S–S ligand is more attractive in view of eq 4 and the unreasonably high oxidation state required for a tungsten simultaneously accommodating two sulfide(2−) ligands and either a carbyne(3−) or a C_3R_3(3−) fragment.

Numerous mechanisms can be pieced together from eq 3–6 and various insertion and coupling sequences.[16] Independent of mechanism, however, it is clear that a dithiocarbamate ligand here serves as a source of one (dimethylamino)carbyne and two sulfide fragments. Efforts to isolate compounds along the reaction coordinate connecting these reagents and products are under way.

Acknowledgment. We thank the National Science Foundation (J.L.T., Grant CHE-8310121) for financial support.

Supplementary Material Available: Tables of positional and thermal parameters and selected bond distances and angles for **1** (4 pages). Ordering information is given on any current masthead page.

Department of Chemistry
The University of North Carolina
Chapel Hill, North Carolina 27514

J. R. Morrow
J. L. Templeton*

Chemical Crystallography Laboratory
Oxford OX1 3PD, U.K.

J. A. Bandy
C. Bannister
C. K. Prout*

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(16) Addition of excess PhC_2D, PhC_2Ph, or HC_2Me to a solution of $W(CO)(PhC_2H)(S_2CNMe_2)_2$ in THF followed by photolysis yielded cyclopentadienyl tungsten products analogous to the PhC_2H product, but extensive alkyne scrambling was evident in the resulting isomer mixtures. Photolysis of reagents containing only internal alkynes did not lead to isolation of comparable products.

Articles

Contribution from the Department of Chemistry,
Northeastern University, Boston, Massachusetts 02115

Transmetalation of Tetranuclear Copper Complexes. 4. Structural Implications of the Kinetics of Direct Transmetalation of Tetranuclear Copper(II) Complexes by $Ni(NS)_2$ Reagents

Geoffrey Davies,* Mohamed A. El-Sayed,*† and Ahmed El-Toukhy†

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The rate laws for direct transmetalations of excesses of tetranuclear copper(II) complexes $(\mu_4\text{-O})[NCu]_4X_6$ (A) (N = monodentate *N,N*-diethylnicotinamide (DENC), pyridine (py); X = Cl, Br) by $Ni(NS)_2$ reagents B and C in nitrobenzene to give $(\mu_4\text{-O})[N_4Cu_3Ni]X_6$ products (D) depends on the molecular geometries of B and C. For B, with cis-coordinated sulfur atoms in a distorted square-planar geometry, rate = $k_B[A]^2[B]$, while C, which is a trans square-planar species, obeys rate = $k_C[A][C]$. It is concluded that rapid exchange of nickel for copper takes place in $\overline{\text{Cu–X–Ni–S}}$ rings.

Introduction

Direct transmetalation is the exchange of metal centers in a polynuclear complex with retention of its core structure.[1,2] Examples of partial and complete metal exchange are shown in eq 1 and 2. Here, N is a monodentate pyridine, X is Cl or Br, and

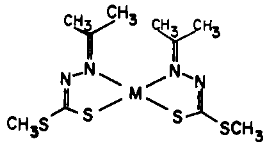
$$(\mu\text{-O})_2[NCuX]_4 + 4Ni(NS)_2 \xrightarrow{H_2O} (\mu\text{-O})_2[NCuNi(H_2O)X_2]_2 + 2Cu(NS)_2 + 2Ni(NS)_2N \quad (1)$$

$$(\mu_4\text{-O})[NCu]_4X_6 + 4Ni(NS)_2 \xrightarrow{H_2O} (\mu_4\text{-O})[NNi(H_2O)]_4X_6 + 4Cu(NS)_2 \quad (2)$$

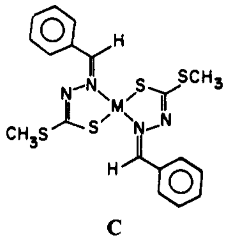
NS is a monoanionic *S*-methyl hydrazinecarbodithioate Schiff base ligand. The thermodynamic driving force for these reactions, which are rapid at room temperature in aprotic solvents like methylene chloride and nitrobenzene, is the formation of very stable $Cu(NS)_2$ coproducts. Efficient gel permeation chromatographic separation of product mixtures results in the coordination of one water molecule by each new nickel center in the original polynuclear core structure.[1,2]

Direct transmetalation has considerable potential in the synthesis of partially and completely substituted polynuclear structures that cannot be obtained by other means. Reactions 1 and 2 are stoichiometric because of favorable thermodynamics. An understanding of the structural–mechanistic factors that also lead to practical rates of metal exchange will be useful in extending direct transmetalation to other polynuclear systems. This information can be obtained from kinetic studies of transmetalation systems involving reactants of known molecular structure.

We demonstrate here that the direct transmetalations of tetranuclear complexes $(\mu_4\text{-O})[NCu]_4X_6$ (A) (N = monodentate *N,N*-diethylnicotinamide (DENC), pyridine (py); X = Cl, Br), by $Ni(NS)_2$ reagents B and C (Figure 1[3-6]) are stoichiometric processes but with rate laws for the first step, eq 3, which depend on the structures of B[5] and C.[6]



B



C

$$A + B \text{ or } C \xrightarrow[\text{solvent}]{\text{aprotic}} \underset{D}{(\mu_4\text{-O})[N_4Cu_3Ni]X_6} + B \text{ or } C \ (M = Cu) \quad (3)$$

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† On leave of absence from the Department of Chemistry, Faculty of Science, University of Alexandria, Alexandria, Egypt.

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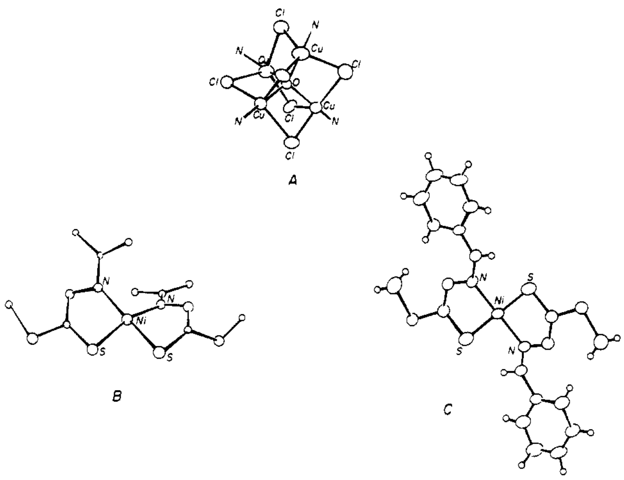

Figure 1. Core structure of A and molecular structures of B[5] and C[6] (M = Ni).

Experimental Section

Materials and Reagents. DENC (Aldrich) was distilled under reduced pressure before use. Anhydrous copper(II) chloride and copper(II) bromide were obtained by heating the respective hydrates (Alfa) under vacuum at 100 °C overnight. Methylene chloride and nitrobenzene were distilled from phosphorus(V) oxide and stored over 4-Å molecular sieves. Reactants A (X = Cl, Br) were obtained by the method of Dickinson;[7] bis(*S*-methyl isopropylidenehydrazinecarbodithioato)nickel(II) (B) and bis(*S*-methyl benzylidenehydrazinecarbodithioato)nickel(II) (C) were prepared as described previously.[1]

Syntheses of $(\mu_4\text{-O})[N_4Cu_3Ni(H_2O)]X_6$ (X = Cl, Br). A solution of B (3 mmol) in 50 mL of anhydrous CH_2Cl_2 was added dropwise over a period of 1 h to a clear brown solution of A (X = Cl, Br; 3 mmol) in anhydrous methylene chloride (50 mL). During the addition the solution turned black. It was then stirred at room temperature for 6 h to ensure complete reaction. The product solution was separated by gel permeation chromatography (positive nitrogen pressure, Biobeads SX-12 resin, 150 cm × 2.5 cm diameter column, anhydrous methylene chloride eluent),[1,2] to give first a yellowish brown band and then a black band. Quantitative yields of dry solid products $(\mu_4\text{-O})[N_4Cu_3Ni(H_2O)]X_6$ (X = Cl, Br) and black $Cu(NS)_2$[1,2] were obtained by vacuum evaporation of the solvent from the respective chromatographic fractions. The same procedure for the corresponding reaction of A with C gave $(\mu_4\text{-O})[N_4Cu_3Ni(H_2O)]X_6$ (X = Cl, Br) and reddish brown $Cu(NS)_2$[1,2] as isolated dry solids. Products $(\mu_4\text{-O})[N_4Cu_{4-x}(Ni(H_2O))_x]X_6$ were prepared by reaction of 1 mol of A and *x* mol of B or C and isolated as above. Analytical data are given in Table I. The molecular weights of all isolated tetranuclear products were determined cryoscopically in nitrobenzene (mp 5.70 °C, K_f = 7.00 °C/m).[1,2]

Physical Measurements. Solution electronic spectral measurements were made with a Beckman DK-1A spectrophotometer in matched quartz cells at room temperature. Infrared spectra, in KBr disks, were obtained with a Perkin-Elmer Model 599 b spectrometer calibrated with the 906.5- or 3026.3-cm^{-1} absorptions of polystyrene.

Kinetic Measurements. Kinetic measurements of reactions of A with B or C in nitrobenzene were always conducted with A in sufficient excess to ensure pseudo-first-order conditions ($[A]_0 = (1.00\text{–}3.00) \times 10^{-3}$ M, $[B]_0$ and $[C]_0 = (5.0\text{–}10.0) \times 10^{-5}$ M). The experimental temperature range was 14.0–42.0 °C. The highest value of $[A]_0$ was limited by solubility.

The rates of formation of B or C (M = Cu) were monitored spectrophotometrically in the wavelength range 500–700 nm. A computer-assisted stopped-flow spectrophotometer[8] was employed for all rate measurements at temperatures controlled within ±0.05 °C of the desired value.

Results and Discussion

We showed in part 2[1] that tetranuclear copper(II) complexes A (N = DENC; X = Cl, Br) react stoichiometrically in aprotic solvents with 4 mol of B to give completely transmetalated tetranuclear products $(\mu_4\text{-O})[(DENC)Ni(H_2O)]_4X_6$ (eq 2). These

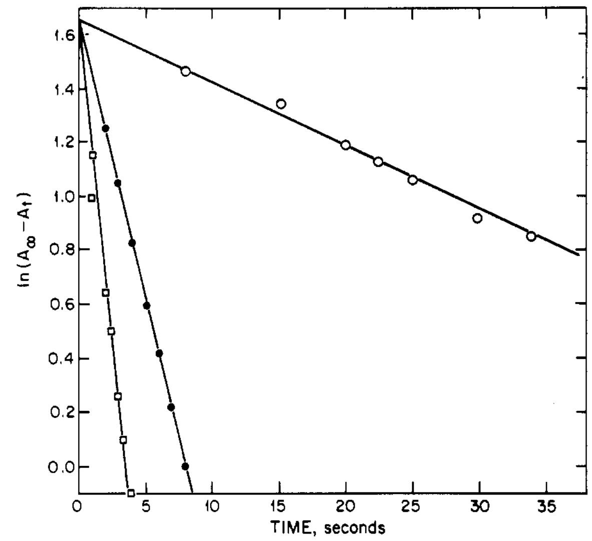

Figure 2. First-order plots of reaction of A (N = py; X = Cl) with B in nitrobenzene at the following temperatures (°C): (○) 16.9; (●) 27.8; (□) 38.1.

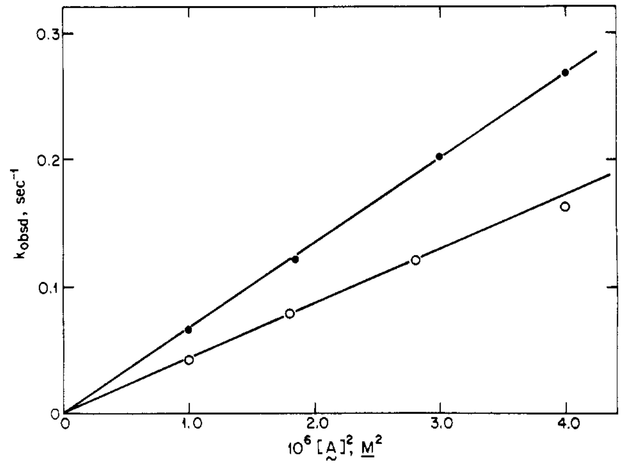

Figure 3. Plots of k_{obsd} vs. $[A]^2$ for the reaction of A ((●) N = DENC, X = Cl, 21.3 °C, (○) N = py, X = Cl, 27.8 °C) with B in nitrobenzene.

products contain 6-coordinate nickel(II) centers with much lower molar absorptivities than the respective copper(II) reactants A. A water molecule is coordinated to each new nickel(II) center during gel permeation chromatographic product separation.

The data in Table I indicate that reaction 2 can be broken down into 4 separate stoichiometric steps to give the series $(\mu_4\text{-O})[N_4Cu_{4-x}(Ni(H_2O))_x]X_6$, where *x* = 1, 2, 3, or 4. Quantitative yields of the same tetranuclear products are obtained with either B or C as the transmetalating agent at any particular molar reactant ratio.

All copper-containing products exhibit two broad absorption maxima in the near-IR region (Table I). The maximum molar absorptivities with fixed N and X are approximately proportional to the number of copper(II) centers in each product, with little variation in the wavelength of maximum absorption.

Unfortunately, attempts to obtain product crystals suitable for X-ray structural determination have been unsuccessful. Crystalline[1] A is often obtained as one product of attempted crystallization of $(\mu_4\text{-O})[N_4Cu_{4-x}(Ni(H_2O))_x]X_6$; with *x* = 1 or 2 and with *x* = 3 or 4 we have only obtained small, very fragile, water-sensitive crystals that are not of sufficient quality or stability for single-crystal measurements.

Kinetic Measurements. Formation of D was ensured in stopped-flow kinetic studies by reacting B or C with a large excess of A in nitrobenzene. Reactions monitored at 500–700 nm were single events that are first order in [B] or [C] (Figure 2). No reaction precursors or intermediates were detected. The pseu-

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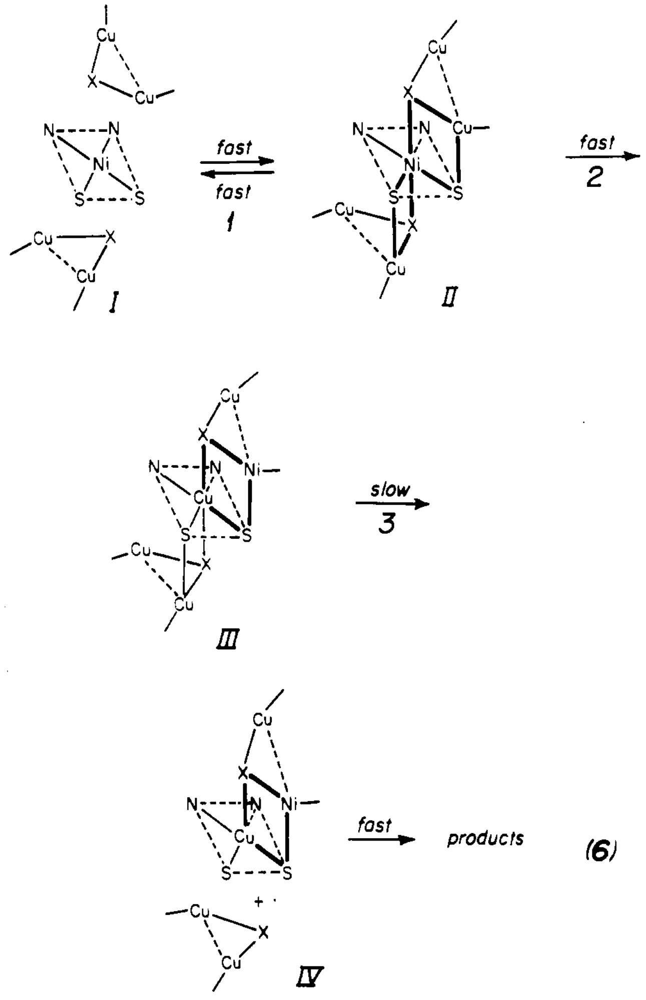
do-first-order rate constants, k_{obsd}, obtained from linear (to at least 85% reaction) plots of ln $(A_\infty - A_t)$ vs. time, where A_t is absorbance at time t, were reproducible to ±5% or better under fixed experimental conditions and were accurately proportional to $[\mathrm{A}]^2$ (Figure 3)[9] and [A] (Figure 4)[9] in the transmetalation of A by B and C, leading to overall rate laws 4 and 5, respectively. Kinetic parameters obtained by linear least-squares analysis[8] of the data are given in Table III.

$$d[\mathrm{Cu(NS)_2}]/dt = k_{\mathrm{B}}[\mathrm{B}][\mathrm{A}]^2 \qquad (4)$$

$$d[\mathrm{Cu(NS)_2}]/dt = k_{\mathrm{C}}[\mathrm{C}][\mathrm{A}] \qquad (5)$$

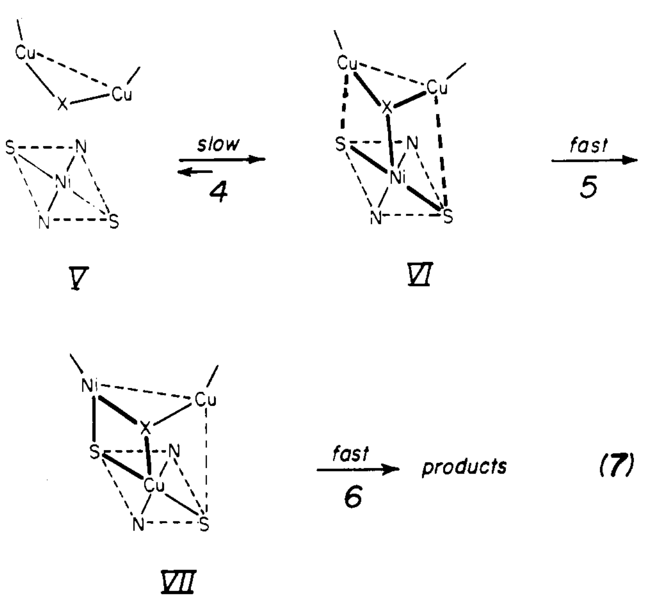
Origin of Different Rate Laws. The different rate laws for transmetalation of A apparently are due to geometrical differences in the transmetalating agents B and C (Figure 1). Transmetalating agent B is a slightly tetrahedrally distorted square-planar complex[5] (the angle between planes Ni, S(1), N(1) and Ni, S(3), N(3), which would be 90° for a perfect tetrahedron, is 27.71°) with *cis*-carbodithioate sulfurs. Its tetrahedral distortion has been neglected for clarity in eq 6. Complex C is a square-planar complex with *trans*-carbodithioate sulfurs (S–S = 4.36 (4) Å).[6]



(6)

Pertinent data for A are as follows: (N = DENC; X = Cl) Cu–Cl = 2.41 (4) Å, Cu- - -Cu = 3.2 (1) Å, Cu–Cl–Cu = 80.3°;[1] (N = py; X = Cl) Cu–Cl = 2.41 (3) Å, Cu- - -Cu = 3.1 (1) Å, Cu–Cl–Cu = 80°;[3] (N = DENC; X = Br) Cu–Br = 2.79 (4) Å, Cu- - -Cu = 3.5 (1) Å, Cu–Br–Cu = 83.1°.[4]

Structural Mechanisms for Transmetalation. On the basis of the known *cis*-[5] and *trans*-carbodithioate[6] geometries of B and C, we propose the structural mechanisms in eq 6 and 7 for reactions of A with B and C, respectively.



(7)

Examination of space-filling models indicates that the halogen atoms on each tetrahedral edge of A[1,3,4] are geometrically accessible for axial coordination to the nickel centers of B and C. If this were the only point of attachment, we might expect the rate law for the reaction of C with A also to be second order in [A] because C is a stronger Lewis acid (at least for monodentate pyridine bases)[10] than is B. This is not observed (eq 5). We therefore propose weak but specific additional interactions between the copper centers in A and the carbothioate sulfur atoms of B and C primarily because these coordinated S atoms of $\mathrm{Ni(NS)_2}$ are derived from the enol form of the ligand[5,6] and are thus more nucleophilic than the N donor atoms. If coordination of the latter and of the thioether groups of B and C are both neglected and each carbothioate sulfur coordinates just one copper(II) center in A, then transmetalation precursor structures II and VI follow. These structures are consistent with the respective rate laws 4 and 5, in particular the fact that C·2A is not involved in transmetalation of A by C.

We calculate Cu–S to be at least 3.5 Å for a symmetrical structure VI, but two such interactions provide a straightforward and consistent way of explaining the presence of 1 mol of A and only 1 mol of C in the activated complex for transmetalation (see below). The cis geometry of B in II favors the binding of just one copper center of each Cu–X–Cu unit of A, perhaps resulting in a shorter Cu–S interaction. The *cis*-carbothioate sulfurs in B[5] are in van der Waals contact (3.2 Å),[11] which appears to preclude a Ni–X interaction in the $\mathrm{NiS_2}$ plane in B (Figure 1).

The simple rate laws 4 and 5 confirm that all interactions of A with B and C are weak. By comparison of the predicted[12,13] and observed rate law 4 for reaction of A with B via II we estimate[12,13] the equilibrium constants β_2 for the rapid formation of structure II to be less than ca. 10^4 $\mathrm{M^{-2}}$ at 21 °C in nitrobenzene; β_2 is probably much less because β_2 for formation of B·2py is only 0.38 $\mathrm{M^{-2}}$ in benzene at 25 °C.[10]

Precursor structures II and VI both contain $\overline{\mathrm{Cu{-}S{-}Ni{-}X}}$ rings, which we fell are important in facilitating metal exchange through coordination to shared bridging ligands, as postulated in the isomerizations of $[\mathrm{NCuNi(H_2O)X_2}]_2\mathrm{Y_2}$ structures (Y = O, $\mathrm{CO_3}$).[1,2]

Entropic Considerations. Steps 1–3 of eq 6 are expected to result

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[9] Supplementary data in Table II.

[10] Iskander, M. F.; El-Sayed, L.; Labib, L.; El-Toukhy, A. *Inorg. Chim. Acta* **1984**, *86*, 197.

[11] Huheey, J. E. *Inorganic Chemistry*; 3rd ed.; Harper and Row: New York, 1983; p 258.

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

product	anal., %: C	H	N	Cu	Ni	M_r	λ_{max},[b] cm^{-1} (ϵ, M^{-1} cm^{-1})	ν_{M-O}, cm^{-1}
$(DENC)_4Cu_4Cl_6O$[c]	40.0 (40.18)	4.7 (4.72)	9.2 (9.37)	21.0 (21.25)		1180 ± 20 (1196)	850 (1630), 775 (1400)	510
$(DENC)_4Cu_3Ni(H_2O)Cl_6O$	40.0 (39.7)	4.9 (4.8)	8.9 (9.3)	16.3 (15.86)	4.6 (4.96)	1240 ± 20 (1208)	850 (1160), 775 (1030)	495
$(DENC)_4Cu_2Ni_2(H_2O)_2Cl_6O$	33.6 (39.36)	4.6 (4.93)	8.7 (9.18)	11.0 (10.39)	10.2 (9.6)	1250 ± 20 (1223)	850 (840), 775 (760)	490
$(DENC)_4CuNi_3(H_2O)_3Cl_6O$	36.5 (38.95)	4.7 (5.06)	8.7 (9.08)	5.5 (5.14)	15.1 (14.25)	1260 ± 20 (1236)	837 (360), 767 (340)	500
$(DENC)_4Ni_4(H_2O)_4Cl_6O$[c]	37.79 (38.48)	5.1 (5.17)	8.7 (8.98)		18.5 (18.81)	1270 ± 20 (1249)	*d*	500
$(DENC)_4Cu_3Ni(H_2O)Br_6O$	32.5 (32.5)	4.0 (3.9)	7.7 (7.6)	14.1 (12.9)	3.86 (4.0)	1500 ± 20 (1475)	850 (1700), 790 (1590)	420
$(py)_4Cu_3Ni(H_2O)Cl_6O$	29.8 (29.66)	2.6 (2.7)	7.0 (6.9)	24.04 (23.46)	6.01 (7.23)	*e*	860 (1420), 775 (1280)	500

[a] Calculated values in parentheses. [b] In nitrobenzene. [c] Reference 1. [d] Negligible molar absorptivities in the region 775–860 nm. [e] Solubility too low for cryoscopy in nitrobenzene.

Table III. Kinetic Data for Monotransmetalation of $(\mu_4\text{-}O)N_4Cu_4X_6$ Complexes by $Ni(NS)_2$ Reagents in Nitrobenzene

N, X	$Ni(NS)_2$	$10^{-4}k_B$[a]	$\Delta H_B^{\ddagger}$[b]	$\Delta S_B^{\ddagger}$[c]	k_C[d]	$\Delta H_C^{\ddagger}$[b]	$\Delta S_C^{\ddagger}$[c]
DENC, Cl	B	1.62	20.0	29			
py, Cl	B	1.89	20.4	30			
DENC, Br	B	0.025	24.0	35			
DENC, Cl	C				12.6	4.2	-38

[a] Units are M^{-2} s^{-1} at 21 °C; typical error is ±5%. [b] Units are kcal mol^{-1}; typical error is ±0.4 kcal mol^{-1}. [c] Units are cal deg^{-1} mol^{-1} at 25 °C; typical error is ±3 cal deg^{-1} mol^{-1}. [d] Units are M^{-1} s^{-1} at 21 °C; typical error is ±5%.

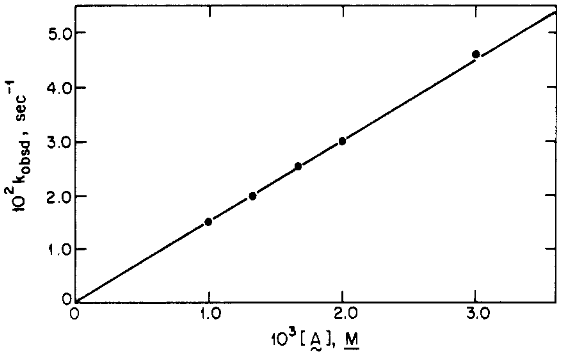

Figure 4. Plot of k_{obsd} vs. [A] for the reaction of A (N = DENC; X = Cl) with C at 27.8 °c in nitrobenzene.

in negative,[10] near-zero and positive entropy changes, respectively, as are steps 4–6, respectively, of eq 7.

Interpretation of the Kinetic Data. Since $\Delta S_B^{\ddagger}$ is positive (Table III) we propose step 3, eq 6, as rate-determining in the reactions of A with B. The increase in $\Delta H_B^{\ddagger}$ in changing X from Cl to Br in A is ascribed to stronger Cu–Br bonds to be broken in step 3.[1,2] Changes of N from DENC to py in A have little effect on the kinetics of reaction of A with B (Table III).

The low $\Delta H_C^{\ddagger}$ and very negative $\Delta S_C^{\ddagger}$ values are typical of reactions of neutral molecules in which precursor assembly is rate-determining.[8] This situation seems to arise because of the relative difficulty in forming a significant Cu–S interaction in VI (see above).

Conclusions. Strong Cu–S bond formation is a major driving force for transmetalation,[1] and some Cu–S interaction should be expected to facilitiate metal exchange. It appears that the formation of Cu–S–M–X rings in the precursors allows very facile metal exchange in these systems, and thus we propose Cu–Y–M–X ring formation (X and Y nucleophilic) as a minimum structural requirement for rapid metal exchange in transmetalation of copper(II) complexes by $M(YZ)_2$ reagents. Once this requirement is met, it then appears that metal exchange will only become rate-determining in systems involving B and C where the copper(II) centers are strongly coordinated by polydentate ligands.

Acknowledgment. We thank the Department of Health and Human Services (Grant RR07183) for support and Professors Thomas R. Gilbert and Kay D. Onan for experimental assistance.

Supplementary Material Available: Table II, kinetic data for monotransmetalation of $(\mu_4\text{-}O)N_4Cu_4X_6$ complexes by $Ni(NS)_2$ reagents in nitrobenzene (1 page). Ordering information is given on any current masthead page.