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Cooperativity in metal exchange reactions of bis(acetylacetonato)copper(II) with $Co(NS)_2$ and $Zn(NS)_2$ reagents in methylene chloride

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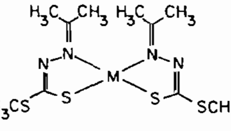
Abstract

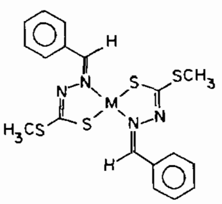
Neutral monomeric target bis(acetylacetonato)copper(II), ($Cu(acac)_2$, **C**), reacts reversibly with transmetalators $Co(NS)_2$ (**A_3**) and $Zn(NS)_2$ (**A_4**) (NS is monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate) in methylene chloride to give products $Co(acac)_2$ (**D**) and $Zn(acac)_2$ (**E**), respectively, and co-product $Cu(NS)_2$ (**A_2**). The reaction of excess **C** with **A_3** proceeds in two kinetically resolvable steps, the rates of which are both independent of [**C**]. This indicates metal exchange through an especially stable precursor **P** to give a successor complex **S**, as found in the corresponding complex formation reaction of **C** with $Cu(NS)_2$ (**A_2**). By contrast, the reactions of excess **C** with $Ni(NS)_2$ (**A_1**) and $Zn(NS)_2$ (**A_4**) proceed through precursors with measurable thermodynamic parameters to give different forms of successor complexes **S**. The kinetic and thermodynamic data for metal exchange in **C** are compared with those for irreversible transmetalation of heteropolymetallic targets with $M(NS)_2$ reagents.

Introduction

About seven years ago it was discovered that the copper centers in simple polynuclear oxo(halo)-copper(II) targets are stoichiometrically replaced with other metals from neutral reagents $M(NS)_2$, where M is Co, Ni and Zn and NS are easily made, monoanionic *S*-methyl hydrazinecarbodithioate Schiff base ligands in structures **A** and **B** [1–3]. This gave birth to transmetalation chemistry, which is now established as an excellent source of many new heteropolymetallic molecules [3].



A



B

The great virtue of this chemistry is that transmetalation reactions proceed in discrete stoichiometric steps [4–6]. For example, reactions (1) with stoichiometric amounts x of one or more of three different transmetalators $M(NS)_2$, $M'(NS)_2$ and $M''(NS)_2$ theoretically give 35 different polymetallic products [7]. An example is $(\mu_4\text{-O})N_4CuCoNiZnCl_6$, where N is a monodentate pyridine, which contains four different metals and cannot be made in any other way [7]. Another indication of wide potential scope is that transmetalation is not restricted to copper targets [3, 8].

$$(\mu_4\text{-O})N_4Cu_4Cl_6 + xM(NS)_2 \longrightarrow (\mu_4\text{-O})N_4Cu_{4-x}M_xCl_6 + xCu(NS)_2 \quad (1)$$

Practical transmetalation chemistry is limited in a general sense by four factors. First, there needs to be a strong thermodynamic driving force so that all the metal replacement steps are irreversible: reactions (1) are driven by the formation of especially stable co-product $Cu(NS)_2$ [2, 3, 6, 8]. Second, the reactions should proceed at useful rates under mild conditions. This calls for labile targets and transmetalators: reactions (1) occur on the stopped-flow time scale at room temperature [7, 9–12]. Third, the transmetalation products should be easy to separate:

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the heteropolymetallic products of reactions (1) are easily separated from co-product $Cu(NS)_2$ (A_2) by gel permeation chromatography [2, 6, 7]. Fourth, the primary heteropolymetallic products should not spontaneously fragment, because this will limit the extent of their further transmetalation [3, 7]: heteropolymetallic products of reactions (1) that contain fewer than three zinc centers are isolatable tetranuclear molecules [7].

These desirable characteristics led us to another question. Suppose we have a target containing two different metals in equivalent target sites, either of which theoretically [8] can be replaced with M from transmetalator $M(NS)_2$. An example is the target $(\mu_4\text{-}O)N_4Cu(Ni(H_2O))_3Cl_6$ [6, 11] reacting with equimolar $Co(NS)_2$ (A_3), which is capable of replacing either copper or nickel in the target with cobalt [8]. We observe that only copper is replaced [11].

One factor responsible for this specific replacement of copper by cobalt is that co-product $Cu(NS)_2$ is more thermodynamically stable than alternative co-product $Ni(NS)_2$ (A_1) [8]. Another is that $Co(NS)_2$ specifically associates with the copper center in the target $(\mu_4\text{-}O)N_4Cu(Ni(H_2O))_3Cl_6$ to form a rapidly equilibrated 1:1 reaction precursor **P** (eqn. (2) [11] that is converted to metal-exchanged products in rate-determining reaction (3). This supposition is indicated by kinetic data for the reaction, which is governed by rate law (4) [11].

$$(\mu_4\text{-}O)N_4Cu(Ni(H_2O))_3Cl_6 + Co(NS)_2 \rightleftharpoons \mathbf{P} \quad \beta_2,\ \text{fast} \tag{2}$$

$$\mathbf{P} \longrightarrow \text{products} \quad k_3,\ \text{slow} \tag{3}$$

$$\text{rate} = \frac{\beta_2 k_3[\mu_4\text{-}O)N_4Cu(Ni(H_2O))_3Cl_6][Co(NS)_2]}{(1+\beta_2[(\mu_4\text{-}O)N_4Cu(Ni(H_2O))_3Cl_6])} \tag{4}$$

The same situation holds for reaction of $(\mu_4\text{-}O)N_4Cu(Ni(H_2O))_3Cl_6$ with $Zn(NS)_2$ (A_4), but now there are two different 1:1 precursor forms **P** and **P′** whose proportions depend on the experimental temperature and whose rates of conversion to metal-exchanged products are different [11].

Copper in the whole target family $(\mu_4\text{-}O)N_4Cu_{4-x}M_xCl_6$ ($x = 1$–3, M = Co or Ni) is specifically replaced by Co or Zn from reagents A_3 and A_4 [11, 12]. Rate law variations in the reactions with transmetalator A_4 as a function of M and x in $(\mu_4\text{-}O)N_4Cu_{4-x}M_xCl_6$ targets indicate that the strongest precursor interactions occur when M is $Ni(H_2O)$ and x is 2 or 3 [12]. This corresponds to the maximum number of Cu–Cl–Ni edges and $CuNi_2$ faces in the target. It suggests interactions of transmetalators A_3 and A_4 with more than one target metal center despite the fact that metal replacement in $(\mu_4\text{-}O)N_4Cu_{4-x}M_xCl_6$ is specific to copper [11, 12].

Our goals are (i) to try to understand the manner in which a transmetalator replaces a metal in the target and (ii) to account for the existence of different precursor interactions that lead to specific metal replacement.

Precursor interactions involving more than one target metal center can be avoided by studying the transmetalation of monomeric targets that contain only one kind of target donor atom. A recent paper from our laboratory [13] describes the transmetalation of neutral monomeric target $Cu(acac)_2$ (**C**: acac is acetylacetonate) by $Ni(NS)_2$ (A_1) in methylene chloride. This reversible metal exchange reaction proceeds through two different precursors **P** and **P′** whose proportions depend on the experimental temperature. Also reported were the kinetics of complexation of **C** by $Cu(NS)_2$, which proceeds through an especially stable precursor to give the successor complex **C**·A_2 [13].

Conclusions regarding the possible structures of the precursors, activated complexes and successors in these reactions of **C** need to be tested by varying the transmetalator. This paper reports that target **C** also reacts reversibly with transmetalators A_3 and A_4 and that the reaction with A_4 proceeds through a single precursor with measurable thermodynamic parameters. The kinetic data are compared with previous results [13] and with data for monotransmetalation of heteropolynuclear copper(II) targets with $M(NS)_2$ reagents.

Experimental

Materials

Methylene chloride (Aldrich) was purified as described previously [2]. Bis(acetylacetonato)copper(II) (**C**: Aldrich) was recrystallized from ethanol/methylene chloride. Transmetalators A_3 and A_4 were obtained by literature methods [2, 4].

Separations and analyses

Reactants A_3, A_4 and **C** and the products of their reactions were subjected to chromatography on silica gel (70–270 mesh, 60 Å: Aldrich) with methylene chloride as the eluent. Metal analyses of each eluted fraction were performed after standard sample preparation with a Leeman Labs PlasmaSpec inductively coupled plasma emission spectrometer equipped with a computer-controlled scanning Echelle grating monochromator. The instrument was programmed to monitor emission intensity at each analytical wavelength for three, 3-s intervals. Analytical wavelengths (nm) and detection limits (ng/ml) were Co (228.62, 8), Cu (324.75, 3) and Zn (213.86, 7). C, H. N and S analyses of isolated solid samples were performed by Desert Analytical Laboratories, Tucson, AZ.

Physical measurements

The electronic spectra of reactants and products in methylene chloride were measured with Perkin-Elmer Lambda 4B and Beckman DK-1A spectrophotometers in matched quartz cells at room temperature.

Kinetic measurements of the reaction of **C** with A_3 or A_4 in methylene chloride were performed with a thermostatted (±0.05 °C), computer-assisted Hi-Tech Scientific Model SFL41 stopped-flow spectrophotometer [12]. All the reactions were monitored under dinitrogen (reagent A_3 is air-sensitive [4]). The monitoring wavelength for all measurements was 600 nm, where A_2 is the principal absorber [1]. Temperature was varied in the range 10.0–30.0 °C. Target **C** was always present in sufficient excess to ensure pseudo-first-order conditions [13]. Concentrations were varied in the range $[C]_0 = 2.5$–25.0 mM with $[A_3$ or $A_4]_0$ fixed at 0.25 mM. These experimental conditions are almost exactly the same as in our previous study [13]. All reactions were monitored for at least ten half-lives. Pseudo-first-order rate constants k_{obs} from the slopes of linear plots of $\ln|(A_\infty - A_t)|$ versus time, where A_t is the absorbance at time t, were reproducible to ±5% or better under fixed experimental conditions.

Results and discussion

The following questions are addressed in this paper.

1. Do cobalt and zinc from transmetalators A_3 and A_4 replace the copper in monomeric target **C** as found with transmetalator A_1, which reversibly replaces copper with nickel to give Ni(acac)$_2$ [13]? If so, are the reactions reversible?

2. Do the reactions proceed through precursors whose stability varies with **A**? If so, are the thermodynamic parameters for precursor formation measurable?

3. How do the rates and activation parameters for metal exchange in **C** vary with **A**? How do they compare with those for replacement of one copper center in polynuclear copper targets with M from transmetalators **A**? Do the reactions have similar mechanisms?

4. Are the reaction products separate metal-exchanged species (e.g. Co(acac)$_2$ (**D**) and Cu(NS)$_2$ (A_2)) or do the products remain associated as successor complexes?

Reactant structures

Figure 1 shows the molecular structures of the reactants of this study. All are highly soluble in methylene chloride.

Target **C** is a flat molecule with D_{4h} symmetry [14]. It forms mono- and bis-complexes with a wide variety of ligands [15]. Transmetalator A_1 also is nearly flat (the dihedral angle is 27°) with a *cis*-configuration [16]. Although transmetalation coproduct A_2 cannot be obtained as single crystals because of slow spontaneous decomposition in solution, we have concluded from its electronic and EPR spectra that it is a flat molecule with a *cis*-configuration [13]. Transmetalators A_3 and A_4 are isomorphous in the solid state and have tetrahedral geometry [17].

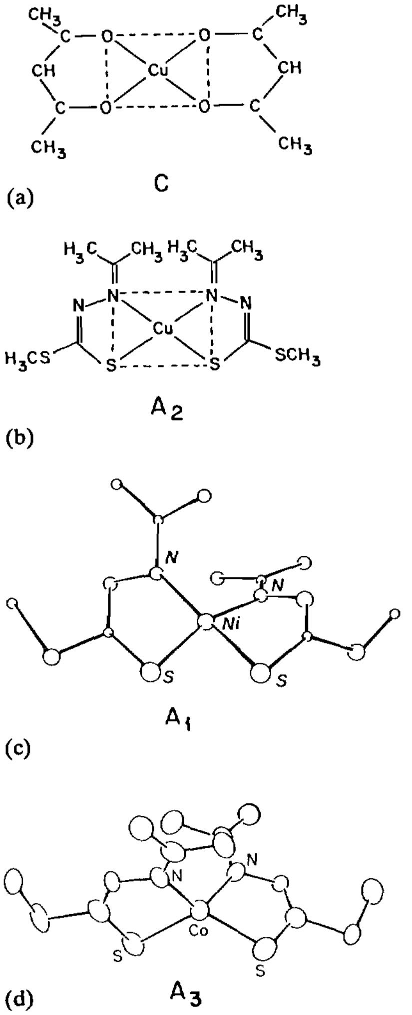


Fig. 1. Molecular structures of: (a) square-planar **C** [14]; (b) *cis*-square planar Cu(NS)$_2$ (A_2) [13]; (c) Ni(NS)$_2$ (A_1) [16]; (d) Co(NS)$_2$ (A_3) (Zn(NS)$_2$ (A_4) is isomorphous with A_3 [17]).

Reactions of $Cu(acac)_2$ (C) with $Co(NS)_2$ (A_3) and $Zn(NS)_2$ (A_4) in methylene chloride. Spectral and chromatographic observations

Mixing excess target C with transmetalators A_1 [13], A_3 and A_4 results in large absorbance increases at 600 nm that are characteristic of the formation of co-product $Cu(NS)_2$ (A_2) as a result of metal exchange (see eqn. (1)) [2, 6, 7–13]. Reversible exchange of M for copper in C was confirmed by the following chromatographic experiments.

Equimolar solutions of C and A_3 were allowed to react to completion in methylene chloride at room temperature and were then chromatographed on silica gel with methylene chloride as the eluent. No precautions were taken to exclude dioxygen in the chromatography. Four fractions, which were shown by isolation and analysis to be A_2, A_3, $Co(acac)_2$ (**D**) and C were easily eluted in that order. The low yield of A_3 compared to that of A_2 (they should be equimolar if metal exchange is reversible and there are no other complications) was shown to be due to air-oxidation of A_3 [4] during the chromatography, which gives unidentified cobalt(III) products that are difficult to elute with methylene chloride.

The experiment was repeated exactly as above with reactants C and A_4. Two eluted colored bands were isolated and shown by analysis to be A_2 and C. The other expected eluates of a reversible metal exchange reaction between C and A_4 are colorless A_4 [1] and $Zn(acac)_2$ (**E**).

These results indicate that the reactions of C with transmetalators A_3 and A_4 result in reversible metal exchange, eqn. (5) and (6), as found for the corresponding reaction of C with transmetalator A_1 [13].

$$\mathrm{C}+\mathrm{A}_3 \rightleftharpoons \mathrm{D}+\mathrm{A}_2 \tag{5}$$

$$\mathrm{C}+\mathrm{A}_4 \rightleftharpoons \mathrm{E}+\mathrm{A}_2 \tag{6}$$

Kinetic analysis

Before describing and comparing the kinetics of the reactions of excess target C with four reagents A, we will briefly review our strategy for analyzing the data [13].

Equations (2)–(4) are recast in general form with excess C as the target, A as the transmetalator and provision for reaction reversibility, as indicated in eqns. (5) and (6). This gives eqns. (7)–(9). Here, P is a reaction precursor in rapid equilibrium with C and A. Successor complex S is the result of rate-determining metal exchange in P. If equilibrium constant β is moderately large, the observed pseudo-first-order rate constant k_{obs} is expected from eqn. (9) to increase to a limiting value k_8+k_{-8} with increasing [C]. In other words, plots of k_{obs} versus $[\mathrm{C}]_0$ at fixed temperature will be curved with finite intercepts k_{-8} [13].

$$\mathrm{C}+\mathrm{A} \rightleftharpoons \mathrm{P} \quad \beta,\ \text{fast} \tag{7}$$

$$\mathrm{P} \rightleftharpoons \mathrm{S} \quad k_8,\ k_{-8},\ K_8,\ \text{slow} \tag{8}$$

$$k_{obs}=\beta k_8[\mathrm{C}]_0/(1+\beta[\mathrm{C}]_0)+k_{-8} \tag{9}$$

Equation (9) can be rearranged to eqn. (10). Linear plots of $1/(k_{obs}-k_{-8})$ versus $1/[\mathrm{C}]_0$ at fixed temperature validate the mechanism of eqns. (7) and (8) and allow the calculation of individual values of β, k_8 and k_{-8} [11–13].

$$1/(k_{obs}-k_{-8})=1/\beta k_8[\mathrm{C}]_0+1/k_8 \tag{10}$$

An important situation is where $\beta[\mathrm{C}]_0 \gg 1$ in eqn. (9). The result is eqn. (11). This equation predicts that k_{obs} will be independent of $[\mathrm{C}]_0$ and that we cannot (i) determine β or (ii) separate k_8 from k_{-8}. This is because we can only detect the limiting form (resulting from large β) of the full curve predicted by eqn. (9) [9–13].

$$k_{obs}=k_8+k_{-8} \tag{11}$$

Kinetics of reaction of excess C with $Co(NS)_2$ (A_3) in methylene chloride

Mixing excess C with transmetalator $Co(NS)_2$ (A_3) in methylene chloride under dinitrogen [4] results in two clearly resolved absorbance changes at 600 nm (Fig. 2). Both absorbance changes were independent of $[\mathrm{C}]_0$.

The first process (resulting in an absorbance increase) is expected for formation of transmetalation co-product $Cu(NS)_2$ (A_2, eqn. (5)) [13]. The second process (yet to be identified) results in a smaller absorbance decrease (Fig. 2). The pseudo-first-order rate constants for these kinetically separable processes are defined as k_{obs} (1) and k_{obs} (2) for the title system.

Figure 3 shows plots of k_{obs} (1) versus $[\mathrm{C}]_0$ at five different temperatures. The horizontal plots indicate rate law (11). A plot of log (k_{obs} (1)) versus $1/T$ exhibited excellent linearity. This, together with ab-

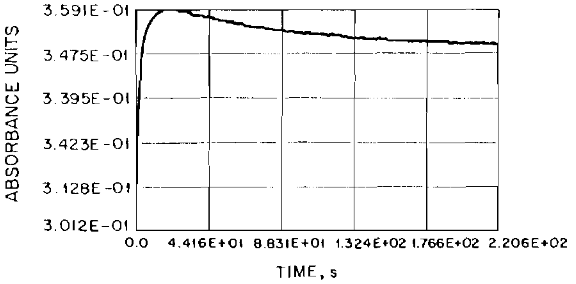


Fig. 2. Absorbance–time curve in the reaction of C (2.5 mM) with A_3 (0.25 mM) in methylene chloride at 30 °C.

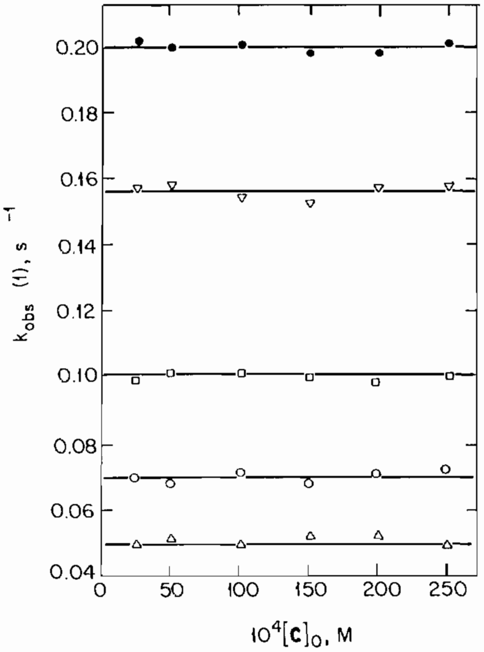


Fig. 3. Plots of k_{obs} (1) vs. $[C]_0$ for the reaction of excess C with A_3 in methylene chloride at the following temperatures (°C): 10.0, △; 17.0, ○; 22.0, □; 27.0, ▽; 30.0, ●.

sorbance changes that are independent of $[C]_0$, suggests that $k_8 \gg k_{-8}$ in this particular system. The kinetic data for the first observed process in the title reaction are collected with other data for reactions of C in Table 1.

Figure 4 shows plots of k_{obs} (2) versus $[C]_0$ at four different temperatures. We again observe pseudo-first-order rate constants that are independent of $[C]_0$ at fixed temperature. A plot of log (k_{obs} (2)) versus $1/T$ was accurately linear over the whole temperature range of this study, indicating only one second reaction step. The kinetic data for this step are collected with other data for successor complex formation [13, 18] in Table 2.

Kinetics of reaction of excess C with $Zn(NS)_2$ (A_4) in methylene chloride

Mixing excess C with transmetalator $Zn(NS)_2$ (A_4) in methylene chloride results in an exponential absorbance increase at 600 nm, as expected for the formation of co-product $Cu(NS)_2$ (A_2) from a metal exchange reaction [9–13]. Increasing $[C]_0$ at fixed temperature and $[A_4]$ caused larger absorbance increases, consistent with reversible overall metal exchange reaction (6).

Figure 5 shows plots of k_{obs} versus $[C]_0$ for the title reaction at five different temperatures. The data clearly indicate rate law (9), as confirmed by the linear plots of eqn. (10) in Fig. 6. Values of β, k_8

TABLE 1. Measured and derived parameters for the reactions of excess **C** with reagents **A** in methylene chloride (Scheme 1)[a]

Reagent	Parameter	M[b]	ΔH_i[c]	ΔS_i[d]
Equilibrium parameters				
A_1	β	490±15	10.3±0.6	47±5
	β'	110±10	−1.0±0.5	6±4
A_4		90±8	−5.7±0.5	−10±4
A_1	β_p	4.5	11.4±0.6	41±5
	K_8	2	−2.0±0.6	−10±5
A_4		2	−4.6±0.5	−14±4
A_1	K'_8	4.6	−2.0±0.6	−3±5
A_4		1.9	−20.5±0.4	−68±5
A_1	β_s	2	11.4±0.6	34±5
A_4		1	16.0±0.5	54±6
			$\Delta H_i^{\ddagger}$[c]	$\Delta S_i^{\ddagger}$[d]
Kinetic parameters				
A_1	k_8	0.068	9.3±0.6	−33±5
A_3		0.12	13.1±0.5	−7±4
A_4		0.049	6.1±0.4	−49±5
A_1	(k'_8	0.068	9.3±0.6	−33±5[e])
A_1	k_{-8}	0.032	11.8±0.5	−24±5
A_4		0.025	10.7±0.5	−30±5
A_1	k'_{-8}	0.014	10.8±0.5	−31±5
A_4		0.023	26.6±0.4	24±4

[a] Data for reactions of A_1 are from ref. 13. All other data from this work. [b] Magnitude of the cited parameter at 23 °C in methylene chloride. [c] Units are kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1} at 25 °C. [e] Quantities in parentheses are assumed on the basis of considerations in ref. 13.

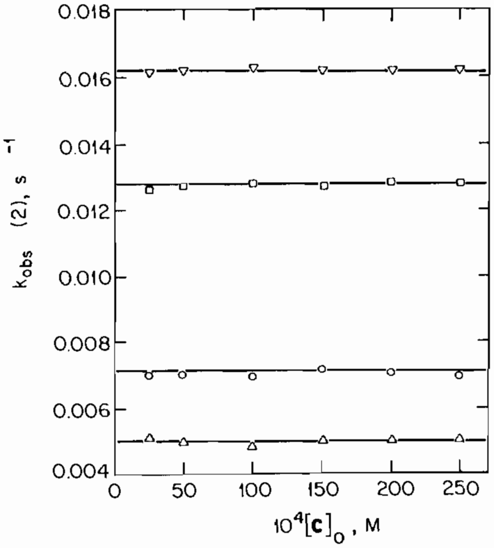


Fig. 4. Plots of k_{obs} (2) vs. $[C]_0$ for the reaction of excess C with A_3 in methylene chloride at the following temperatures (°C): 10.0, △; 16.0, ○; 25.0, □; 30.0, ▽.

TABLE 2. Kinetic data for first-order successor complex formation in the reactions of excess **C** and of excess dimeric target **E** with reagents **A**[a]

Target	M in A	$k_{obs}(2)$[b]	$\Delta H^{‡}$[c]	$\Delta S^{‡}$[d]	Reference
C	Co	0.012	10.3	−33	this work
	Cu	1.40	5.5	−39	13
E[e]	Co	0.11	5.9	−43	18
	Ni	0.90	9.0	−30	18
	Cu	1.2	12.7	−15	18
	Zn	0.70	13.4	−18	18

[a] Data for **C** in methylene chloride; data for **E** in nitrobenzene. [b] Units are s^{-1} at 23 °C. [c] Units: kcal mol^{-1}. Typical error is ±0.5 kcal mol^{-1}. [d] Units: cal deg^{-1} mol^{-1} at 25 °C. Typical error is ±5 cal deg^{-1} mol^{-1}. [e] **E** is the dimeric copper(II) target $N_2ClCu(Cl,Cl)CuClN_2$ (N is *N*,*N*-diethylnicotinamide): see ref. 18.

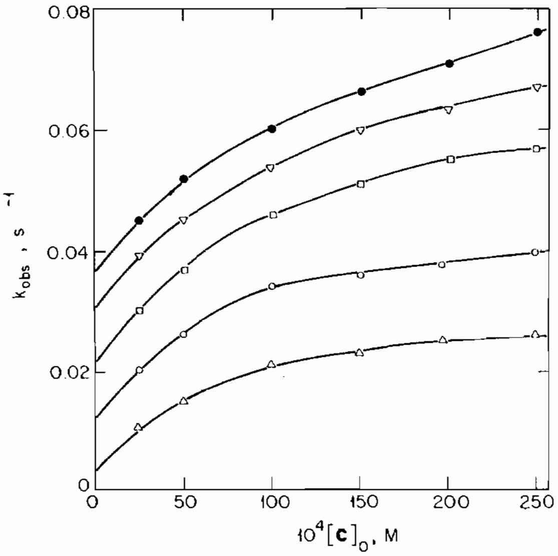


Fig. 5. Plots of k_{obs} vs. $[C]_0$ for the reaction of excess **C** with A_4 in methylene chloride at the following temperatures (°C): 10.0, △; 17.0, ○; 22.0, □; 27.0, ▽; 30.0, ●.

and k_{-8} at each experimental temperature can be obtained from eqns. (9) and (10).

A linear plot of log β versus $1/T$ indicates that there is only one precursor involved in the title system over the temperature range of this study [11–13]. This was confirmed by an excellent linear plot of log k_8 versus $1/T$, which shows that there is only one discernable rate-determining forward step for metal exchange in the C/A_4 system.

Reverse rate constants k_{-8} at the respective experimental temperatures can be obtained from the intercepts of Fig. 5. A plot of log k_{-8} versus $1/T$ (Fig. 7) reveals that there are two successor complexes formed in the reversible title reaction. These successors are converted to the single precursor **P**′ (see below) with first-order rate constants k_{-8} and k'_{-8} in the high and low experimental temperature range, respectively. This means that there are different equilibrium constants, $K_8 = k_8/k_{-8}$ and $K'_8 = k_8/k'_{-8}$ that link **P** to the two successor complexes S_{Zn} and S'_{Zn} at high and low temperatures, respectively. Kinetic and equilibrium parameters for the title reaction are given with data for the reactions of **C** with other reagents **A** [13] in Table 1.

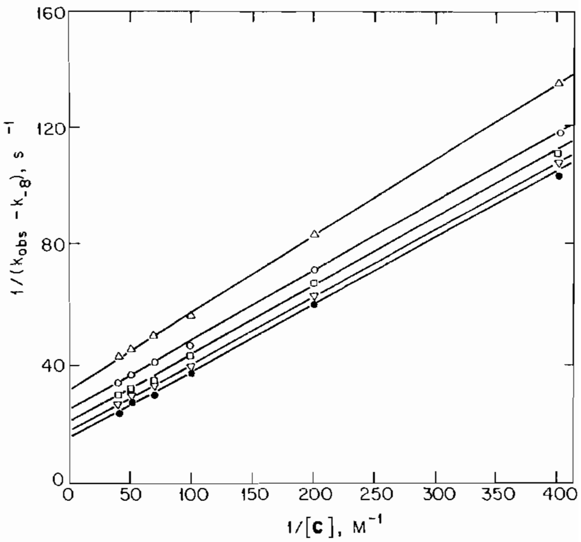


Fig. 6. Plots of $1/(k_{obs} - k_{-8})$ vs. $1/[C]_0$ for the reaction of excess **C** with A_4 in methylene chloride at the following temperatures (°C): 10.0, △; 17.0, ○; 22.0, □; 27.0, ▽; 30.0, ●.

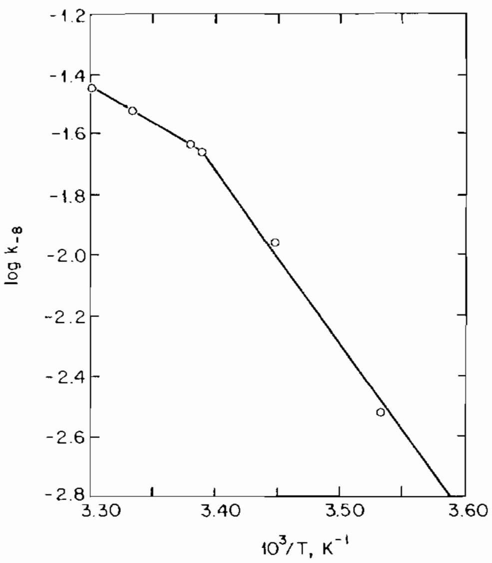


Fig. 7. Plot of log k_{-8} vs. $1/T$ for the reaction of excess **C** with A_4 in methylene chloride.

Interpretation

Equilibrium processes

We previously offered Scheme 1 to account for the reactions of excess target C with reagents Ni(NS)$_2$ (A$_1$) and Cu(NS)$_2$ (A$_2$) [13]. Its main features are as follows.

Reactant A$_1$ (M = Ni) was assumed for simplicity to be planar. In methylene chloride C and A$_1$ rapidly and reversibly form moderately stable 1:1 precursor P$_M$ or P$'_M$, depending on the experimental temperature. Equilibrium constant β_p links P$'_M$ to P$_M$. Either precursor is reversibly interconverted with metal-exchanged successor complex S$_M$ or S$'_M$ with forward rate constant k_8 and reverse rate constants k_{-8} and k'_{-8}, respectively. Equilibrium constant β_s links S$'_M$ to S$_M$. This part of Scheme 1 accounts for a rate law of the form of eqn. (9) and will be used with M = Zn to discuss the reversible reaction of C with zinc reactant A$_4$.

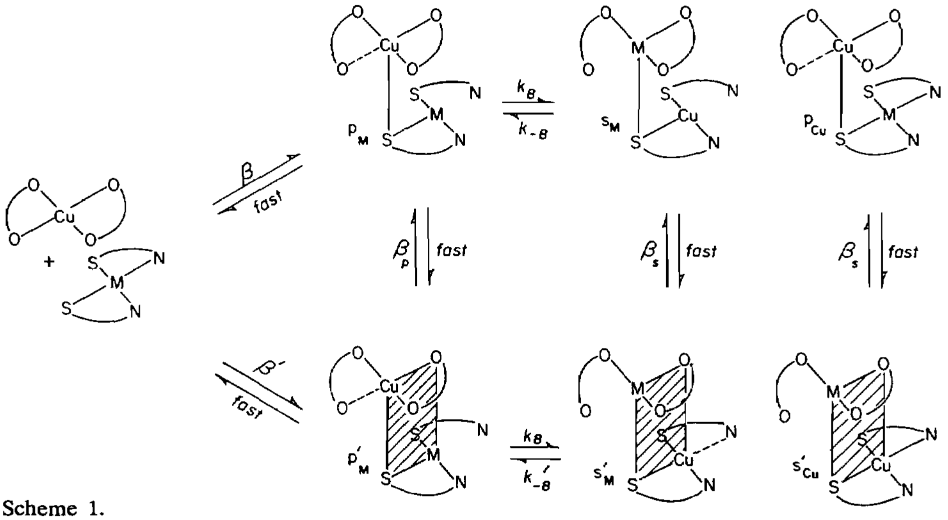
The right hand column of Scheme 1 (M = Cu) was used to discuss the rapid complex formation reaction of C with Cu(NS)$_2$ (A$_1$), which proceeds with rate law (11) [13]. We will use it here to discuss the reaction of C with Co(NS)$_2$ (A$_3$), which also proceeds with rate law (11).

The reactions of C with A$_1$–A$_4$ proceed with rate laws (9) [13], (11) [13], (11) and (9), respectively. Rate law (9) results from the existence of moderately stable precursors, while rate law (11) indicates much more stable precursors. On this basis alone we can tell that reagents A$_2$ and A$_3$ are much 'stickier' [11] reactants for C than are reagents A$_1$ and A$_4$.

This result is difficult to understand for the following reason. The relative stabilities of transmetalators A increase in the order A$_4$ < A$_3$ < A$_1$ < A$_2$ [8], while the apparent stickiness order for reaction with C at ambient temperatures is A$_1$, A$_4$ ≪ A$_2$, A$_3$. The stability order is a measure of the relative ease with which the chelate rings of reagents A can be opened. Thus, if precursor interactions always involved ring opening in A then the stability and stickiness orders would be the same. The fact that they are not indicates specific interactions of C with A that may (perhaps with least stable reagent A$_4$ [8]) or may not (with especially stable A$_2$) involve chelate ring opening in A. In other words, the interactions of C with any particular A are *cooperative* so that their connection with a particular single property of A is hard to identify.

The reaction of C with A$_4$ proceeds via rate law (9), as demonstrated by Figs. 5 and 6. It thus has the same kind of mechanism, involving a moderately stable precursor, as the corresponding reaction with A$_1$. However, the reaction with A$_4$ involves only one precursor form, as indicated by a linear plot of log β versus $1/T$ over the same temperature range as employed in our previous study of the reaction of C with A$_1$, which involves two precursors [13]. Our first task is to compare the properties of the three precursors found in the C/A$_1$, A$_4$ systems.

The data in Table 1 indicate that the precursor in the C/A$_4$ system resembles that detected in the lower temperature range in the C/A$_1$ system: the equilibrium constants β' are of similar magnitude at 23 °C and both precursors are formed exothermically and with an average entropy change near zero. As indicated in Scheme 1, we conclude that these precursors contain four-membered rings in P$'_M$ that facilitate metal exchange [9–13]. Table IV of ref. 11 reports equilibrium constants β and βK_8 for interaction of A with a range of polynuclear halo-



Scheme 1.

(amine)copper complexes. These parameters vary from 250 to 3300 in nitrobenzene at 23 °C. The corresponding values for interactions of A_1 and A_4 with C (Table 1) are smaller, indicating that C is only a moderately sticky target for A_4. However, it is worth repeating that C behaves as a very sticky target for A_2 and A_3.

The other equilibrium parameters for the C/A_1, A_4 systems in Table 1 are comparable except that formation of successor S'_M from precursor P'_M in the C/A_4 system is especially exothermic and results in a very large entropy decrease (Table 1).

Figure 8 shows a correlation of all known thermodynamic data for transmetalation reactions involving reversible components that are governed by measurable equilibrium constants β, β', β_p, β_s, K_8 and K'_8. Points 15–18 are the new data from this study. It appears that there are three major classes of equilibrium interaction.

The first class, which accounts for the majority of the data, involves equilibria that are established with little enthalpy or entropy change. This class accommodates data for formation of precursors P'_M that are supposed to contain a closed four-membered ring between the reactants (Scheme 1).

Formation of the second class of associated species (points 1, 2, 8–10, 18) results in an enthalpy increase of about 10 kcal mol^{-1} and an entropy increase of about 40 cal deg^{-1} mol^{-1}. One of these data sets (point 18) refers to equilibrium constant β_s that links the low and high temperature successors S'_{Zn} and S_{Zn} in the C/A_4 system. It appears to refer to species without closed four-membered rings. The third class of interaction (points 5, 15, 17) is very exothermic and results in very negative entropy changes.

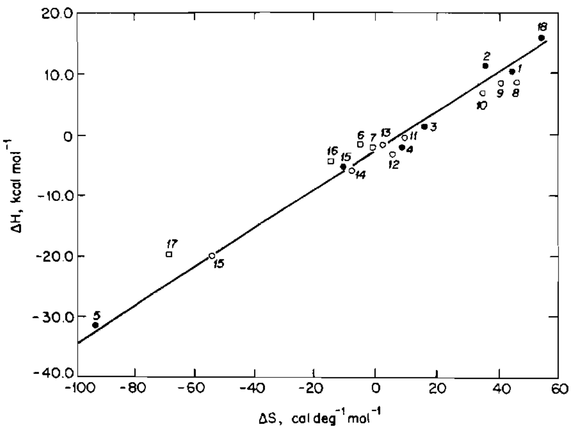


Fig. 8. Plot of enthalpy vs. entropy changes for reversible processes in transmetalation reactions. Figure 9 of ref. 13 has been supplemented by addition of the data for reactions of **C** with A_4 from Table 1.

Figure 8 correlates data for a wide range of reactants and processes, including reversible metal exchange. Marked but compensated variations of thermodynamic parameters for association of a fixed target or transmetalator indicate that all interactions between the reactants are cooperative. In other words, no single property of the target or transmetalator determines their magnitude.

Kinetic processes

Table 1 contains all the kinetic data for C/A systems that refer to metal exchange. In order to compare the first-order rate constants we have to assume that $k_8 \gg k_{-8}$ in rate law (11) because k_{-8} cannot be determined independently. This seems justified by linear plots of log k_8 versus $1/T$ over the whole temperature range of our C/A_2 [13] and C/A_3 studies.

Metal exchange in the C/A systems is orders of magnitude slower than for first-order irreversible replacement of single copper centers in (μ_4-O)$N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ targets by A_3 and A_4 (see Table III of ref. 11). This is because P_M/S_M interconversion in Scheme 1 requires rupture of similarly strong complexes C and $Cu(NS)_2$ (A_2). This similar strength is responsible for reversible metal exchange. The similar magnitudes of k_8 and k_{-8} in Table 1 indicate that the properties of C and A_2 largely determine the interconversion rates. An activated complex containing copper and M centers that are each bonded to at least one donor atom of each acac and NS ligand is necessary to explain the absence of any mixed ligand products M(acac)NS [13].

Plots of $\Delta H_8^{\ddagger}$ versus $\Delta S_8^{\ddagger}$, $\Delta H_{-8}^{\ddagger}$ versus $\Delta S_{-8}^{\ddagger}$ and $\Delta H'_{-8}$,‡ versus $\Delta S'_{-8}$,‡ (5 points) from the data in Table 1 are colinear, which again emphasizes the essential cooperativity of equilibrium and kinetic processes in transmetalation reactions. The exception is the data for conversion of the low temperature successor S_M to precursor P'_M in the C/A_4 system, which exhibit an activation enthalpy that is *c.* 7 kcal mol^{-1} greater than expected from the other data.

We previously demonstrated that increased stability of the precursors formed in the (μ_4-O)$N_4Cu(Ni(H_2O))_3Cl_6$/A_3,A_4 transmetalation systems leads to lower metal exchange rates [11]. This demonstration was possible because the three precursors involved in these systems are converted to products at different rates. It is not possible to demonstrate this trend in the C/A_1, A_4 systems because the plots of log k_8 versus $1/T$ are linear, which indicates (unexpectedly [11]) that successors can be formed from one precursor even though another may also be present.

Figure 9 shows reaction profiles for all transmetalation reactions that are known to proceed

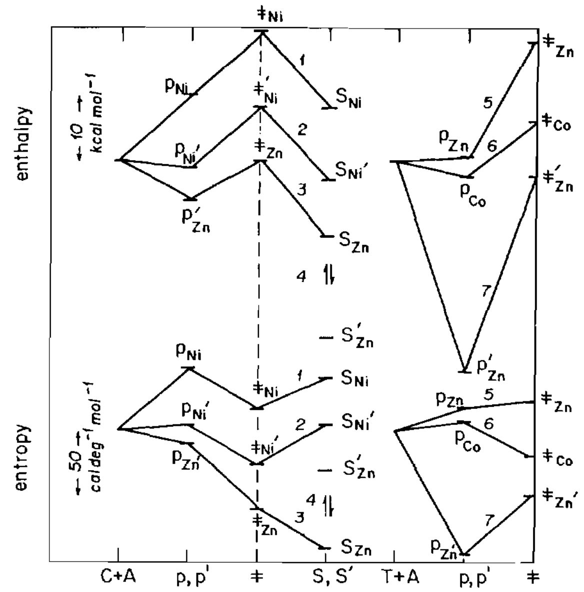


Fig. 9. Enthalpy and entropy profiles for the reversible reactions of C with A_1 and A_4 (left column, data from Table 1) and for the irreversible transmetalation of (μ_4-O)$N_4Cu(Ni(H_2O))_3Cl_6$ with A_3 and A_4 (right column, data from ref. 11).

through precursors with measurable thermodynamic parameters. The profiles in the first column refer to reversible reactions of C with reagents A_1 [13] and A_4. Those in the second column are for reactions of target (μ_4-O)$N_4Cu(Ni(H_2O))_3Cl_6$ with A_3 and A_4 [11]. The latter profiles are comparable to those in the first column only up to the indicated dashed vertical line because the reactions of (μ_4-O)$N_4Cu(Ni(H_2O))_3Cl_6$ with A_3 and A_4 are irreversible [11].

The important features of these profiles are as follows.

(i) The reaction of C with A_1 proceeds through two different precursors [13], one of which resembles the C/A_4 precursor (compare profiles 2 and 3).

(ii) Parallel behavior is exhibited in the enthalpy and entropy profiles except for entropy profile 3 that describes formation of successor complex S_{Zn} in the C/A_4 system. This successor has exceptionally low entropy.

(iii) The formation of precursors and activated complexes in the reactions of C with A_1 (at low temperatures, profile 2), C with A_4 (profile 3), (μ_4-O)$N_4Cu(Ni(H_2O))_3Cl_6$ with A_4 (at high temperatures, profile 5) and (μ_4-O)$N_4Cu(Ni(H_2O))_3Cl_6$ with A_3 (profile 6) involves similar enthalpy and entropy changes. But the primary interactions of A with (μ_4-O)$N_4Cu(Ni(H_2O))_3Cl_6$ involve halide [11], while those with C can only involve the oxygen donor atoms of acac. Could there be any better indication that *all* the interactions between these reactants are responsible for the structures and stabilities of the species involved? This conclusion is strengthened by the existence of unusual (but still compensated) profiles like 7. The course of transmetalation reactions clearly depends on the breaking and making of particular bonds in the reactants and thus, by its very nature, is metal-specific.

Direct evidence for successor complex formation

There are four categories of evidence for the existence of successor complexes in transmetalation reactions. The first is the observation of slow Cu(NS)(s) precipitation in the transmetalation of copper(I) targets with $M(NS)_2$ reagents [20, 21]. Second, we can sometimes observe absorbance changes when transmetalation products are remixed [19]. The third category is when plots with finite intercepts like Fig. 5 are obtained: metal exchange reactions can only be reversed by association of the products, as demonstrated here and in ref. 13. The fourth is the kind of absorbance–time behavior shown in Figs. 2 and 3 of ref. 18. The new data for the second stage of reaction of C with A_3 (Fig. 2 and Table 2) fit the activation parameter plot in Fig. 11 of ref. 13. This demonstrates that the formation or rearrangement of successor complexes in transmetalation reactions also is cooperative in the sense that no one property of either reactant determines the activation parameters.

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