cl–Ni edges at $x = 2$, (b) Cu_2Ni faces at $x = 1$, and (c) CuNi_2 faces at $x = 3$.

Table VII indicates that the greatest number (6) of Cu–Cl–Ni edges and CuNi_2 faces is found in $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_{4-x}(\text{Ni}(\text{H}_2\text{O}))_x\text{Cl}_6$ targets at $x = 2$ and $x = 3$.[22] Saturated kinetic behavior (rate law 4 or 6) is observed at these same values of x. The indication is that Cu–Cl–Ni edges and CuNi_2 faces both contribute to precursor stability, with the edges playing the dominant role. However, we cannot strongly favor one factor over the other, since small temperature variations can cause transmetalation rate law changes from eq 6 to eq 4 (see, for example, Figures 3 and 4 of ref 9).

Conclusions. The rate laws for monotransmetalation of $(\mu_4\text{-O})(\text{N,py})_4\text{Cu}_{4-x}(\text{Co,Ni}(\text{H}_2\text{O}))_x\text{X}_6$ targets with $\text{M}'(\text{NS})_n$ transmetalators B_1–B_3 and E are a sensitive function of x and M′ because Co–X and Ni–X bonds are weaker than Cu–X bonds in these targets and $\text{M}'(\text{NS})_n$ have different affinities for a fixed target. Precursor formation leads to specific association of M′ in $\text{M}'(\text{NS})_n$ with a copper(II) center of the target. This association helps to direct specific replacement of copper(II) with M′.

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Supplementary Material Available: Table III, containing kinetic data for monotransmetalation of D (6 pages). Ordering information is given on any current masthead page.

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(22) (N,py)Cu_3NiX complexes contain no CuNi_2 faces (Table VII).

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Thermal Isomerization of Regiospecifically ^{10}B-Labeled Icosahedral Carboranes

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Thermal treatment of regiospecifically ^{10}B-enriched (96%) $3\text{-}(^{10}\text{B})\text{-}1,2\text{-C}_2{}^{n}\text{B}_9\text{H}_{12}$ and $2\text{-}(^{10}\text{B})\text{-}1,7\text{-C}_2{}^{n}\text{B}_9\text{H}_{12}$ (^{n}B = boron with normal isotopic abundances) followed by ^{10}B and ^{11}B NMR analysis reveal that (1) $3\text{-}(^{10}\text{B})\text{-}1,2\text{-C}_2{}^{n}\text{B}_9\text{H}_{12}$ undergoes rearrangements that completely scramble the enriched boron atom, (2) these rearrangements occur at a rate faster than the conversion of $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ to $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$, (3) the $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ that is formed does not re-form $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ at a detectable rate, and (4) at temperatures at which $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ forms $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$ at a significant rate, the latter undergoes no further rearrangements. The movement of ^{10}B at 350 °C in $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ is compared to the movement predicted by various isomerization mechanisms. The mechanism that appears to give the closest agreement involves a 12-vertex nido intermediate. It was found that a number of previously considered mechanisms, including simple exchange between two boron sites, triangular face rotation in an icosahedron, diamond–square–diamond twist, and rotation of pentagonal pyramids, are extensions of the nido intermediate mechanism. The synthesis and thermal rearrangement of $3\text{-F-}3\text{-}(^{10}\text{B})\text{-}1,2\text{-C}_2{}^{n}\text{B}_9\text{H}_{11}$ demonstrate that independent intramolecular fluorine migration does not occur during rearrangement.

Introduction

o-Carborane,[1] $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$, was first prepared from the reaction of decaborane with acetylene in Lewis basic solvents.[2] This icosahedral molecule with adjacent carbons was found to undergo an irreversible thermal rearrangement at 450 °C to produce a meta isomer,[3] $1,7\text{-C}_2\text{B}_{10}\text{H}_{12}$, in which the carbons are no longer adjacent. At 620 °C the meta isomer rearranges reversibly to the para isomer, $1,12\text{-C}_2\text{B}_{10}\text{H}_{12}$ (Figure 1).[4,5] The chemistry of the carboranes and their applications in the synthesis of high-temperature polymers has been reviewed.[6]

Postulates regarding isomerization mechanisms followed closely on the heels of the thermal rearrangement studies. The principal mechanistic proposals are shown in Figure 2. The conversion of *o*- to *m*-carborane, for example, may be viewed as an intramolecular rearrangement based on a cuboctahedral intermediate[7] (Figure 2a), a rotation of the two fused pentagonal-pyramid cluster halves[2] (Figure 2b), a triangular face rotation in an icosahedron (Figure 2c), a diamond–square–diamond twist (Figure 2d), or a 12-vertex nido intermediate (Figure 2e).

The use of boron-halogenated carborane derivatives provided an additional external cluster atom label and allowed somewhat more detailed analysis of possible rearrangement pathways. The product distribution from the thermal isomerization of 9-bromo-*o*-carborane, for example, appeared to be consistent with a variation of the cuboctahedral intermediate mechanism in which selected triangular faces rotated in the transition state.[8] The products from the thermal isomerization of 9-chloro-*m*-carborane were also consistent with the cuboctahedral intermediate mechanism, but in this case a different set of triangular faces was required to rotate.[9] Rotation of pentagonal pyramids (Figure 2b) and rotation of a triangular face in the ground icosahedral state[10] (Figure 2c) were considered unlikely mechanisms at the

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(1) the following nomenclature is used in this paper: carborane = dicarba-*closo*-dodecaborane(**12**); *o*-carborane, *m*-carborane, and *p*-carborane = 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane(12), respectively; ^{n}B = boron atoms with normal isotopic abundances (80% ^{11}B, 20% ^{10}B).

(2) (a) Fein, M.; Bobinski, J.; Mayes, N.; Schwartz, N.; Cohen, M. S. *Inorg. Chem.* **1963**, *2*, 1111–1115. (b) Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Ibid.* **1963**, *2*, 1089–1092.

(3) Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128–1133.

(4) Papetti, S.; Heying, T. L. *J. Am. Chem. Soc.* **1964**, *86*, 2295.

(5) Stanko, V. I.; Brattsev, V. A.; Gol'tyapin, Yu. V. *Zh. Obshch. Khim.* **1969**, *39*, 2686–2688.

(6) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970.

(7) Hoffmann, R.; Lipscomb, W. N. *Inorg. Chem.* **1963**, *1*, 231–232.

(8) Kaesz, H. D.; Bau, R.; Beall, H. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1967**, *89*, 4218–4220.

(9) Hart, H. V.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1969**, *91*, 771–772.

(10) Muetterties, E. L.; Knoth, W. N. *Polyhedral boranes*; Marcel Dekker: New York, 1968; p 70.