

TRANSMETALATION MECHANISMS

By

G. DAVIES, A. ALI*, S. AL-SHEHRI**, N. EL-KADY***‡, M. A. EL-SAYED***§ and A. EL-TOUKHY***‡

Chemistry Department and The Barnett Institute, Northeastern University, Boston, Massachusetts 02115, USA

*Chemistry Department, College of Science and Technology, Abu-Deis, Jerusalem

**Chemistry Department, Leicester University, Leicester LE1 7RH, UK

***Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

‡Present address: Chemistry Department, Faculty of Science, University of Qatar, Doha, Qatar

§Present address: Chemistry Department, Faculty of Science, United Emirates University, Al-Ain, United Arab Emirates

ميكانيكية تفاعلات التبادل الفلزي

جيفري ديفز و عدنان علي و سعد الشهري و نجوى القاضي
محمد عبد الرحمن السيد و أحمد الطوخي

يناقش هذا البحث حركية وميكانيكية تفاعلات التبادل الفلزي الأحادية للمتراكبات المتعادلة (T) مع عوامل التبادل الفلزي المتعادلة (TM) في المذيبات غير القطبية . وقد وجد أن المعدلات والقوانين الحركية للأنظمة محل الدراسة تتغير بتغير التركيب الكيميائي والفراغي لكل من (T) ، (TM) كما أن التفاعل يتم من خلال نواتج إضافة وسيطة (P) أو (P') يحدث التبادل الفلزي بداخلها لتنتج عوامل وسيطة أخرى (S) أو (S') تنفصل منها النواتج بعد ذلك . وتعتمد تركيزات P ، P' ، S ، S' على نوع المتفاعلات ودرجة حرارة التفاعل . وقد وجد أن معدلات التفاعل واختيارية تعتمد على ثبات عوامل التبادل الفلزي (TM) .

Key Words: Transmetalation, Target, Transmetalator, Heteropolymetallic complexes, Kinetics, Mechanisms, Precursors, Metal exchange, Successors.

ABSTRACT

Transmetalation is the stoichiometric replacement of the metals in a polymetallic target T with different metals from reagents called transmetalators, TM. Transmetalation at useful rates under mild conditions is an excellent source of large families of discrete heteropolymetallic complexes. Direct transmetalation gives heteropolymetallic products containing the same number of metal atoms as T. Replacement of just one metal center in T with a different metal from TM is called monotransmetalation. Replacement of a particular metal in a heteropolymetallic target T with another metal from TM is specific. Preferred reaction of T with one of a mixture of TM and TM' is selective. This paper discusses the kinetics and mechanisms of real and model monotransmetalations of neutral T with neutral TM in aprotic solvents. Transmetalation requires the breaking and making of many different bonds, but most monotransmetalation systems exhibit just one kinetic event whose rates and rate laws vary with T and TM. The observed event can be formation of reaction precursors P or P', metal exchange within P or P', rearrangement of successor complexes S or S' or their dissociation to separate products. The concentrations and proportions [P]/[P'] and [S]/[S'] depend on the reactants and the experimental temperature. Overall rates and transmetalation selectivity depend on TM stabilities. Transmetalation specificity results from correlated thermodynamic factors in P/P' assembly and kinetic factors in activated complex formation. The most common slow transmetalation step is metal exchange.

INTRODUCTION

Heteropolymetallic complexes and clusters are very desirable materials. Better ways of making them continue to be sought (Adams, 1990; Andres *et al.*, 1989; Bender, 1988;

Braunstein, 1988, 1992; Mashuta, 1989; Steggarda, 1992). Some years ago we discovered that large families of discrete heteropolymetallic complexes can be made by a process called transmetalation (Davies *et al.*, 1984; El-Toukhy *et al.*, 1984). Ongoing work 1) seeks to understand how the metals

in heteropolymetallic transmetalation products interact to give specific molecular and catalytic properties (Abu-Raqabah *et al.*, 1989; El-Sayed *et al.*, 1992a) and 2) converts these products to highly dispersed alloys, mixed metals and mixed metal oxides by thermal and electrochemical methods for materials and catalytic applications (Abdel-Fattah and Davies, 1992; Abdel-Fattah *et al.*, 1993; Davies, Giessen and Shao, 1991, 1992; Kounaves *et al.*, 1993).

Transmetalation is defined as the stoichiometric replacement of the metals in a polymetallic target T with other metals from reagents called transmetalators, TM (Fig.1)

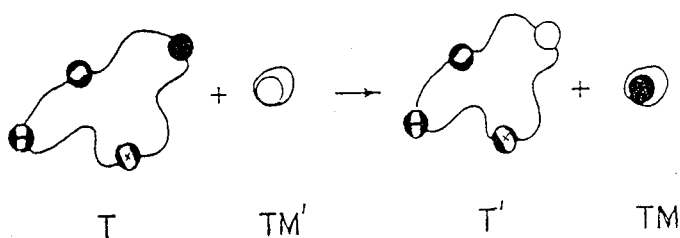


Fig. 1: Pictorial representation of a direct, specific monotransmetalation reaction.

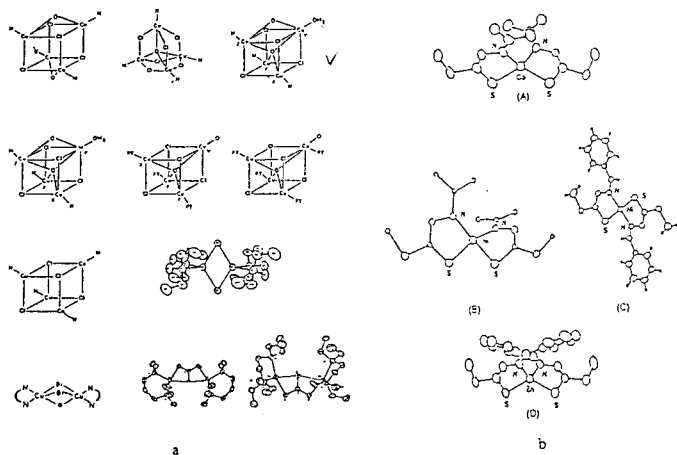
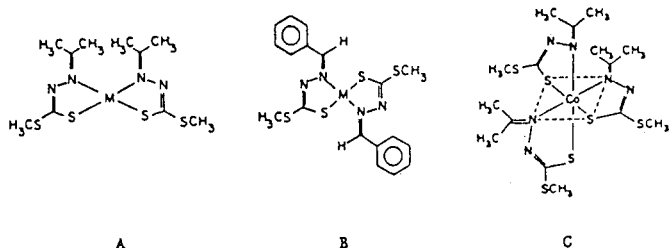
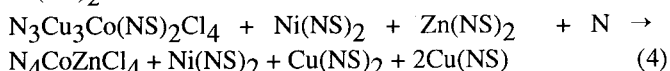
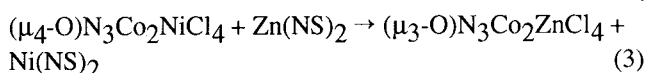
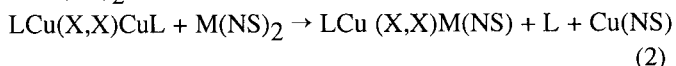
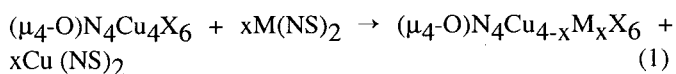


Fig. 2: Typical (a) targets and (b) transmetalators. The NS ligand is S-methyl isopropylidenehydrazinecarbodithioate in transmetalators (A) and (B) and S-methyl benzylidenehydrazinecarbodithioate in transmetalators (C) and (D). The drawings are not to scale (Davies, El-Sayed and El-Toukhy, 1989).

Typical neutral targets (Fig. 2a) contain common monodentate pyridine ligands N or bidentate N,N,N',N'-tetraalkyldiamine ligands L, oxide, carbonate and X = Cl⁻ or Br⁻. Excellent transmetalators M(NS)_n (Fig. 2b) contain monoanionic S-methyl hydrazinecarbodithioate ligands NS in molecules A-D. Published transmetalation work involves the metals Fe, Co, Ni, Cu, Zn, Cd, Hg and Sn (Caulton, Davies and Holt, 1990; Davies, El-Sayed and El-Toukhy, 1989, 1992).



Direct transmetalation gives heteropolymetallic products containing the same number of metal atoms as target T (Fig. 1, eqs. 1 (x=1-4), 2 and 3). It is good chemistry because only one part of the target is altered at a time. Replacement of just one metal center in T with a different metal from TM is called monotransmetalation (Fig. 1 and eqs. 1-3). Replacement of a particular metal center in a heteropolymetallic target T is specific (Fig. 1 and eq 3). Preferred reaction of a target with one of a mixture of different transmetalators TM and TM' is selective (eq. 4). Transmetalation is not restricted to copper targets (see, for example, eq. 3) and is of wide potential applicability.



Practical use of transmetalation for materials and catalyst synthesis requires 1) easily made reactants; 2) stoichiometric metal replacement at useful rates under mild conditions; and 3) an ability to generate families of discrete, easily separated heteropolymetallic products. All these requirements are met by reactions 1-4 (Abu-Raqabah *et al.*, 1989).

The products and potential applications of transmetalation chemistry have been reviewed (Caulton, Davies and Holt, 1990; Davies, El-Sayed and El-Toukhy, 1989, 1992). Here we focus on transmetalation kinetics and try to account mechanistically for transmetalation stoichiometry, specificity and selectivity. Our presentation has six main sections.

First, we describe the characteristics of transmetalation and our strategy for kinetic measurements. Next we outline experimental conditions and what is observed when excesses of different targets T react with different transmetalators TM in aprotic solvents. Third, finding the number of observable events and their reaction orders allows sub-classification of the data and comparison of overall rates. Fourth, we assign an event (precursor P information, metal exchange, successor complex S rearrangement or S dissociation) to each observable step by comparing its activation parameters with those of known processes. Model transmetalation systems are especially useful for this purpose. Fifth, we compare the thermodynamic and kinetic components of different systems to substantiate and correlate the assignment. Lastly, we offer a general transmetalation mechanism to describe the slow steps in different systems.

CHARACTERISTICS AND STRATEGY

Polymetallic targets containing cobalt, nickel, copper(I) and copper(II) react stoichiometrically, specifically and selectively with known M(NS)_n reagents. Stoichiometric, stepwise reactions are indicated by 1) linear spectrophotometric absorbance changes with clear breaks indicating complete reaction on titration of a target with increasing amounts of TM (El-Toukhy *et al.*, 1984); 2) gravimetric determination of the Cu(NS)_n(s) co-product of copper(I) transmetalation (Davies *et al.*, 1986c); 3) elemental and molecular weight analysis of the isolated heteropolymetallic products (Abu-Raqabah *et al.*, 1989); and 4) evidence for irreversible reactions from kinetic

measurements (see below). The reactions are stoichiometric because the respective co-products $\text{Co}(\text{NS})_2$, $\text{Ni}(\text{NS})_2$, $\text{Cu}(\text{NS})_2$ and $\text{Cu}(\text{NS})_2$ are much more thermodynamically stable than reactants $\text{M}(\text{NS})_n$. Selectivity is expected because the stability of $\text{M}(\text{NS})_n$ varies with M and NS (Davies *et al.*, 1986c). Specificity arises from particular interactions between T and TM in reaction precursors P to be discussed below. The result of these characteristics is stoichiometric reactions that give predictable, discrete heteropolymetallic products.

Other factors that facilitate kinetic analysis and mechanistic understanding are that 1) we know the reactant core structures (Fig. 2), which are a basic requirement for mechanism studies (Wilkins, 1974); 2) the reactants are neutral, so ionic strength effects are absent; 3) use of weakly coordinating aprotic solvents simplifies interpretation of the events; 4) there are many possible combinations of structurally known reactants in different solvents at different temperatures; and 5) we can work under pseudo-first-order conditions with a large excess of target to ensure replacement of only one metal center in T.

EXPERIMENTAL CONDITIONS AND OBSERVED EVENTS

Kinetic work under pseudo-first-order conditions has distinct advantages (Wilkins, 1974). We use target T in large excess to ensure monotransmetalation. Typical concentration ranges are $[\text{T}] = 0.25\text{--}25.0\text{ mM}$, with $[\text{TM}] = 0.025\text{--}0.25\text{ mM}$. Temperature is varied over a wide range to obtain precise activation parameters. We use methylene chloride and nitrobenzene as aprotic solvents. Both are weak ligands. The much higher dielectric constant of nitrobenzene favors any polar intermediates and allows their detection (Davies *et al.*, 1988a).

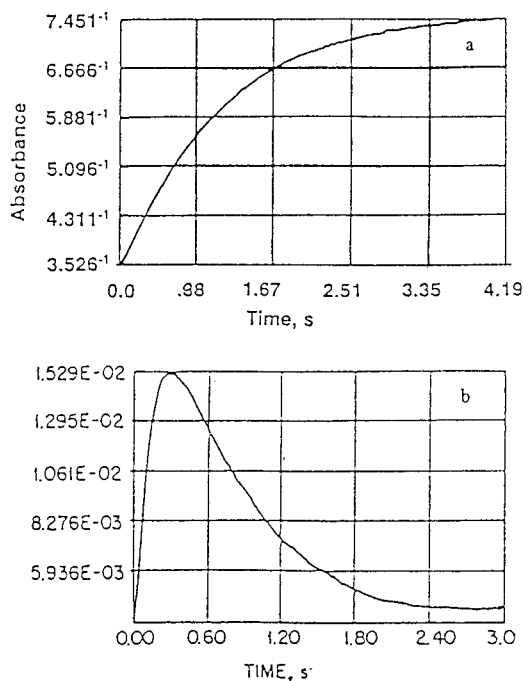


Fig. 3: Absorbance-time records for (a) a typical monotransmetalation reaction and (b) the reaction of $\text{N}_2\text{CuCl}(\text{Cl},\text{Cl})\text{ClCuN}_2(\text{N}=\text{N},\text{N}$ -diethylnicotinamide, 0.83mM) with A ($\text{M} = \text{Ni}$) (0.10 mM) in nitrobenzene at 22.6° C (El-Sayed and Davies, 1990). The monitoring wavelength is 575 nm in both cases.

Depending on the reactants, transmetalation is monitored spectrophotometrically at a wavelength in the range $350\text{--}750\text{ nm}$. We vary the monitoring wavelength to see if this changes the number of observed events or their rates. The reactions often proceed on the stopped-flow time scale. We most often find just one exponential absorbance-time record (Fig. 3a) with experimental first-order rate constants k_{obsd} up to 100 sec^{-1} .

There are many possible slow processes in transmetalation reactions but we most often observe only one of them (Fig. 3a). For this reason we need a way to assign each observed event to a particular process. Fortunately, neutral target Cu(acac)₂ (Fig. 4) serves as a good model for a metal center in a polymetallic target T (Ali and Davies, 1991).

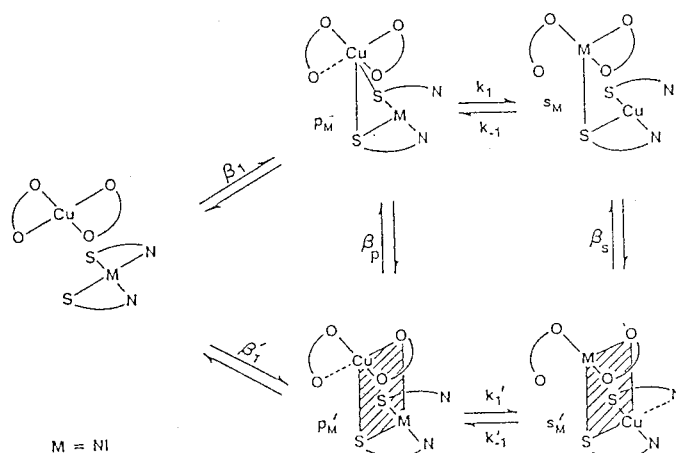
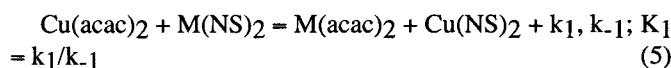


Fig. 4: Proposed mechanism for the reversible reaction of excess Cu (acac is acetylacetonate) with A ($\text{M} = \text{Ni}$) in methylene chloride. Primed parameters refer to low experimental temperatures, where the four membered rings are the counterparts of proposed ring R in Fig. 5. Full, partial and broken bonds are suggested by the measured enthalpy and entropy changes on very fast precursor formation and for kinetic activation in either direction (Ali and Davies, 1990).

THE ASSIGNMENT OF EVENTS

Transmetalation reactions like 1-4 require the breaking and making of many different bonds. They involve at least four major processes in the following logical order: 1) formation of reaction precursors P and/or P'. These precursors are formed by sharing of one or more of the ligand atoms that are exchanged by the metals; 2) metal exchange to give successor complexes S and S'. Metal exchange requires ligand transfer to give species resembling the products. Entities P, P', S, or S' in a model (Fig. 4) or real transmetalation reaction could have common structural features; 3) possible slow rearrangement of S/S'; or 4) dissociation of S/S' to give separate product molecules, as implied in eqs 1-5 (acac is acetylacetonate). Most of the possibilities are featured in the model system of Fig. 4.



except that practical transmetalations are irreversible (that is, k_1 and k_{-1} are zero).

Mechanistic tools used to assign the observed events are as follows.

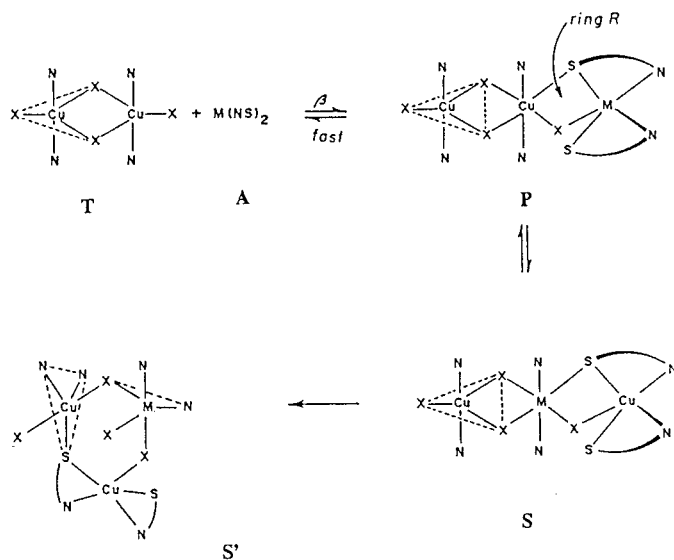


Fig. 5: Proposed mechanism for the reaction of dimeric target $N_2CuX(X,X)XCuN_2$ ($N = N,N$ -diethylnicotinamide) with transmetalator A ($M = Ni$) in nitrobenzene consisting of three components. Equilibration to form precursor P is too rapid to measure on the stopped-flow time scale. It involves formation of proposed four-membered ring R. Equilibrium constant is small, as indicated by a linear plot of $\ln [N_2CuX(X,X)XCuN_2]$. The second step involves reversible metal exchange in P and successor complex S and accounts for the first process in Fig. 3b. The third component is irreversible conversion of S to a different for the first-order absorbance decrease in Fig. 3b. Changing M in A from Ni to Co or Zn results in only the last absorbance decrease being measurable under the same conditions. The proposed structures are based on structural information on the reactants and the measured enthalpy and entropy changes for reaction (El-Sayed and Davies, 1990).

1) Count the number of absorbance changes in each transmetalation reaction. Compare each with what is expected from reactant and product spectra. For example, an absorbance increase is expected at 575-600 nm when copper (II) in a target is replaced by $M = Co, Ni$ or Zn . So, the first absorbance increase at 575 nm in the reaction of excess target $LCuCl(Cl, Cl)ClCuL$ with A ($M = Ni$) (Fig. 3b) corresponds to monotransmetalation to give formal $LCuCl(Cl, Cl)ClNiL$ and $Cu(NS)_2$ products. This step is followed by an absorbance decrease due to successor complex S rearrangement (Fig. 5) that decreases the absorptivity of coordinated co-product $Cu(NS)_2$: only the second process is kinetically measurable when M in A is Co, Cu or Zn (El-Sayed and Davies, 1990). Reversible processes are signalled by a dependence of the size of the absorbance change on the target concentration [T], as in reaction 5 and by intercepts on the ordinate axis in plots of k_{obsd} vs $[T]^n$ (see below and Fig. 6f: Ali and Davies, 1990).

2) Observe absorbance changes with time on re-mixing the separated reaction products. As noted above, formation of $Cu(NS)_2$ by metal exchange results in absorbance increases at 575 or 600 nm, but mixing $Cu(NS)_2$ with polymetallic T gives small absorbance decreases for $Cu(NS)_2$ complexation for form S (Al-Shehri *et al.*, 1993). Thus, the sequence $P \rightarrow S \rightleftharpoons$ products would only be resolvable near 600 nm if the second step were slower than the first.

3) Determine the kinetic order of each step. Compare the data with those for known processes at the same target (Ali and Davies, 1990, 1991; Al-Shehri *et al.*, 1990a, 1993).

4) Change the solvent from methylene chloride to polar nitrobenzene to see effects on the number of events, rates, rate laws and activation parameters (Davies *et al.*, 1988).

5) Plot experimental activation enthalpies ΔH_{n+1}^\ddagger vs activation entropies ΔS_{n+1}^\ddagger for systems with the same order $n + 1$ (see below: Davies *et al.*, 1988; Davies, 1989).

6) Where possible, construct reaction profiles, establish the largest enthalpy and entropy changes and compare one profile with others (Ali and Davies, 1991).

Kinetic Order Determination

Linear first-order plots of absorbance-time data for real and model monotransmetalation reactions with excess [T] indicate an invariant first-order dependence of the rate on [TM], eq 6a. Every species involved in these reactions thus contains one TM molecule. The plot slopes give the experimental pseudo-first-order rate constant k_{obsd} for each observed event under fixed conditions.

$$\text{rate} = k_{n+1} [TM][T]^n \quad (6a)$$

The observed rate constant for most measurable monotransmetalation events is eq 6b, where n is 0, 1 or 2. We find n by plotting k_{obsd} vs $[T]^n$ and adjust n until a linear plot is obtained (Fig. 6a-c). Plots 6a and 6b pass through the origin, indicating kinetic irreversibility. Determination of n allows sub-classification of each observed event as an overall first-, second- or third-order process, eq 6a. The rate constant for a particular event is k_{n+1} .

$$k_{obsd} = k_{n+1} [T]^n \quad (6b)$$

Special Systems

A virtue of transmetalation is that it generates families of structurally similar heteropolymetallic molecules. For example, direct transmetalation of a fixed target with three different transmetalators in eq 1 can, in principle, generate a family of thirty-five other polymetallic targets. An example is $(\mu_4-O)N_4CuCo(NiH_2O)_2Cl_6$ (the water molecules are coordinated during its chromatographic isolation (Davies, El-Sayed and El-Toukhy, 1989, 1992)). We find in practice that heteropolymetallic products containing more than two zinc centers are too unstable to be isolated, but most of the other possible products have been obtained from reaction 1 (Abu-Raqabah *et al.*, 1989).

Use of $(\mu_4-O)N_4Cu_{4-x}(NiH_2O)_xCl_6$ ($x = 1-4$) as individual targets for reaction with transmetalators A ($M = Co, Ni$ and Zn) reveals one or other version of rate law 6 or very special rate law 7 when x is 3 and M is Co or Zn (Fig. 6d: Al-Shehri *et al.*, 1990).

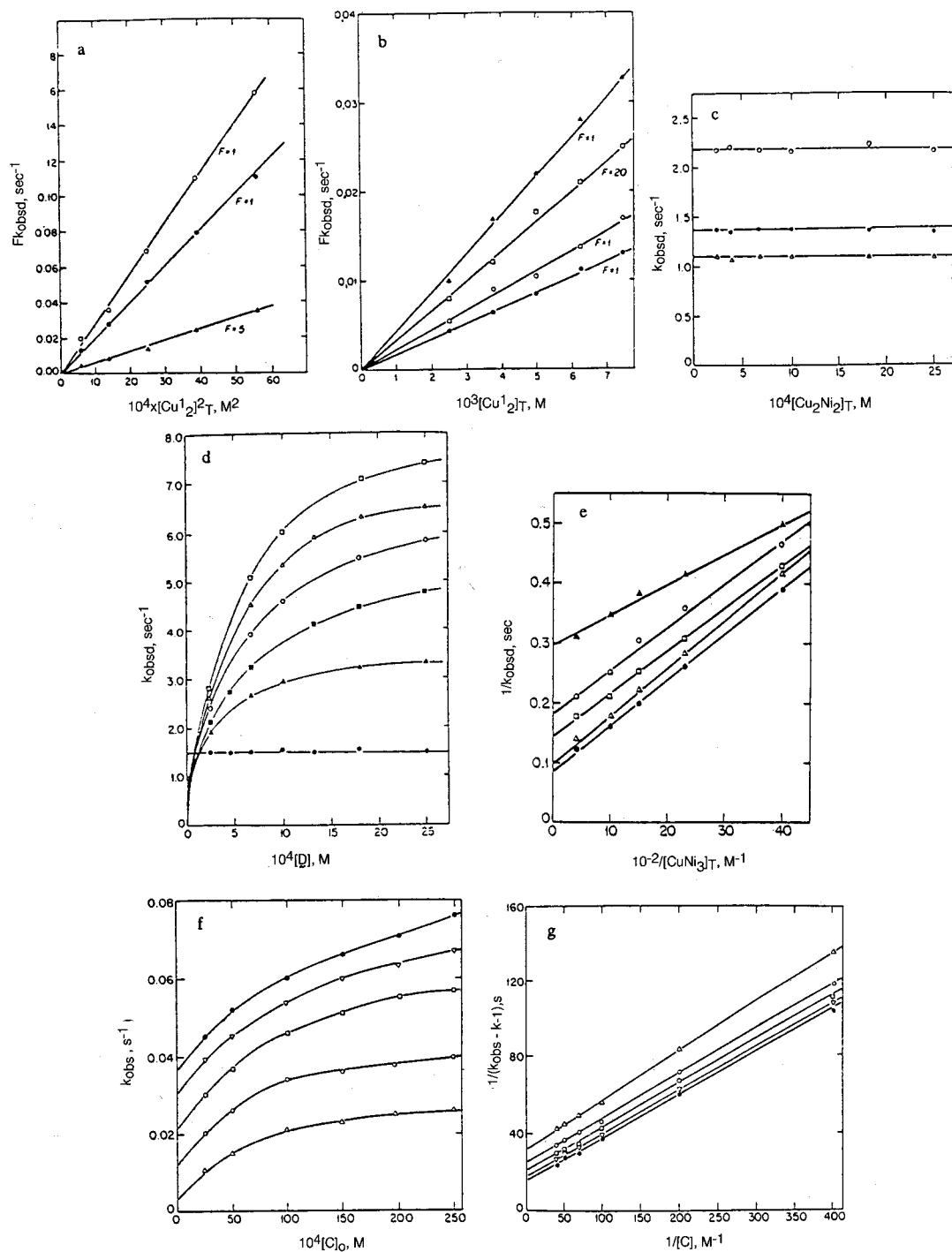


Fig. 6: Plots of (a) Fk_{obsd} vs $[L_2Cu_2X_2Y]^2$ for systems 39 (at 24.5°C, Δ), 26 (30.3°C, \bullet) and 24 (30.3°C, \circ) of Table 1b; (b) Fk_{obsd} vs $[L_2Cu_2X_2CO_3]$ for L = TMPD, X = Cl with A (M = Ni) (at 30.3°C, \circ), L = TMPD, X = Br with A (M = Ni) (35.4°C, \bullet), L = TMED, X = Cl with A (M = Ni) (28.0°C, Δ) and L = TEED, X = Cl with B (M = Ni) (31.0°C, \square). See Table 1 for abbreviations (Davies *et al.*, 1986b); (c) k_{obsd} vs $[T]$ for reaction of T = $(\mu_4-O) N_4Cu_2 (NiH_2O)_2 Cl_6$ with A (M = Zn) (at 12.0°C, Δ), $(\mu_4-O)py_4Cu_2 (NiH_2O)_2 Cl_6$ with A (M = Zn) (12.0°C, \bullet) and $(\mu_4-O) N_4Cu_2 (NiH_2O)_2 Cl_6$ with A (M = Zn) (18.0°C, \circ) in nitrobenzene (rate law 6, $n = 0$: Al-Shehri *et al.*, 1990b); (d) k_{obsd} vs $[D]$ for the reaction of D = $(\mu_4-O) N_4Cu(NiH_2O)_3 Cl_6$ with A (M = Zn) in nitrobenzene at 8.0°C (\bullet), 10.0°C (Δ), 12.0°C (\blacksquare), 15.0°C (\circ), 17.5°C (\square) and 18.5°C (\square) (Al-Shehri *et al.*, 1990a); (e) $1/k_{\text{obsd}}$ vs $1/[D]$ for the data in panel (d); (f) k_{obsd} vs $[C]$ for the reaction of C = Cu(acac)₂ with A (M = Zn) in methylene chloride at 10.0°C (Δ), 17.0°C (\square), 27.0°C (Δ) and 30.0°C (\bullet); (g) $1/k_{\text{obsd}}$ vs $1/[C]$ for the data in panel (f) (Ali and Davies, 1991).

$$k_{\text{obsd}} = k_1 \beta_1 [T] / (1 + \beta_1 [T]) \quad (7)$$

$$1/k_{\text{obsd}} = 1/k_1 \beta_1 [T] + 1/k_1 \quad (8)$$

Rate law 7 is valuable because it can be inverted to give eq. 8. A linear plot of $1/k_{\text{obsd}}$ vs $1/[T]$ (Fig. 6e) validates rate law 7 and allows the separation of equilibrium constant β_1 from first-order rate constant k_1 . This is direct proof that transmetalation involves pre-association of the reactants in precursors P, eq. 9, and allows separate consideration of equilibrium and kinetic components in any observable event with rate law 7 (*vide infra*).

$$\text{TM} + \text{T} = \text{P} \beta_1 \quad (9)$$

Eq. 7 has two important limits: 1) $\beta_1 [T] \ll 1$, which gives eq. 6 with $k_2 = k_1 \beta_1$ in a second-order process with $n = 1$; 2) $\beta_1 [T] \gg 1$, which corresponds to eq. 6 with $n = 0$ and first-order behavior with rate constant k_1 . The rates in this second limit are independent of $[T]$ because β_1 in eq. 9 is very large at typical temperatures (Fig. 6c).

Eq. 7 is the general rate law for events involving one T and one TM. What we find experimentally (Fig. 6a-d) depends on the magnitude of β_1 in eq. 9. The exception to this statement is when $n = 2$ in rate law 6, which refers to an overall third-order process with one TM and two T in the activated complex. Eq. 9 can be modified to describe reactant association in precursors $\text{TM} \cdot \text{T}_2$ with formation constant β_2 , but the simple experimental form $k_{\text{obsd}} = k_3 [T]^2$ ($n=2$ in eq. 6b) leaves $\beta_2 = k_3/k_1$ inseparable. Formation constants β_2 are very small in known third-order monotransmetalations under typical conditions (Ali-Shehri *et al.*, 1990a).

So, the observable events in most monotransmetalations are first-, second- or third- order, depending on the reactants. A few of them are governed by informative rate law 7. A study of rate law variations as a function of x in monotransmetalations of targets $(\mu_4\text{-O})\text{N}_4\text{Cu}_{4-x}(\text{NiH}_2\text{O})_x\text{Cl}_6$ with A ($M = \text{Zn}$) strongly suggests that formation of precursors P involves target Ni-Cl-Cu edges and/or CuNi_2 faces (Ali-Shehri *et al.*, 1990b). In other words, more than one target metal center is involved with the transmetalator. This conclusion and the need to find more examples of rate law 7 led us to model the metal centers of polynuclear targets with neutral mononuclear target $\text{Cu}(\text{acac})_2$ (Ali and Davies, 1990). This flat target contains only O-donor atoms (Fig. 4). The choice was fortunate because it revealed rate law 10 (Fig. 6f), which predicts that highest $k_{\text{obsd}} = k_1 + k_{-1}$.

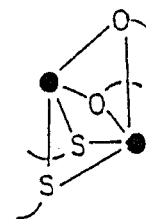
$$k_{\text{obsd}} = k_1 \beta_1 [T] / (1 + \beta_1 [T]) + k_{-1} \quad (10)$$

$$1/(k_{\text{obsd}} - k_{-1}) = 1/k_1 \beta_1 [T] + 1/k_1 \quad (11)$$

Rate law 10 has the extra term k_{-1} because it governs reversible metal exchange reactions 5, as indicated in Fig. 6f and verified chromatographically. Eq. 10 can be rearranged to eq. 11. Linear plots of $1/(k_{\text{obsd}} - k_{-1})$ vs $1/[T]$ (Fig. 6g) validate rate law 10 and allow separation of kinetic parameters k_1 and k_{-1} from equilibrium parameters β_1 and K_1 (Fig. 4). This adds to the store of k_1 and β_1 data for

monotransmetalation. It also allows comparison of k_{-1} data for the reverse of reactions 5, which, of course, describe metal exchange in the opposite direction.

The product of monotransmetalation of $(\mu_4\text{-O})\text{N}_4\text{Cu}_2(\text{NiH}_2\text{O})_2\text{Cl}_6$ with A ($M = \text{Zn}$) is $(\mu_4\text{-O})\text{N}_4\text{Cu}(\text{NiH}_2\text{O})_2\text{ZnCl}_6$. Analytical data indicate that copper in the whole family of targets $(\mu_4\text{-O})\text{N}_4\text{Cu}_{4-x}(\text{NiH}_2\text{O})_x\text{Cl}_6$ is specifically replaced by zinc (Ali-Shehri *et al.*, 1990). This is despite the fact that Zn (NS)₂ is thermodynamically capable of replacing either copper or nickel in these targets (Davies *et al.*, 1986c). Precursor and activated complex structures must account for transmetalation specificity. Another important finding is that there are no detectable products $\text{M}(\text{acac})\text{NS}$ from the reactions of $\text{Cu}(\text{acac})_2$ with $\text{M}(\text{NS})_2$, eq. 5. This indicates that transferring ligand donor atoms (one from each bidentate ligand acac and NS) are shared by the exchanging metals in the activated complex as shown below (Ali and Davies, 1990). First-order rate constant k_{-1} indicates very strong interaction between products $\text{M}(\text{acac})_2$ and $\text{Cu}(\text{NS})_2$ in successor complexes S, which are the primary metal exchange products and analogues of precursors P (Fig. 4).



The temperature dependences of β_1 , β_p , k_1 , k_{-1} , β_s and K_1 (symbols in eq. 5 and Fig. 4) reveal different precursors P and P' and different successor complexes S and S' in some systems at different experimental temperatures (see below and the examples in Figure 7). Those labelled P' and S' in Fig. 4 are favored at low experimental temperatures (Ali and Davies, 1990, 1991).

This detail is welcome because it completes more of the mechanistic picture. But we still have to appreciate what we are seeing in Fig. 3. We will start by comparing rates.

COMPARISON OF RATES

Table 1 lists kinetic data for 43 monotransmetalation events at 23°C in methylene chloride and nitrobenzene. All come from records like Fig. 3a. The sources are given in footnote e. We have calculated each k_{obsd} (sec^{-1}) by substituting $[T] = 10 \text{ mM}$ (a typical high experimental target concentration) into eq. 6b with the published rate constant and order n . Another 15 systems with calculated $k_{\text{obsd}} = 0.15 - 1.5 \text{ sec}^{-1}$ from the same sources are not included in Table 1. The data span a k_{obsd} range of about 25,000, with half-lives under the specified conditions from 7 msec to 3 min. Typical precision is $\pm 4\%$. Thus, several entries in Table 1 have essentially the same rate under the comparison conditions.

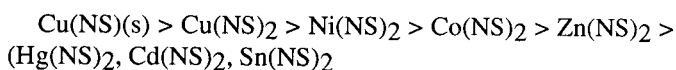
We might expect the least thermodynamically stable transmetalators to be the most reactive. This is at least partially true: the fastest known system is with transmetalator A ($M = \text{Hg}$), which is one of the least stable $\text{M}(\text{NS})_n$ complexes A in the order

Table 1
Fast and slow monotransmetalations of copper targets with M(NS)₂ Transmetalators A and B at [T] = 10 mM and 23°C in aprotic solvents^a

Entry	Target	TM	M ^b	Solvent	n ^c	k _{obsd} ^d	Ref ^e
(a) fast systems							
1	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	A	Hg	NB	2	98	1
2	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	A	Zn	NB	1	87	2
3	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	A	Co	NB	2	86	2
4	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	A	Zn	MC	2	48	2
5	(μ ₄ -O) N ₄ Cu ₄ Br ₆	B	Zn	MC	1	40	2
6	(μ ₄ -O) N ₄ Cu ₄ Br ₆	B	Zn	NB	1	39	2
7	(μ ₄ -O) N ₄ Cu(NiH ₂ O) ₃ Cl ₆	A	Ni	NB	2	36	3
8	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	A	CO	MC	2	34	2
9	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	B	Zn	NB	1	21	2
10	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	A	Zn	NB	2	16	2
11	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	A	Ni	MC	2	9.7	2
12	(μ ₄ -O) N ₄ Cu(NiH ₂ O) ₃ Br ₆	A	Zn	NB	0	7.3	3
13	(μ ₄ -O) N ₄ Cu(NiH ₂ O) ₃ Cl ₆	A	Zn	NB	<i>f</i>	5.6	3
14	(TEED) ₂ Cu ₂ Cl ₂	A	Co	MC	1	5.3	4
15	(TEED) ₂ Cu ₂ Cl ₂	A	Ni	MC	2	4.6	4
16	(μ ₄ -O) N ₄ Cu ₂ (NiH ₂ O) ₂ Cl ₆	A	Zn	NB	0	4.0	3
17	(TEED) ₂ Cu ₂ Cl ₂	A	Co	NB	1	3.7	4
18	(μ ₄ -O) N ₄ Cu(NiH ₂ O) ₃ Cl ₆	A	Co	NB	<i>f</i>	3.6	3
19	(μ ₄ -O) N ₄ Cu ₄ Br ₆	A	Zn	NB	1	2.8	2
20	(TEED) ₂ Cu ₂ Cl ₂	A	Co	NB	1	3.5	4
21	(TEED) ₂ Cu ₂ Cl ₂	A	Ni	NB	2	2.3	4
22	(μ ₄ -O) py ₄ Cu ₄ Cl ₆	A	Ni	NB	2	1.9	2
23	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	A	Ni	NB	2	1.6	2
(b) slow systems							
24	(TEED) ₂ Cu ₂ Br ₂ CO ₃	A	Ni	NB	2	0.14	5
25	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	B	Ni	NB	1	0.13	2
26	(TEED) ₂ Cu ₂ Cl ₂ CO ₃	A	Ni	NB	2	0.11	5
27	(μ ₄ -O) N ₄ Cu ₃ NiH ₂ OCl ₆	A	Zn	NB	0	0.10	6
28	(TEED) ₂ Cu ₂ Br ₂	A	Ni	MC	2	0.083	4
29	(TEED) ₂ Cu ₂ Br ₂	A	Ni	NB	1	0.060	4
30	(μ ₄ -O) N ₄ Co ₃ CuCl ₆	A	Zn	NB	1	0.055	3
31	(TEED) ₂ Cu ₂ Br ₂ O	A	Ni	NB	1	0.052	5
32	(TEED) ₂ Cu ₂ Br ₂ CO ₃	A	Co	NB	1	0.045	5
33	(μ ₄ -O) N ₄ Cu ₄ Cl ₆	B	Ni	MC	1	0.038	2
34	(TEED) ₂ Cu ₂ Cl ₂ O	A	Co	NB	1	0.027	5
35	(μ ₄ -O) N ₄ Cu ₄ Br ₆	A	Ni	NB	2	0.025	2
36	(TEED) ₂ Cu ₂ Cl ₂ CO ₃	A	Ni	NB	1	0.024	5
37	(TEED) ₂ Cu ₂ Cl ₂ CO ₃	A	Zn	NB	0	0.023	5
38	(TMPD) ₂ Cu ₂ Cl ₂ O	A	Ni	NB	1	0.011	5
39	(TEED) ₂ Cu ₂ Br ₂ CO ₃	B	Ni	NB	1	0.0063	5
40	(TMED) ₂ Cu ₂ Cl ₂ CO ₃	B	Ni	NB	1	0.0063	5
41	(TEPD) ₂ Cu ₂ Cl ₂ CO ₃	A	Co	NB	0	0.0046	5
42	(TMPD) ₂ Cu ₂ Br ₂ CO ₃	A	Co	NB	1	0.0040	5
43	(TEED) ₂ Cu ₂ Cl ₂ CO ₃	A	Co	NB	0	0.0039	5

^a Abbreviations: N = N,N'-diethylnicotinamide; NB = nitrobenzene; MC = methylene chloride; TEED = N,N,N',N'-tetraethylethylenediamine; TMED = N,N,N',N'-tetramethylethylenediamine; TMPD = N,N,N',N'-tetramethyl-1,3-propanediamine;

^b M is the metal in transmetalator A or B; ^c In rate law 6; ^d Units are sec⁻¹; ^e References: 1, Abu-Raqabah *et al.*, 1989, Davies *et al.*, 1986b; 3, Al-Shehri *et al.*, 1990a; 4, Davies *et al.*, 1988a; 5, Davies *et al.*, 1988b; 6, Al-Shehri *et al.*, 1990b; ^f Rate law 7 applies.



(Davies *et al.*, 1986c; Abu-Raqabah *et al.*, 1989). We find that the fastest and slowest reactions in Table 1a are those with metals Hg and Ni, respectively, which points to transmetalator stability as an important rate-determining factor.

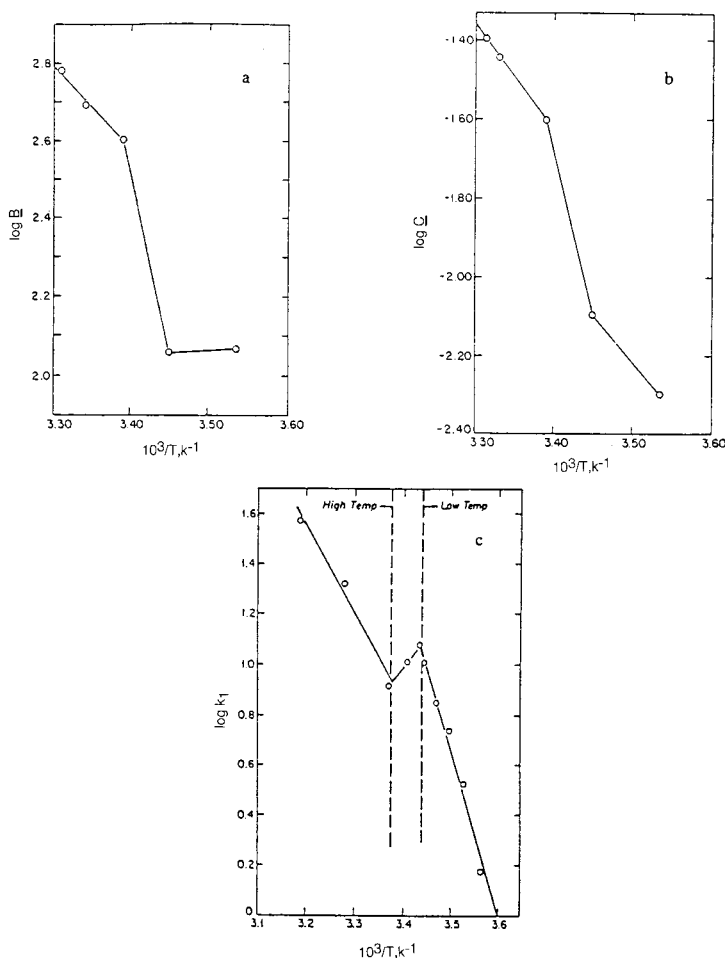


Fig. 7: Temperature dependences of parameters (a) $B = \beta_1$ and (b) $C = k_{-1}$ for the reaction of $\text{Cu}(\text{acac})_2$ with A ($M = \text{Ni}$) in methylene chloride. The plots indicate the existence of two precursors and two successor complexes in this system (Fig. 4) (Ali and Davies, 1990); (c) temperature dependence of k_1 in the reaction of $(\mu_4\text{-O})\text{N}_4\text{Cu}(\text{NiH}_2\text{O})_3\text{Cl}_6$ with A ($M = \text{Zn}$) in nitrobenzene. The data indicate the existence of two reaction precursors (Al-Shehri *et al.*, 1990a).

The most reactive $A(M = \text{Hg})$ would be a great transmetalator except for the fact that primary product $(\mu_4\text{-O})\text{N}_4\text{Cu}_3\text{HgCl}_6$ very rapidly loses NHgCl_2 to give $(\mu_3\text{-O})\text{N}_3\text{Cu}_3\text{Cl}_4$. This is a disadvantage because there are more potential transmetalated derivatives $(\mu_4\text{-O})\text{N}_4(M, M', M'', M''')_4\text{X}_6$ than $(\mu_3\text{-O})\text{N}_3(M, M', M'')_3\text{X}_4$ (Abu-Raqabah *et al.*, 1989). Primary product fragmentation explains why we

have not worked extensively with $A(M = \text{Hg})$. Nevertheless, the form of the rate law for entry 1 indicates that monotransmetalation is the slowest step in the production of $(\mu_3\text{-O})\text{N}_3\text{Cu}_3\text{Cl}_4$.

Complexes B appear to be more thermodynamically stable than A with the same M. The actual stability order for B has not been established but is probably much the same as with A. Consistent with this idea, we find that the six fastest known events are with metals Co, Zn and Hg that form the weakest complexes A. Other notable features of Table 1a are as follows.

Eighteen of the fastest known events are with copper(II) targets $(\mu_4\text{-O})\text{N}_4\text{Cu}_4\text{X}_6$ or their transmetalated derivatives. These especially labile targets commend reactions 1 for synthesis. The remainder in Table 1a are the earliest events in the reactions of copper(I) $\text{L}_2\text{Cu}_2\text{Cl}_2$ targets with various A, which are not transmetalations because the slowest overall step is precipitation of co-product $\text{Cu}(\text{NS})(s)$ (Davies *et al.*, 1988a). Data pairs (14, 15) and (20, 21) indicate little effect on the rate of changing M in A (but the rate law changes), that changing L can affect the rate with fixed M in the same rate law and that changing the solvent has little effect on the rate (see also data pair 5, 6).

Data pairs (2, 3), (4, 5), (9, 10) and (20, 21) indicate that you can change M and NS, X and NS, NS, or L and M, respectively, and observe the same rate but a different rate law. The rate law is different with X = Cl and Br in the target $(\mu_4\text{-O})\text{N}_4\text{Cu}_4\text{X}_6$ (12, 13), but changing the N ligand in $(\mu_4\text{-O})\text{N}_4\text{Cu}_4\text{Cl}_6$ has essentially no effect (22, 23).

Eleven of the fastest reactions have a third-order rate law (eq. 6a, $n = 2$). Of these, six involve relatively stable complex $A(M = \text{Ni})$. By contrast, only five systems in Table 1b have a third-order rate law and all involve $A(M = \text{Ni})$. Thus, third-order events tend to be fast (despite the different stabilities of A) and essentially planar transmetalator $A(M = \text{Ni})$ has a preference for third-order events. These events all involve very weak complexes $\text{TM}\cdot\text{T}_2$ but we have no idea of their relative stabilities because of the form of the rate law. Perhaps the most fragile precursors have the highest metal exchange rates (Al-Shehri *et al.*, 1990)? Third-order behavior is never observed with transmetalators B despite the square planar geometry of B ($M = \text{Ni}$) (Davies *et al.*, 1988b). However, there is evidence for the involvement of terminal target X in $\text{B}\cdot\text{T}$ precursors (El-Sayed and Davies, 1990).

Changing the solvent for the slower reactions can change the order with little effect on the rate (data pair 28, 29). Altering NS causes a large decrease in rate and changes the rate law (11, 33), but altering X sometimes just lowers the rate (11, 35).

Seventeen of the entries in Table 1b are for copper(II) complexes $\text{L}_2\text{Cu}_2\text{X}_2\text{Y}$, which have strong bridging systems (Fig. 2a). For this reason they are relatively unreactive targets. Changing the bridging system or ligands L may not have much effect on the rate, but it can change the rate law (entries 38-43).

It is interesting to find that monotransmetalation rate laws are different: transmetalators TM can associate quite differently with the same T (Davies *et al.*, 1986a; 1988b). A knowledge of rates as a function of target and transmetalator is useful for synthetic strategy. However, rate comparisons

have limited mechanistic utility because different systems have different rate laws and quite subtle experimental variations can change both rate law and rate. Rate law 6 gives no separate information about reactant preassociation or the primary products of metal exchange (Al-Shehri *et al.*, 1990a). We have to employ a different strategy for thinking about systems with rate law 6.

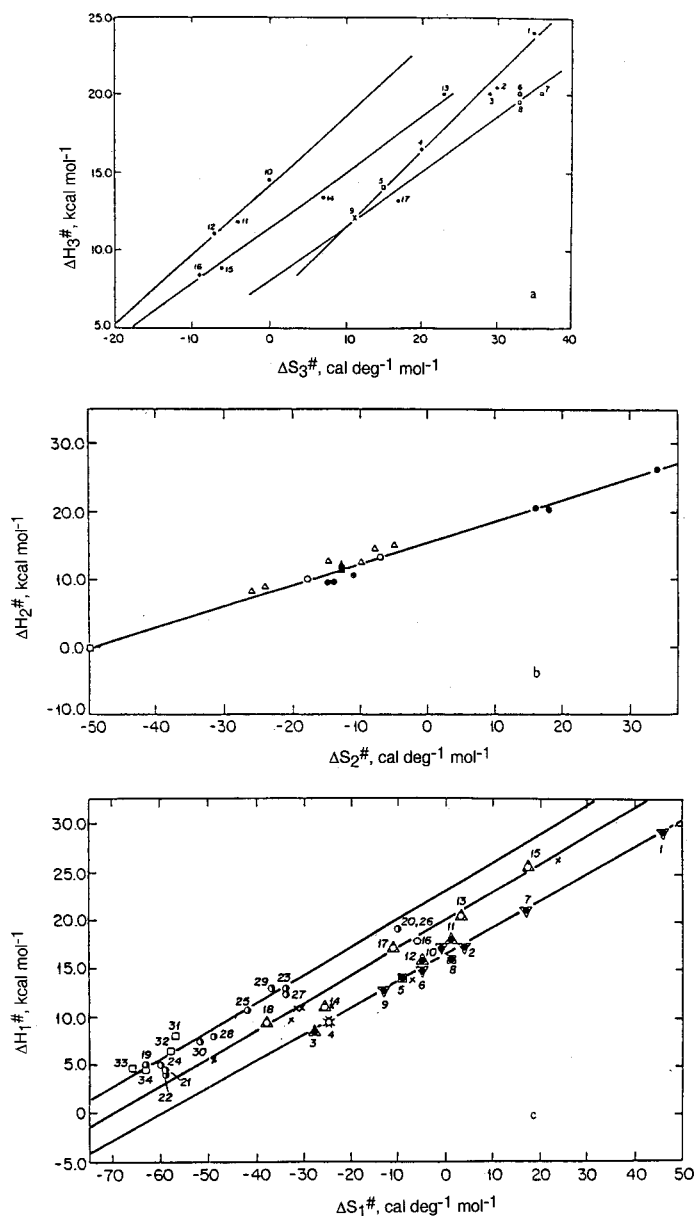


Fig. 8: Enthalpy-entropy correlations for (a) third-order events (Al-Shehri *et al.*, 1990a); (b) second-order events (Davies *et al.*, 1988b; Al-Shehri *et al.*, 1990b); and (c) first-order monotransmetalation and isomerization systems (Fig. 11 of Al-Shehri *et al.*, 1990a has been supplemented with data (x) from Table 1 of Ali and Davies, 1991).

ASSIGNMENT THROUGH ACTIVATION PARAMETER CORRELATIONS

Activation parameter plots are useful for examining systems with the same order to see if they have common features. Plots for simple third-, second-, and first-order processes (that is, with $n = 2, 1$ or 0 in eq 6 or with $\beta_1 [T] \ll$

1 or $\beta_1 [T] \gg 1$ in eq 7 or 10), Figure 8, reveal compensated enthalpy and entropy changes. This characteristic feature of transmetalation reactions is taken to indicate thermodynamic and kinetic components of β_n and k_1 that vary in a correlated manner with common slow steps for each event (Davies *et al.*, 1988b; Davies, 1989; Al-Shehri *et al.*, 1990a).

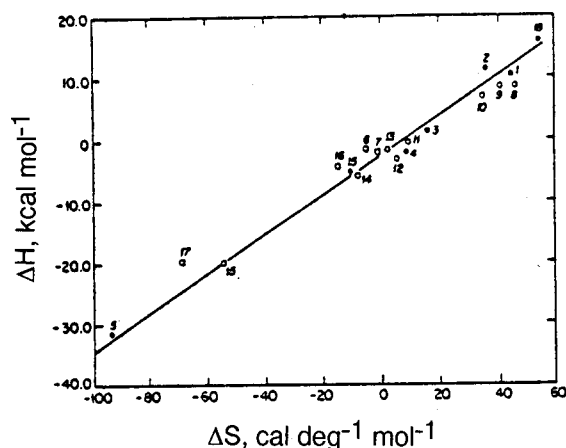


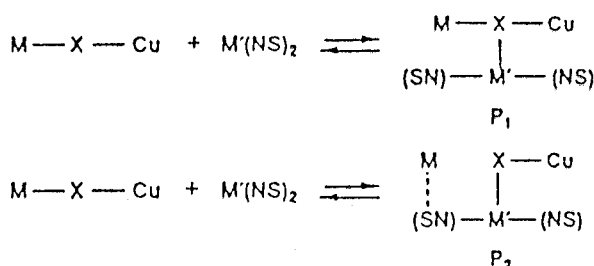
Fig. 9: Plot of ΔH vs ΔS for all known measurable equilibrium parameters in real and model monotransmetalation reactions (Ali and Davies, 1991).

Enthalpy and entropy changes associated with measurable precursor P formation by different T and TM are strongly correlated (Fig. 9). Net bond breaking or making in precursor formation thus leads to predictable entropy changes. The same effects are indicated by Figures 8a and 8b, which embody inseparable thermodynamic and kinetic activation factors in the measured slow step. Again we see that bond breaking on activation leads to predictable entropy increases.

Our understanding has improved with the accumulation of data for many different systems. We will now consider each experimental reaction order in turn, starting with third-order events.

Third-order Events

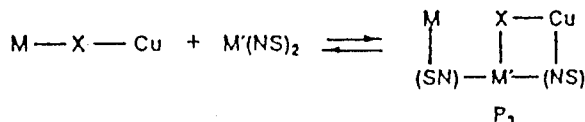
The correlations for observed third-order events in Figure 8a have slopes of 500 ± 20 and 370 ± 20 K, respectively. The first line from the left correlates data for the transmetalation of targets $L_2Cu_2X_2Y$ ($Y = CO_3$) that are known to contain terminal X (Davies *et al.*, 1988b). The second line from the left is for the earliest events in the transmetalation of copper(I) targets $L_2Cu_2X_2$ that contain no terminal X (Davies *et al.*, 1988a). The separable, parallel lines in Figure 8a indicate that we can sub-classify the data and suggest that 1) the first and third lines from the left refer to precursors P₂ containing terminal halide X in T;



and 2) the structures of either "half" of precursors $TM \cdot T_2$ can be changed from P_1 to P_2 by changing T to one that contains or can generate terminal X , by using low stability transmetalators A ($M = Co$ or Zn : Davies *et al.*, 1986c) or by replacing some of the copper in target $(\mu_4-O)N_4Cu_4Cl_6$ with $Ni(H_2O)$ centers.

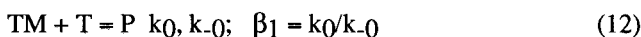
The structures of P_1 and P_2 differ in the extent of competition between M and M' for bridging X ($M-X-Cu$ represents an intact target edge). Stronger $M'-X$ bonding favors P_2 . These ideas are fairly firm despite the fact that $TM \cdot T_2$ precursors are generally too weak to characterize thermodynamically. Absorbance increases for $Cu(NS)_2$ production in all known third-order events and the involvement of relatively stable transmetalator A ($M = Ni$) in most of them imply metal exchange within weak precursors $TM \cdot T_2$ as the observed slow step. But $TM \cdot T_2$ structures are a mystery: the "halves" of the interaction could be different (Al-Shehri *et al.*, 1990a). Very recent work with dithiophosphate transmetalators $M(PS)_2$ indicates that metal exchange in characterizable $TM \cdot T_2$ precursors may only be a little slower than in $TM \cdot T$ with TM and T common (Ali *et al.*, 1993).

So, third-order events refer to metal exchange in weak precursors $TM \cdot T_2$ with different structures like P_1 and P_2 . Proposed P_2 has the structural features needed for specific copper replacement (Al-Shehri *et al.*, 1990). It contains only weak $M-(NS)$ bonds. Stronger bonding of this sort would favor $TM \cdot T$ precursors like P_3 and either second- or first-order behavior, depending on the magnitude of β_1 .



Second-Order Events

Second-order behavior is quite common in transmetalation systems (Davies *et al.*, 1988b and Table 1). The very good correlation of second-order data is shown in Fig. 8b. Its slope and intercept are $a = 325 \pm 20$ K and $b = 15 \pm 1$ kcal mol⁻¹, respectively. There is no particular grouping of targets and transmetalators, but the correlation suggests a common slow step. Precursor formation and metal exchange in a thermodynamically weak precursor $TM \cdot T$ would both be second-order. The "product" could be P , S or rapidly dissociating S . The following model helps us decide which is the more likely observed step.



Assumption of a steady state for $[P]$ gives eq 14, which has two limits. One is $k_{-0} \gg k_1$.

$$\text{rate} = k_0 k_1 [TM][T]/(k_{-0} + k_1) \quad (14)$$

This leads to eq. 15, which is of the same form as eq. 6a with $n = 1$ and $k_2 = \beta_1 k_1$. Eq. 15 corresponds to rate-determining reaction 13. The second limit has $k_{-0} \ll k_1$ and leads to eq. 16. Formation of P is now the slowest

process. The experimental activation parameters associated with these limits are given by eqs. 17 and 18, respectively. Eq 18 implies no relationship of ΔH_2^\ddagger or ΔS_2^\ddagger with any thermodynamic quantities $\Delta H\beta_1$ or $\Delta S\beta_1$ that can be extracted from systems with rate law 7 or 10. We will assign the second-order data in Fig. 8b with this idea in a later section.

$$\text{rate} = (k_0 k_1 / k_{-0}) [TM][T] = \beta_1 k_1 [TM][T] \quad (15)$$

$$\text{rate} = k_0 [TM][T] \quad (16)$$

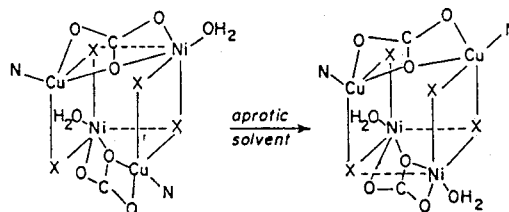
$$\Delta H_2^\ddagger = \Delta H\beta_1 + \Delta H_1^\ddagger; \quad \Delta S_2^\ddagger = \Delta S\beta_1 + \Delta S_1^\ddagger \quad (17)$$

$$\Delta H_2^\ddagger = \Delta H_0^\ddagger; \quad \Delta S_2^\ddagger = \Delta S_0^\ddagger \quad (18)$$

First-order Systems

First-order behavior is often seen in the transmetalation of copper(II) targets, but has never been observed with copper(I) (Davies *et al.*, 1988b). It arises either from eq 6b with $n = 0$ (Fig. 6c), from eq 7 or 10 at large $\beta_1[T]$ or for $S \rightarrow P$ and $S \rightarrow S'$ processes (Fig. 3b, 4 and 5). We have supplemented Fig. 11 of (Al-Shehri *et al.*, 1990b) with first-order metal exchange and $S \rightarrow P$ data from Table 1 of Ali and Davies (1991) to get Fig. 8c. Eight of nine new points fit the middle plot of Fig. 8c, which refers to first order monotransmetalation of targets $L_2Cu_2X_2Y$ ($Y=O$ or CO_3). The latter contain terminal X and we took the correlation to indicate that $L_2Cu_2X_2O$ targets can supply terminal X for precursor formation, perhaps as in P_3 (Davies *et al.*, 1988b). The correlation in Fig. 8c supports the structures of precursors and successors shown in Fig. 4 for reactions 5.

All the lines in Fig. 8c have slope $d = 300 \pm 25$ K. The top line in Fig. 8c refers to first-order isomerizations of the type shown below (Davies *et al.*, 1986d), which require substantial bond-breaking. This confirms that target requirements play a major role in determining the energetics of monotransmetalation reactions. However, it is still hard to pinpoint rate contributions from different transmetalators.



Events with Separable Thermodynamic and Kinetic Components

The discovery of rate laws 7 and 10 was a real breakthrough in our search for transmetalation mechanisms: it allows the separation of thermodynamic (β_1 , K_1) from kinetic (k_1 , k_{-1}) factors and separate consideration of their associated enthalpy and entropy changes.

The kinetic components of rate laws 7 and 10 are correlated in Fig. 8c. Fig. 9 (Ali and Davies, 1991) demonstrates correlated enthalpy and entropy changes on precursor and successor complex formation. Its slope and intercept are $c = 310 \pm 20$ K and $w = -3 \pm 1$ kcal mol⁻¹, respectively. These data can be used with the slope $d = 300 \pm 25$ K and intercept $x = 17 \pm 1$ kcal mol⁻¹ of the bottom plot in Fig. 8c to assign the data for second-order transmetalations in Fig. 8b as follows.

The correlations in Fig. 8c and 9 are given by eqs 19 and 20, respectively. Suppose the correlation in Fig. 8b is given by eq. 21.

$$\Delta H_1^\ddagger = d\Delta S_1^\ddagger + x \quad (19)$$

$$\Delta H\beta_1 = c\Delta S\beta_1 + w \quad (20)$$

$$\Delta H_2^\ddagger = \Delta H\beta_1 + \Delta H_1^\ddagger = a\Delta S_2^\ddagger + b = a(\Delta S\beta_1 + \Delta S_1^\ddagger) + b \quad (21)$$

We then predict that $a = c = d$ and that $w + x = b$. The predictions are satisfied within experimental error, indicating that all the second-order systems correlated in Fig. 8b have metal exchange as the slowest step.

Experimental parameters ΔH_2^\ddagger and ΔS_2^\ddagger range from 0 to 23 kcal mol⁻¹ and from -50 to 33 cal deg⁻¹ mol⁻¹, respectively, because their thermodynamic and kinetic components change in a correlated manner with different T and TM. However, no single property of T or TM determines their magnitude (Fig. 8c and 9: Ali and Davies, 1991).

The Origin of Second- and First-order Rate Laws

The stability of precursors like P₃ varies with its constituents, as reflected by the magnitude of β_1 . The latter is quite sensitive to its thermodynamic parameters. For example, β_1 decreases from 500 to 5 with an increase of $\Delta H\beta_1$ from 10.3 to 11.4 kcal mol⁻¹ at $\Delta S\beta_1 = 44$ cal deg⁻¹ mol⁻¹ (see Table 1 of Ali and Davies, 1991). A β_1 of 500 would result in rate law 7 or 10, while $\beta_1 = 5$ gives second-order behavior under typical conditions. Enthalpic variations like these are possible even in closely similar systems.

REACTION PROFILES

Reaction profiles describe the sequence of events that connects reactants to ultimate products. They can be constructed for reversible systems with separable thermodynamic and kinetic components (as in Fig. 4 and 6f) and compared with those for irreversible transmetalation of polymetallic targets (Fig. 6d). Typical results (Fig. 10: Ali and Davies, 1991) show commonalities (for example between profiles 2, 3, 5 and 6) that point to rate-determining metal exchange. The similar profiles in Fig. 10 commend the use of reactions like 5 as models for monotransmetalation but we still lack understanding of monotransmetalation successors that might slowly rearrange (Fig. 3b and 5). For this reason we leave synthetic scale reactions for many half-lives (6-12hrs) before product isolation (Davies et al., 1988a). Ongoing work addresses the question of successor structures and seeks to model profiles like 7 and the extreme points in Fig. 8b.

A GENERAL TRANSMETALATION MECHANISM

Precursor structures like P' (Fig. 4), P₂ and P₃ are explanations of how transmetalation is organized and the origin of its specificity. Transmetalation selectivity (eq 4 and the rate differences in Table 1) is associated in some way with the thermodynamic stability of transmetalators M(NS)₂ (Davies et al., 1986c). This suggests that opening of NS chelate rings can occur on precursor formation (Fig. 4), as implied in our comparison of rates and consideration of P₂

and P₃. We end our discussion with some new information that bears directly on this question.

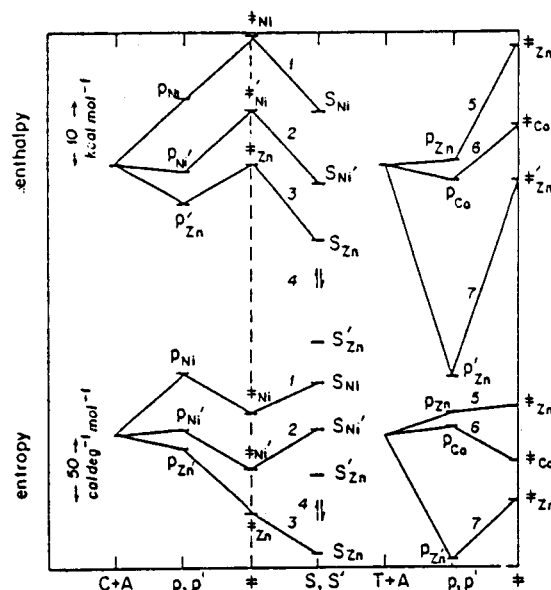
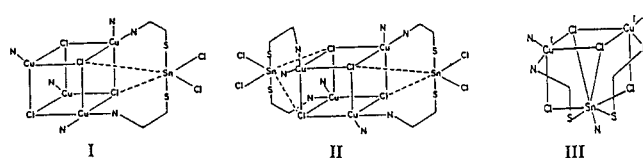


Fig. 10: Enthalpy and entropy profiles for reversible reactions of Cu(acac)₂ with A (M = Ni and Zn) (left column) and for irreversible transmetalation (μ_4 -O)₄N₄Cu(NiH₂O)₃Cl₆ with A (M = Co and Zn). The respective profiles are obtained from experiments at different temperatures (Ali and Davies, 1991).

Electronic and PMR spectral data, cryoscopic measurements and the time dependence of co-product Cu(NS)(s) precipitation indicate that species I and II are precursors in the transmetalation of copper(I) target [NCuCl]₄ with tin(IV) transmetalator Sn(NS)₂Cl₂ and that the product of reaction of the same target with Sn(NS)₄ is molecule III. Here, NS is S-methyl isopropylidenehydrazinecarbodithioate, as in transmetalators A (Abu-Raqabah et al., 1992).



The structures of I-III point to transmetalation as a special kind of ligand exchange.

The proposed transmetalation sequence is summarized in Fig. 11. Ligands N on target Cu have been omitted, are framework atoms (Fig. 2a) and the italic numbers represent likely coordination numbers of Cu and M. The sequence is organized by the target framework and by M's preference for one target site.

Halogen atoms X provide a foothold for precursor formation that results in an increase of coordination number at transmetalator metal M. The stoichiometry and extent of precursor formation (β_n) depend on the coordinative

unsaturation and geometry of M and its affinity for . They vary from one system to another.

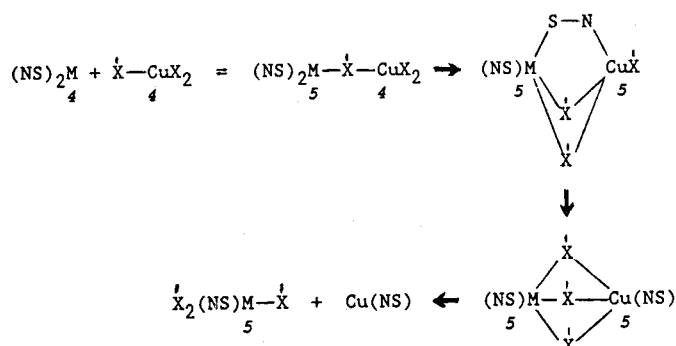


Fig. 11: Proposed mechanism for the reaction of [NCuX]₄ with M(NS)₂ transmetalators. Ligand N is omitted and X are target framework atoms (Fig. 2a). Italic numbers give likely coordination numbers (Abu-Raqabah *et al.*, 1992).

An increase of metal M coordination number weakens M-N and M-S bonds in M(NS)_n. Transfer of NS ligands to Cu then proceeds in steps. The kinetic part of the mechanism probably begins with M-N bond breaking (see I-III: Abu-Raqabah *et al.*, 1992). Breaking M-N bonds lowers the coordination number of M, which now bonds more strongly to foothold ligands X. But Cu-X bonds are weakened by a higher coordination number of Cu on bonding to NS. The result is net replacement of Cu-X bonds with M-X bonds.

Transmetalation is almost complete when an entire NS ligand has been transferred from (NS)_n to Cu to give ≡Cu(NS)Cl₃M(NS)_{n-1}. This species contains one Cu with a higher coordination number than for the other metals in T. With copper(I) targets, the time-dependence of Cu(NS)(s) co-product formation (see, for example, Abu-Raqabah *et al.*, 1992) indicates slow fragmentation of an intermediate containing ≡Cu(NS). Fragmentation as in eq 4 is slow because the coordination number of copper(I) is not impossibly high and strong Cu-Cl bonds have to be broken (Davies *et al.*, 1988a).

All established copper(II) targets contain five-coordinate metal centers (Fig. 2a). Transfer of one complete NS ligand from M(NS)_n would give a seven-coordinate copper(II) center in an active site like (O,N)Cu(NS)Cl₃M(NS)_{n-1}. Copper(II) transmetalation is driven by formation of Cu(NS)₂, but the transfer of just one atom of a second NS ligand would give unprecedented eight-coordinate copper(II). Loss of the copper(II) ligand N might relieve steric congestion (we know that polynuclear copper(II) complexes that contain strongly held amine ligands are poor transmetalation targets (El-Sayed *et al.*, 1992b)). These considerations help to explain the rapid production of Cu(NS)₂ in transmetalations of labile copper(II) targets with labile M(NS)₂ reagents: there is a very marked decrease in Cu^{II}-X bond strengths on NS ligand transfer to copper(II) to increase its coordination number above five.

Fig. 11 has two or three possible slow metal exchange steps. Fig. 8 and 10 imply that they are part of the same net

process but that the rate of any one of them varies with the reaction partners. For any two reactants, new bond breaking leads to about the same entropy increase (Ali and Davies, 1991).

Direct transmetalation is remarkable because the target framework is maintained while M-X bonds are being replaced with M'-X bonds. It is valuable because it generates large heteropolymetallic families. Labile targets and transmetalators in stoichiometric reactions will extend transmetalation to many more elements. Its role in materials and catalytic applications seems assured.

ACKNOWLEDGEMENTS

We gratefully acknowledge the United States National Science Foundation (Grants CHE-8717556, INT-9100117 and INT-9203819) and the Petroleum Research Fund, administered by the American Chemical Society (Grant 24132-AC3-C) for financial support of our work. A. A., S. A.-S., N. E.-K., M. A. E.-S. and A. E.-T. thank their respective institutions for study leave to participate in this project. This is contribution number 532 from the Barnett Institute of Chemical Analysis and Materials Science at Northeastern University.

REFERENCES

- Abdel-Fattah, T.M. and G. Davies, 1993. Treatment of dehydrated Na-Y zeolite with the heteropolymetallic products of transmetalation reactions. In: Multifunctional mesoporous inorganic solids. C. A. C. Sequiera, ed. Dordrecht. Kluwer, in press.
- Abdel-Fattah, T.M., G. Davies, K. J. Balkus, Jr. and J. Leiton, 1993. Highly Selective Zeolite-Encapsulated Heteropolymetallic Catalysts Made from Transmetalation products. J. Amer. Chem. Soc., submitted.
- Abu-Raqabah, A., G. Davies, M. A. El-Sayed, A. El-Toukhy and M. Henary, 1989. Limits of direct transmetalation of polynuclear copper(II) complexes with M(NS)_n reagents. Scissor transmetalators. Synthesis and properties of trimers (μ₃-O)(N,py)₃Cu₃X₄. Inorg. Chem., 28: 1156-1166.
- Abu-Raqabah, A., G. Davies, M. A. El-Sayed, A. El-Toukhy, S. Shaikh, and A. Zubieta, 1992. Transmetalation of tetranuclear copper complexes with tin transmetalators. Molecular structure of *cis*-dichloro-*bis*-(*trans*-S-methyl isopropylidenehydrazinecarbodi-thioato)tin(IV) and consideration of transmetalation mechanisms. Inorg. Chim. Acta, 193: 43-56.
- Adams, R.D., 1990. Metal cluster complexes containing heteroatom-substituted carbene ligands. Chem. Rev., 89: 1703-1712.
- Ali, A. and G. Davies, 1990. Products and kinetics of the reactions of *bis*-(acetylacetonato) copper(II), Cu(acac)₂, with Ni(NS)₂ in methylene chloride. Inorg. Chim. Acta, 177: 167-178.
- Ali, A. and G. Davies, 1991. Co-operativity in the transmetalation of Cu(acac)₂ with Co(NS)₂ and Zn(NS)₂ reagents in methylene chloride. Inorg. Chim. Acta, 179: 245-254.

- Ali, A., H. Abo-El-Dahab and G. Davies, 1993. Stoichiometry and kinetics of transmetalations with dithiophosphate transmetalators, in preparation.
- Al-Shehri, S., G. Davies, M. A. El-Sayed and A. El-Toukhy, 1990a. Products and kinetics of the direct transmetalation of $(\mu_4\text{-O})\text{N}_4\text{Cu}(\text{Ni}(\text{H}_2\text{O}))_3\text{Cl}_6$ (N is N,N-diethylnicotinamide) by $\text{M}(\text{NS})_n$ reagents (NS is S-methyl isopropylidenehydrazinecarbodithioate) in nitrobenzene: A relationship between precursor stabilities and product formation rates. *Inorg. Chem.*, 29: 1198-1205.
- Al-Shehri, S., G. Davies, M. A. El-Sayed and A. El-Toukhy, 1990b. Rate law variations in the specific monotransmetalation of $(\mu_4\text{-O})(\text{N},\text{py})_4\text{Cu}_{4-x}\text{M}_x\text{X}_6$ complexes with $\text{Zn}(\text{NS})_2$ in nitrobenzene. *Inorg. Chem.*, 29: 1206-1210.
- Al-Shehri, S., G. Davies, M. A. El-Sayed and A. El-Toukhy, 1993. Kinetics and mechanisms of complexation of polymeric targets with transmetalation product $\text{Cu}(\text{NS})_2$, in preparation.
- Andres, R.P., W. L. Averback, L. E. Brown, W. A. Goddard, A. Kaldor, S. G. Louie, M. Moscovits, P. S. Peercy, S. J. Riley, R. W. Siegel, F. Spaepen, and Y. Wang, 1989. Research opportunities in clusters and cluster-assembled materials. DOE Report, 4: 704-712.
- Bender, R., P. Braunstein and C. de Meric de Bellefon, 1988. Electronic and steric effects in closely related heteronuclear complexes. Selective pathways in synthetic and catalytic bimetallic chemistry. *Polyhedron*, 7: 2271-2283.
- Braunstein, P., 1988. Clusters moléculaires: matériaux, architectures, finalités. *New J. Chem.*, 10: 367-386.
- Braunstein, P., J. Rose and A. Tiripicchio, 1992. Hexa- and nonanuclear heterometallic clusters based on mercury-capped MCo_3 (M = Fe or Ru) tetrahedral units. *J. Chem. Soc. Dalton Trans.*, 911-920.
- Caulton, K.G., G. Davies, and E. M. Holt, 1990. Synthesis, structures, physical properties and reactions of halo (amine) copper(I) complexes. *Polyhedron Report* 33: *Polyhedron*, 9: 2319-2351.
- Davies, G., A. El-Toukhy, K. D. Onan, and M. Veidis, 1984. Transmetalation reactions of tetranuclear copper (II) complexes. 1. Stoichiometry and the crystal structures of two products of reaction of $(\text{DENC})\text{Cu}_4\text{Cl}_4\text{O}_2$ (DENC = N,N-diethylnicotinamide) with $\text{Zn}(\text{NS})_2$ complexes (NS is a hydrazinato-S-Methyl carbodithioate Schiff base) in aprotic solvents. *Inorg. Chim. Acta*, 84: 41-50.
- Davies, G., M. A. El-Sayed and El-Toukhy, 1986a. Transmetalation of tetranuclear copper complexes. 4. Structural implications of the kinetics of direct transmetalation of tetranuclear copper(II) complexes by Ni (NS)₂ reagents. *Inorg. Chem.*, 25: 1925-1929.
- Davies, G., M.A. El-Sayed, and A. El-Toukhy, 1986b. Transmetalation of tetranuclear copper complexes. 9. Stoichiometry and kinetics of transmetalation of $(\mu_4\text{-oxo})[\text{NCu}]_4\text{X}_6$ complexes by $\text{M}(\text{NS})_2$ reagents in aprotic solvents. *Inorg. Chem.*, 25: 3899-3903.
- Davies, G., M. A. El-Sayed, A., El-Toukhy, M. Henary, T. S. Kasem and C. A. Martin, 1986c. Selective transmetalation and demetalation of heteropolynuclear metal complexes. *Inorg. Chem.*, 25: 3904-3909.
- Davies, G., M. A. El-Sayed, A., El-Toukhy, M. Henary and C. A. Martin, 1986d. Distinguishable sites in tetranuclear oxocopper(II) complexes $(\text{py})_3\text{Cu}_4\text{Cl}_4\text{O}_2$ and $(\text{DENC})_3\text{Cu}_3\text{M}(\text{H}_2\text{O})\text{Cl}_4\text{O}_2$ (M = Co, Ni, Cu, Zn). *Inorg. Chem.*, 25: 4479-4487.
- Davies, G., N. El-Kady, M. A. El-Sayed, A., El-Toukhy and M. R. Schure, 1988. The kinetics of primary events in the reactions of $\text{L}_2\text{Cu}_2\text{X}_2$ complexes with $\text{M}(\text{NS})_2$ reagents. *Inorg. Chem. Acta*, 149: 31-43.
- Davies, G., M. A. El-Sayed and El-Toukhy, 1989. Transmetalation: a new route to heteropolymetallic molecules and materials. *Comments Inorg. Chem.*, 8: 203-220.
- Davies, G., 1989. Correlation of activation parameters and the case of substitution controlled reduction of $\text{CoOH}_{\text{aq}}^{2+}$ and $\text{Co}(\text{NH}_3)_2\text{OH}_{\text{aq}}^{2+}$. Implications for electrocatalysis by aquocobalt(III) and other strongly oxidizing metal species. *Inorg. Chem. Acta*, 160: 83-86.
- Davies, G., B. C. Giessen, and H. L. Shao, 1991. Single-phase $\text{Cu}_{.50}\text{Ni}_{.50}$ alloy preparation by thermolysis of a simple heteropolymetallic precursor. *Materials Letters*, 9: 231-234.
- Davies, G., M. A. El-Sayed and El-Toukhy, 1992. Transmetalation and its applications. *Chem. Soc. Reviews*, 21: 101-104.
- Davies, G., B. C. Giessen, and H. L. Shao, 1992. Mixed metal oxide synthesis by thermolysis of simple heteropolymetallic precursors in dioxygen. *Mater. Res. Soc. Symp. Proc.*, 249: 87-93
- El-Sayed, M.A. and G. Davies, 1990. Stoichiometry, products and kinetics of monotransmetalation and complexation of dimeric complexes $[\text{N}_2\text{CuCl}_2]_2$ and $[\text{N}_2\text{NiCl}_2]_2$ (N is N,N-diethylnicotinamide) with $\text{M}(\text{NS})_2$ reagents in nitrobenzene. *Inorg. Chim. Acta*, 173: 163-173.
- El-Sayed, M.A. A. Abu-Raqabah and G. Davies, 1992a. Effects of transmetalation on the mechanisms of copper-catalyzed phenolic oxidative coupling. *Inorg. Chim. Acta*, 192: 31-42.
- El-Sayed, M.A., A. Ali, A. Davies, S. Larsen and J. Zubieta, 1992b. Properties and reactions of tetranuclear copper(I) complexes $[\text{LCuX}]_4$ (L = N,N-diethylaminomethylferrocene; X = Cl and Br). Crystal and molecular structure of $(\mu_4\text{-O})\text{L}_4\text{Cu}_4\text{Cl}_6$. *Inorg. Chim. Acta*, 194: 139-149.

- El-Toukhy, A. G. Z. Cai, G. Davies, T. R. Gilbert, K. D. Onan, and M. Veidis, 1984.** Transmetalation reactions of tetranuclear copper complexes 2. Stoichiometry and products of reaction of [(DENC)CuCl]₄O₂, [(DENC)CuCl]₄(CO₃)₂, (DENC)₄Cu₄Cl₆O and [(DENC)CuCl]₄Cl₄ complexes (DENC = diethylnicotinamide) with Ni(NS)₂ complexes (NS is a hydrazinato-S-methyl carbothioate Schiff base), the kinetics of product isomerization in aprotic solvents and inhibition of copper-catalyzed phenolic oxidative coupling by dioxygen through transmetalation. *J. Amer. Chem. Soc.*, 106: 4596-4605.
- Kounaves, S.P., A. Robbat, Jr., B. Workie and G. Davies, 1993.** Electrodeposition of heteropolymetallic complexes. *J. Electrochem. Soc.*, submitted.
- Mashuta, M.S., R. M. Buchanan, and W. Pierce, 1989.** Binuclear Schiff base complexes. *Inorg. Chim. Acta*, 158: 227-236.
- Steggarda, J.J., 1992.** Platinum-gold cluster compounds. *Comments Inorg. Chem.*, 11: 113-129.
- Wilkins, R.G., 1974.** The study of kinetics and mechanism of reactions of transition metal complexes. Boston: Allyn and Bacon.