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Products and kinetics of the reactions of bis-(acetylacetonato)copper(II) with $Ni(NS)_2$ and $Cu(NS)_2$ reagents in methylene chloride

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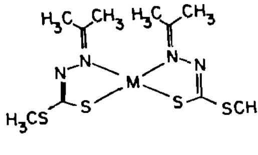
Abstract

Excess neutral monomeric target bis-(acetylacetonato)copper(II), ($Cu(acac)_2$, **C**), reacts reversibly with transmetalator $Ni(NS)_2$ (**A**$_1$: NS is monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate) in methylene chloride to give two temperature-dependent forms of the successor complex $Ni(acac)_2 \cdot Cu(NS)_2$, (**D**·**A**$_2$), S_{Ni} and S_{Ni}'. The overall metal exchange reaction proceeds via two temperature-dependent forms of the 1:1 precursor **C**·**A**$_1$, P_{Ni} and P_{Ni}', whose formation constants are $\beta_4 = 490$ M^{-1} and $\beta_4' = 110$ M^{-1} at 23 °C, respectively. Excess **C** reacts irreversibly at a much higher first-order rate with $Cu(NS)_2$ (**A**$_2$) in methylene chloride to form a complex **C**·**A**$_2$. The data are compared with those for reactions of polynuclear halo(amine)copper targets with $M(NS)_2$ reagents.

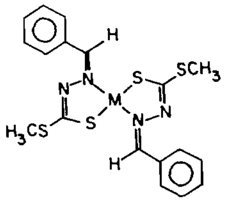
Introduction

Transmetalation is the stoichiometric replacement of the metals in a polymetallic target with other metals from reagents called transmetalators [1][†]. It is a source of many new heteropolymetallic molecules that cannot be obtained by other means [2].

The transmetalation phenomenon has mostly been applied to polynuclear copper(I) [3–7] and copper(II) [1, 7–15] targets, although it also is applicable to targets containing other transition metals [11]. The best known transmetalators are *S*-methyl hydrazinecarbodithioate complexes $M(NS)_2$, where M is Co, Ni, Cu and Zn and NS is monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate and *S*-methyl benzylidenehydrazinecarbodithioate in reagents **A** and **B**, respectively. Transmetalation reactions proceed under mild conditions in aprotic solvents and the heteropolymetallic products are easily separated [1, 2]. The major driving force for stoichiometric copper replacement is the formation of highly stable co-products Cu(NS)(s) and $Cu(NS)_2$, as typified by eqns. (1) [6] and (2) [8], where the transmetalator is **A**, L is an *N,N,N′,N′*-tetraalkyldiamine, N is a monodentate pyridine ligand and X is Cl or Br.



A



B

$$L_2Cu_2X_2 + M(NS)_2 \longrightarrow LCuM(NS)X_2 + L + Cu(NS)(s) \quad (1)$$

$$N_4Cu_4Cl_6O + xM(NS)_2 \longrightarrow N_4Cu_{4-x}M_xCl_6O + xCu(NS)_2 \quad (2)$$

Extensive studies have shown that the patterns and specificity of progressive transmetalation reactions strongly depend on the target core structure [2].

Recent work seeks to establish the structural–mechanistic origins of practical transmetalation systems through kinetic measurements [13–20]. Most

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[†] Other definitions: monotransmetalation refers to the replacement of just one of several metals in a target with another metal; direct transmetalation leaves the target molecularity unchanged; specific transmetalation results in the replacement of just one of several different metallic elements in a heteropolymetallic target [2].

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of our kinetic studies have been of monotransmetalation systems (for example, $x = 1$ in eqn. (2)) [13–15, 18, 19]. The polymetallic targets T all have at least one kind of nucleophilic atom (most often halide, X) to which M of **A** or **B** may attach in an acid–base interaction to form precursors $M(NS)_2 \cdot T_n$, (**P**, eqn. (3)).

$$M(NS)_2 + nT \rightleftharpoons \underset{\mathbf{P}}{M(NS)_2 \cdot T_n}, \quad \beta \tag{3}$$

The existence of unique interactions in **P** is necessary to explain specific replacement of particular elements in heteropolymetallic targets [11, 18, 19].

Among direct evidence for the existence of precursor and successor complexes in transmetalation reactions is that the formation of discrete co-product Cu(NS)(s) in copper(I) replacements like reactions (1) is much slower than events occurring on the stopped-flow time scale [6, 16]. Strong precursor interactions through X of the target and carbothioate S of $M(NS)_2$ result in a simple first-order transmetalation rate law in particular systems [11, 17–19]. Weaker interactions through X or S lead to third- and second-order rate laws that are most often associated with transmetalators **A** (M = Ni) and **B**, respectively [13–18]. The precursor formation constants β of eqn. (3) cannot be determined in any of these cases. However, we have recently discovered specific transmetalation systems for which thermodynamic data for precursor formation can be obtained directly from a new form of the rate law [18, 19]. It was also concluded that the rates of metal replacement in a fixed target decrease with increasing stability of 1:1 reaction precursors **P** [18].

Here we report the products and kinetics of reactions of the neutral, monomeric target $Cu(acac)_2$ (**C**: acac = acetylacetonate) with $M(NS)_2$ reagents **A** (M = Ni ($\mathbf{A_1}$) and Cu ($\mathbf{A_2}$)) in methylene chloride. The impetus for the work was three-fold. First, we wanted to compare the rates and rate laws of transmetalation of a neutral target containing only oxygen donor atoms with our previous data [6, 16, 20] for polynuclear targets with primary halo ligand systems. Second, we wanted to verify that the reaction of **C** with $\mathbf{A_1}$ proceeds with complete ligand exchange to give products $Ni(acac)_2$ (**D**) and A_2. Third, we wished to exclude the complication of interactions of $M(NS)_2$ with more than one target metal center [18, 19] in the precursors for transmetalations of polymetallic targets. The results include the first reported example of a reversible transmetalation reaction with measurable equilibrium constants for precursor and successor complex formation and further evidence [18, 19] that more than one precursor or successor structure can exist in a given metal exchange system.

Experimental

Materials

Methylene chloride (Aldrich) was purified as described previously [13]. Bis-(acetylacetonato)copper(II) (**C**: Aldrich) was recrystallized from ethanol/methylene chloride. Reagents $\mathbf{A_1}$ and $\mathbf{A_2}$ were obtained by literature methods [1].

Separation and analyses

Reactants A_1, A_2 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-second intervals. Analytical wavelengths (nm) and detection limits (ng/ml) were Ni (231.60, 20) and Cu (324.75, 3). C, H, N and S analyses of solid samples were performed by Desert Analytical Services, 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_1 in methylene chloride were performed with the Perkin-Elmer spectrophotometer, which was fitted with a temperature-controlled cell housing (±0.1 °C). A thermostatted, computer-assisted Hi-Tech Scientific Model SFL41 stopped-flow spectrophotometer [16] (±0.05 °C) was employed for monitoring the much faster reaction of **C** with A_2. The monitoring wavelength for all measurements was 600 nm, where A_2 is the principal absorber [1]. Temperature was varied in the range 9.0 to 29.0 °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 $[\mathbf{A_1}$ or $\mathbf{A_2}]_0$ fixed at 0.25 mM. All reactions were monitored for at least 10 half-lives. Pseudo-first-order rate constants k_{obs} obtained 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

General observations

Practical transmetalation reactions are irreversible and stoichiometric, proceed rapidly under mild conditions and give easily separated heteropolymetallic products. These considerations require that useful transmetalation systems have a large driving force and that the reactants be kinetically labile [2].

Polynuclear copper transmetalation targets that satisfy these requirements can contain bidentate *N,N,N′,N′*-tetraalkylamine ligands L, eqn. (1) [6, 16, 17], and even an anionic oxo-pyridine ligand that bridges the target metal centers [3, 4, 21]. Transmetalation of copper requires the ultimate transfer of anionic NS ligands from transmetalators $M(NS)_2$ to copper and formation of discrete metal-exchanged products, as in reactions (1) and (2). The overall transmetalation process thus involves many kinetic events, although only one is usually rate-determining [13–20]. The relative stabilities of transmetalators $M(NS)_2$ are a useful guide to their relative reactivities with a given target. In the context of the present work, previous measurements show that $\mathbf{A}_2$ is more thermodynamically stable than $\mathbf{A}_1$ [1, 11] and that target **C** is much more thermodynamically stable than transmetalation product $Ni(acac)_2$, **D** [22].

The very high stability of transmetalation co-products Cu(NS)(s) and $Cu(NS)_2$ provides a sufficiently large driving force to allow the formation of families of heteropolymetallic transmetalation products that otherwise would not exist [2][*].

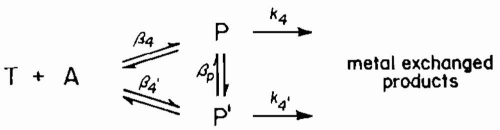
When the target is a heteropolymetallic molecule such as $(\mu_4\text{-}O)N_4Cu_2Ni_2Cl_6$, it also is important that Cu or Ni, but not both, be replaced by M from 1 mol of $M(NS)_2$. The reason for this requirement is that there is no known method of separating the alternative monotransmetalation products $(\mu_4\text{-}O)N_4CuNi_2MCl_6$ and $(\mu_4\text{-}O)N_4Cu_2NiMCl_6$ from each other. Very recent work [18, 19] actually shows that only the copper(II) centers of the target family $(\mu_4\text{-}O)N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ ($x = 1$–3) are replaced with M = Co, Ni or Zn from the respective equimolar $M(NS)_2$ reagents **A** [18, 19] even though replacement of Ni is also thermodynamically possible [11]. This points to specific interactions of $M(NS)_2$ with a copper(II) center in each $(\mu_4O)N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ target [19].

Kinetic studies of monotransmetalations of $(\mu_4\text{-}O)N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ targets T with $M(NS)_2$ reagents have revealed rate law (4) when x in T is 3 and M in **A** is Co or Zn [18].

$$\text{rate} = \beta_4 k_4[\mathrm{T}][\mathrm{M(NS)_2}]/(1+\beta_4[\mathrm{T}]) \quad (4)$$

This discovery is important for several reasons: (i) it is consistent with a transmetalation mechanism like that shown in Scheme 1, where precursors **P** are in rapid equilibrium with the reactants and k_4 governs the rate-determining step; (ii) thus, for the first time we can unambiguously distinguish thermodynamic (β_4) and kinetic (k_4) factors in irreversible transmetalation mechanisms and show that one factor affects the other [18]; (iii) we can demonstrate that transmetalation reactions can proceed through different precursors at different temperatures in the same system (Scheme 1 [18]); (iv) we can compare kinetic data for a range of first-order transmetalation, complex formation and isomerization reactions of polynuclear copper targets to demonstrate marked differences in the strengths of Cu–X and Cu–O bonds that have to be broken for copper replacement (transmetalation) or copper movement (isomerization) [18]; (v) we find that precursor formation constants β_4 are an order of magnitude larger than the largest known equilibrium constant (71 M^{-1} in benzene [24]) for the formation of adducts $M(NS)_2\cdot 2py$, where py is a monodentate pyridine. In other words, $(\mu_4\text{-}O)N_4Cu_{4-x}(Ni(H_2O)_xCl_6$ molecules are better ligands for $M(NS)_2$ than are monodentate py; (vi) variations in the rate laws for specific monotransmetalation of $(\mu_4O)N_4Cu_{4-x}(Ni(H_2O))_xCl_6$ targets by **A** (M = Zn) as a function of x suggest that the primary precursor interactions involve the Ni–Cl–Cu edges and Ni_2Cu faces of $(\mu_4\text{-}O)N_4Cu_{4-x}(Ni(H_2O)_xCl_6$ targets, with the edges playing the major role. Thus, one explanation for large precursor formation constants in particular transmetalation systems is that there can be specific, multiple target–transmetalator interactions that involve more than one target metal center even in 1:1 transmetalation precursors **P** [18, 19].

The present work seeks to eliminate the involvement of more than one target metal center and multiple types of interactions with the O or X atoms of a polymetallic target. Fair comparison with previous work required the selection of a neutral, mono-



Scheme 1.

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[*] Evidence that transmetalation products like $(\mu_4\text{-}O)N_4Cu_{4-x}M_xX_6$ from reactions (2) [1, 8, 13–15] have only temporal existence is as follows: (i) there are no known comparable core molecular structures in M chemistry; (ii) $(\mu_4\text{-}O)N_4Cu_{4-x}M_xX_6$ ($x = 1-3$) readily disproportionate to $(\mu_4\text{-}O)N_4Cu_4X_6$ (a stable structure [1]) on attempted crystallization [1, 8]; (ii) $(\mu_4\text{-}O)N_4Cu_{4-x}M_xX_6$ spontaneously decompose to alloys $Cu_{4-x}M_x$ on heating in argon [23].

meric copper target. Halo(amine)copper complexes at low molar amine:copper ratios were eliminated from consideration because they have a high propensity to aggregate in aprotic solvents [1, 16, 25, 26]. Attempts to prevent this aggregation by employing higher molar amine:copper ratios [27] are inappropriate because this would result in equilibria involving $M(NS)_2 \cdot (amine)_n$ adducts [24] that would greatly complicate mechanistic interpretation.

Structures and properties of the reactants

Target **C** is square planar [28] (Fig. 1(a)). In the context of the present work, its other important virtues are that it only has one kind of ligand atom, O, and that it forms a variety of mono- and bis-adducts with a wide range of ligands [28, 29].

Complex $Cu(NS)_2$ (A_2) decomposes via reaction (5), where N_2S_2 is the corresponding disulfide [5],

$$2Cu(NS)_2 \longrightarrow 2Cu(NS)(s) + N_2S_2 \qquad (5)$$

on attempted growth of single crystals. Microcrystalline solid A_2 exhibits an axial EPR spectrum at room temperature, consistent with a square-planar molecular structure [30]. The EPR spectrum at 130 K in glassy methylene chloride is consistent with a *cis*-geometry of the NS ligands about copper(II). The electronic spectrum of A_2 in methylene chloride contains an intense, broad band at 600 nm (ϵ 1640 M^{-1} cm^{-1}) and another weak feature at *c*. 800 nm. Complexes **A** (M = Co, Ni and Zn) all have a *cis*-geometry [31]. The spectral properties of A_2 are also consistent with a flat *cis*-geometry (Fig. 1(b)).

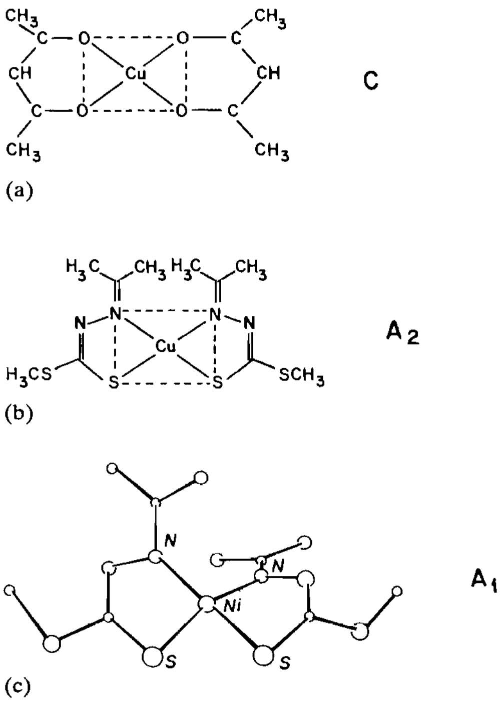


Fig. 1. (a) Square planar structure of target **C** [28]; (b) *cis*-square planar structure of A_2 (see text); (c) molecular structure of A_1 [31a].

Nickel transmetalator A_1 is a nearly flat molecule (the dihedral angle is 27°) with a *cis* geometry [31a] (Fig. 1(c)). As noted above, A_2 is known to be more thermodynamically stable than A_1 [11]. From this point we shall assume that any 1:1 interactions of **C** with A_1 or A_2 give species in which the reactant molecular planes are parallel (Scheme 2).

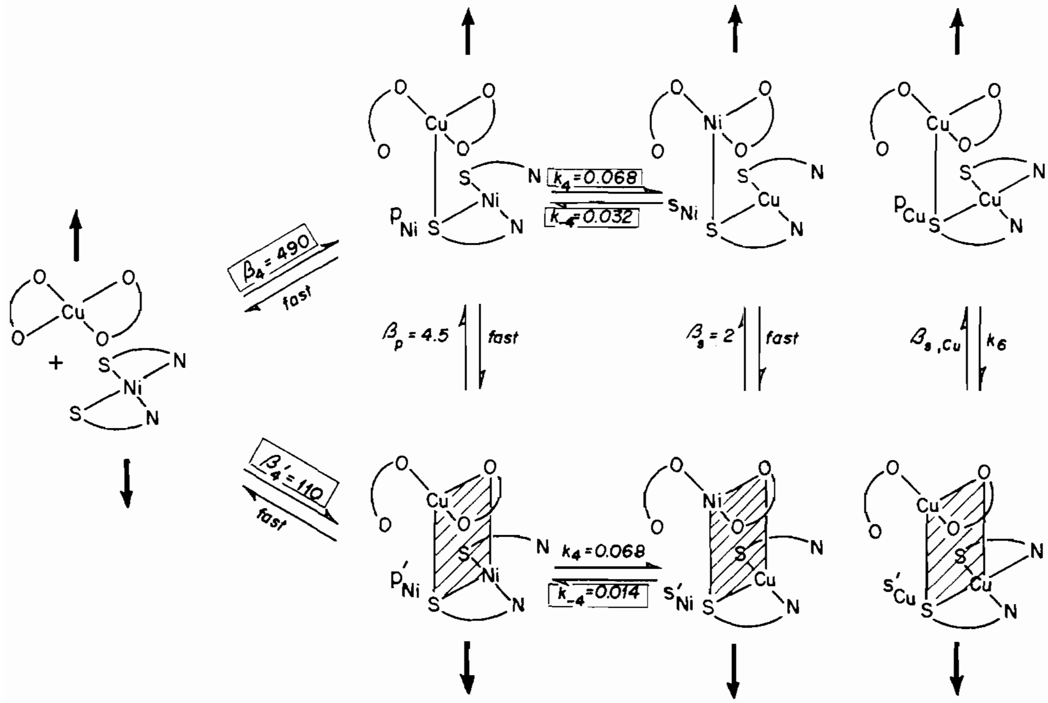
Reaction of $Cu(acac)_2$ (C) with $Cu(NS)_2$ (A_2) in methylene chloride. Spectral and chromatographic observations.

The absorptivity of $Cu(NS)_2$ (A_2) at 600 nm decreases by *c*. 5% on mixing with excess **C** in methylene chloride. The change in absorptivity with $[C]_0/[A_2]_0 > 10$ was independent of $[C]_0$, indicating irreversible complex formation under these conditions, as observed in other systems [20, 32]. However, subjecting such mixtures to chromatography on silica gel with methylene chloride as eluent gave only a first band of A_2 and a second band of **C**. Such chromatography evidently reverses complex formation between A_2 and **C** (see below).

Kinetics of reaction of excess C with A_2 in methylene chloride

The reaction of excess **C** with copper(II) reagent A_2 in methylene chloride occurs on the stopped-flow time scale, as observed in other complex formation systems [20, 32]. Decreased absorbance on reaction is due to a change in the copper environment of A_2 which results in decreased absorptivity at 600 nm, as noted above [20, 32]. Since there is no net metal exchange in the reaction of **C** with A_2, the effects observed must be due to complex formation (Scheme 2, rightmost column).

Absorbance–time data at fixed excess $[C]_0$ and temperature gave plots of $\ln(A_t - A_\infty)$ versus time that were linear for at least four half-lives, indicating a single observable rate-determining step that is first-order in $[A_2]$. Plots of the pseudo-first-order rate constant k_{obs} versus $[C]_0$ at fixed temperature (Fig. 2) indicate rate law (6) for the title reaction. An excellent linear plot of ln k_6 versus $1/T$ was used to calculate the activation parameters, which are given with other first-order data for complex formation [20] in Table 1.



Scheme 2.

$$\text{rate} = k_6[A_2] \tag{6}$$

Reaction of Cu(acac)$_2$ (C) with Ni(NS)$_2$ (A$_1$) in methylene chloride. Spectral and chromatographic observations

Mixing excess **C** with Ni(NS)$_2$ in methylene chloride results in greatly increased absorbance at 600 nm, as observed in other reactions which result in metal exchange to give co-product Cu(NS)$_2$ (A$_2$) [1, 3, 5, 7–9, 11–15, 17–20]. In contrast to the results of the previous section, the total absorbance change on reaction increased with increasing [C]$_0$. This indicates that metal exchange to form successor complexes S_{Ni} and S_{Ni}' is reversible (Scheme 2), as verified by kinetic measurements (see below). Chromatography of a reacted 1:1 mixture of **C** and **A$_1$** on silica gel with methylene chloride as the eluent gave four bands analyzed in the order **A$_2$**, **A$_1$**, **C** and **D** at comparable concentrations. Mixed ligand products M(acac)NS were not detected. This verifies reversible metal exchange in overall reaction (7)*.

$$\underset{\textbf{C}}{\mathrm{Cu(acac)_2}} + \underset{\textbf{A}_1}{\mathrm{Ni(NS)_2}} \rightleftharpoons \underset{\textbf{D}}{\mathrm{Ni(acac)_2}} + \underset{\textbf{A}_2}{\mathrm{Cu(NS)_2}} \tag{7}$$

Kinetics of reaction of excess **C** *with Ni(NS)$_2$ (A$_1$) in methylene chloride*

The reaction of excess **C** with nickel reagent **A$_1$** in methylene chloride is much slower than that with **A$_2$** and was easily monitored at 600 nm by conventional spectrophotometry. Absorbance–time data at fixed excess [C]$_0$ and temperature gave plots of $\ln(A_\infty - A_t)$ versus time that were linear for at least four half-lives, indicating a single rate-determining step that is first-order in [A$_1$]. Plots of the pseudo-first-order rate constant k_{obs} versus [C]$_0$ at fixed temperature (Fig. 3(a)) are curved and have finite intercepts. This suggests rate law (8) where A, B and C are empirical constants with units of s^{-1}, M^{-1} and s^{-1}, respectively. Equation (8) can be rearranged to eqn. (9). Plots of $1/(k_{obs} - C)$ versus 1/[C] from eqn. (9) at five fixed temperatures in the range 10.0 to 29.0 °C are shown in Fig. 4.

$$k_{obs} = A[C]/(1 + B[C]) + C \tag{8}$$

$$1/(k_{obs} - C) = 1/A[C] + B/A \tag{9}$$

Data analysis and comparison

Figure 3 shows our results for two monotransmetalation reactions involving transmetalator

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*The observation of only **A** and **B** bands on chromatography of the equilibrium system $\mathbf{A} + \mathbf{B} \leftrightarrows \mathbf{C}$ is due to preferential retention of **A** and **B** and dissociation of **C** that is rapid on the chromatographic time scale [20]. All of the associated species in Scheme 2 are evidently dissociated by chromatography on silica gel, as indicated by the heavy arrows in Scheme 2.

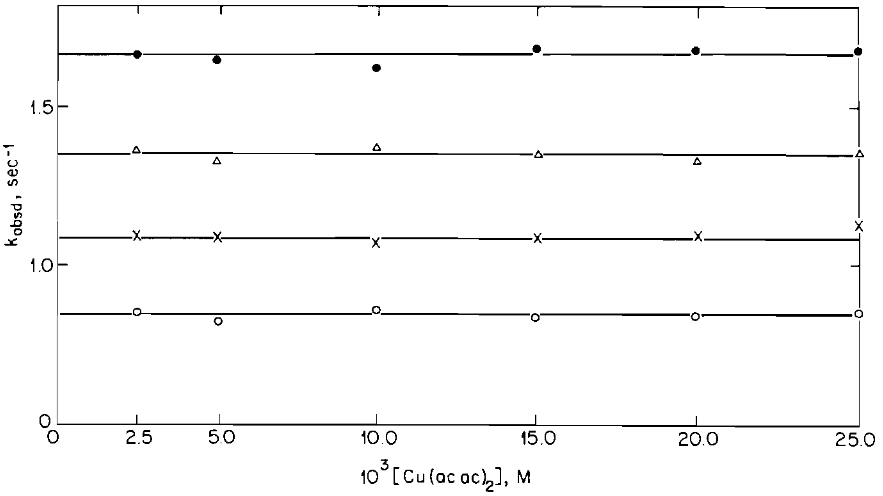

Fig. 2. Plots of k_{obs} vs. [C] for the reaction of excess C with A_2 (rate law (6)) in methylene chloride at the following temperatures (°C): 9.0, ○; 15.0, X; 22.0, △; 29.0, ●.

Ni(NS)$_2$ (A$_1$). The data in Fig. 3(a) refer to the first observed reaction of excess C with A$_1$ in methylene chloride (this work). The data in Fig. 3(b) refer to the first observed reaction of the (μ,μ)-dichlorobridged dimer N$_2$ClCu(Cl,Cl)CuClN$_2$ (E: N = *N*,*N*-diethylnicotinamide) with A$_1$ in nitrobenzene [20]*. Comparison of these data reveals the following.

(i) Changing the target from C to E results in much higher reaction rates. This indicates that E is a significantly more labile target than C.

(ii) Both reactions are reversible, as indicated by the finite intercepts at $[C]_0$ or $[E]_0 = 0$ in Fig. 3. These are the only known reversible reactions of transmetalator A$_1$ with copper targets. The reaction of C with A$_1$ also is the only known reversible reaction of this type in methylene chloride (all the others have been detected in nitrobenzene [16, 20, 32]).

(iii) Plots of k_{obs} versus $[E]_0$ are linear, while those of k_{obs} versus $[C]_0$ are curved and clearly approach a limiting rate at high $[C]_0$. This indicates that the reaction of C with A$_1$ involves the formation of precursors with measurably large formation constants β_4, as introduced in eqn. (4) [18]. Modification of eqn. (4) to incorporate (i) the known first-order dependence on [A$_1$] and (ii) reaction reversibility (that is, term *C*) gives eqn. (10), where T denotes C or E. Assumption of $1 \gg \beta_4[T]$ in the denominator of the first term of eqn. (10) gives eqn. (11), which is the form of the data for the reaction of E with A$_1$ in Fig. 3(b). The reaction of E with A$_1$ thus involves much weaker precursors (smaller β_4) than the corresponding reaction with C*. That is, C is a 'stickier' [18, 19] target than E. Equation (10) can be rearranged to eqn. (12) (see Fig. 4).

$$k_{obs} = \beta_4 k_4[T]/(1 + \beta_4[T]) + k_{-4} \qquad (10)$$

$$k_{obs} = \beta_4 k_4[T] + k_{-4} \qquad (11)$$

$$1/(k_{obs} - k_{-4}) = 1/\beta_4 k_4[T] + 1/k_4 \qquad (12)$$

Comparison of eqns. (8), (9), (10) and (12) indicates the same forms, with $C = k_{-4}$, $A = \beta_4 k_4$, $B = \beta_4$, $A/B = k_4$ and $A/BC = K_4$ for a system with only one precursor, single forward and reverse rate-determining steps and only one overall equilibrium constant $\beta_4 K_4$. We next show that the rate law for the reaction of C with A$_1$ is somewhat more complicated than expected from eqn. (10).

Temperature dependences

Figures 5–8 show the temperature dependences of *B*, *A*/*B*, *C* and *A*/*BC*, respectively, for the reaction of C with A$_1$.

Figure 5 indicates the involvement of more than one precursor in the reaction of excess C with nickel transmetalator A$_1$. Precursor P$_{Ni}$ (Scheme 2)** is

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*Two first-order processes are observed in the reaction of excess E with A$_1$ in nitrobenzene (see Fig. 3 of ref. 20). The first reaction is summarized in Fig. 3(b). In this paper we compare data for the second observed reaction of E with those for other rapid, first-order reactions of E with M(NS)$_2$ reagents [20] and with the data for reaction of excess C with A$_2$ (Table 1).

*If $\beta_4[E] < 0.1$ at the highest [E] in Fig. 3(b), then $\beta_4 < 50$ M^{-1} in the reaction of E with A$_1$ at all the previously reported temperatures [20].

**In Scheme 2 we have enclosed all quantities that are determinable from the relationships in Figs. 3(a) and 5–8. Precursor formation constants β_4 and β_4' have units M^{-1}, while β_p and β_s are unitless. The units of rate constants k_4, k_4', k_{-4} and k_{-4}' are s^{-1}. All quoted values refer to 23 °C in methylene chloride and are given with other derived quantities in Table 2.

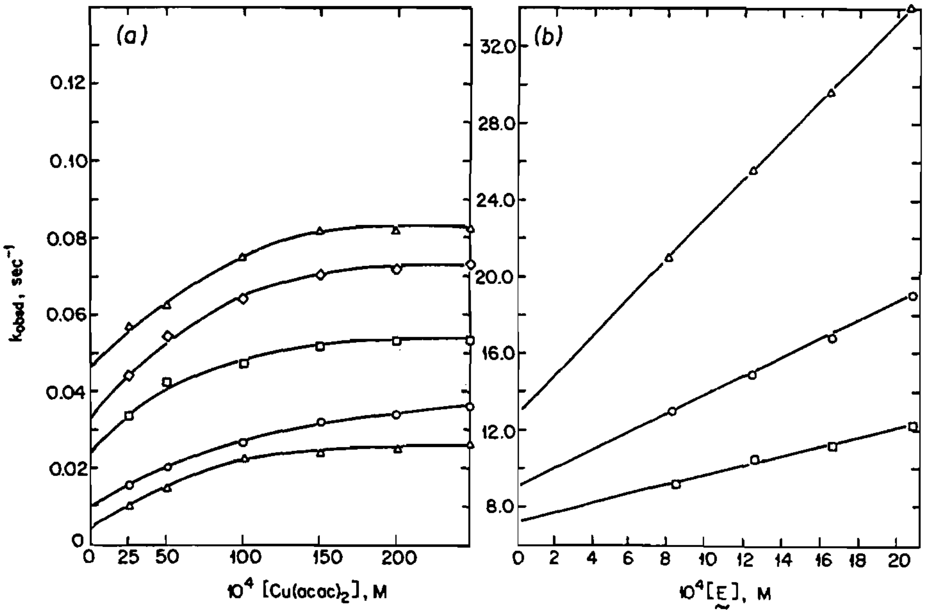

Fig. 3. (a) Plots of k_{obs} vs. [C] for the reaction of excess C with A_1 in methylene chloride at the following temperatures (°C): 10.0, △; 17.0, ○; 22.0, □; 27.0, ◇; 29.0, △. (b) Plots of k_{obs} vs. [E] for the first observed reaction of excess E with A_1 in nitrobenzene at the following temperatures (°C): 17.9, □; 22.6, ○; 30.6, △. The data are from ref. 20.

TABLE 1. Kinetic data for first-order successor complex formation in the reactions of excess C and of excess dimeric target E with reagents

Target	M in A	k_6^b	ΔH_6^{*c}	ΔS_6^{*d}	Reference
C	Cu	1.40	5.5	−39	this work
E	Co	0.11	5.9	−43	20
	Ni	0.90	9.0	−30	20
	Cu	1.2	12.7	−15	20
	Zn	0.70	13.4	−18	20

[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 $^{-1}$.

formed endothermically in the upper temperature range of this study*, while the formation of P_{Ni}, at lower temperatures is essentially thermoneutral. The latter behavior is similar to that of the precursors formed between target (μ_4-O)N_4Cu(Ni(H_2O))$_3$$Cl_6$ and A (M = Co and Zn (the latter only at relatively high temperatures)) in nitrobenzene [18]. The rapid conversion of P_{Ni} to P_{Ni}' has equilibrium constant $\beta_p = \beta_4/\beta_4' \simeq 4.5$ at 23 °C in methylene chloride and is endothermic (Table 2). Conversion of the 'low temperature' precursor to the 'high temperature' precursor in the (μ_4-O)N_4CuNi$_3$$Cl_6$/A (M = Zn) system has $\beta_p \simeq 5.5$ at 23 °C in nitrobenzene and also is endothermic (see Table IV of ref. 18).

The linear plot of log (*A*/*B*) versus 1/*T* in Fig. 6 suggests only one rate-limiting metal-exchange step. However, the temperature dependence of *C* in Fig. 7 demonstrates kinetically distinguishable reverse reactions of two different successor complexes S_{Ni} and S_{Ni}'. These reverse processes have about the same activation enthalpy (Table 2). On the basis of the linearity of the plot in Fig. 6, we assume that the conversions of P_{Ni} to S_{Ni} and P_{Ni}' to S_{Ni}' in Scheme 2 have the same rate constant and activation parameters.

The equilibrium constants for successor complex formation from the respective precursors in Scheme 2 are given by $K_4 = k_4/k_{-4}$ and $K_4' = k_4'/k_{-4}'$. Figure 8 indicates that these equilibrium processes are both slightly exothermic and involve slightly negative entropy changes (Table 2).

Reversible reactions of copper targets with M(NS)$_2$ reagents

Before turning to a more detailed consideration of proposed Scheme 2 and the data in Table 2, we will examine a correlation of thermodynamic data for all known reversible reactions of M(NS)$_2$ complexes with copper targets.

Figure 9 was constructed as follows. We first plotted the heat and entropy of formation of all known precursors P from the respective transmetalation

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*The boiling point of methylene chloride is 40 °C, which restricts the upper limit of the experimental temperature range.

reactants (β values from Table IV of ref. 18 and from Table 2), which are shown as closed circles. We then computed equilibrium constant products $\beta_4 K_4$ and $\beta_4' K_4'$ from Table 2 and added them along with enthalpies and entropies calculated from the temperature dependence of the slope/intercept ratios of plots like Fig. 3(b), which refer to reversible systems with small β_4 and measurable forward and reverse rate constants (eqn. (11)) [18, 20, 32]. Finally, we added points 6 and 7, which refer to equilibrium constants $K_4 = k_4/k_{-4}$ and $K_4' = k_4'/k_{-4}'$ for the reaction of **C** with $\mathbf{A}_1$ in methylene chloride (Table 2, Scheme 2).

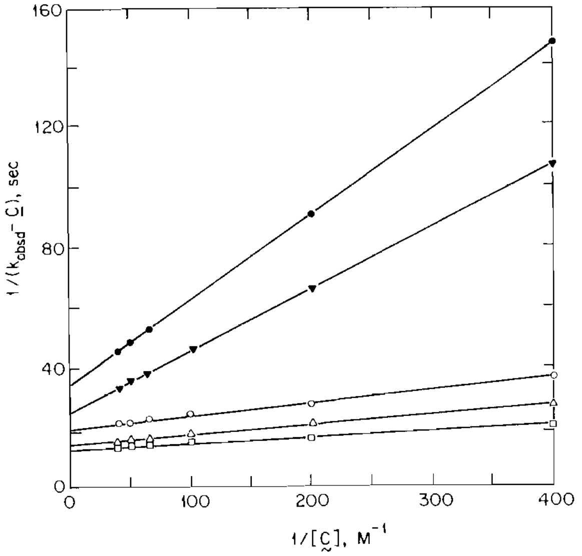


Fig. 4. Plots of $1/(k_{obs} - C)$ vs. $1/[\mathbf{C}]$ for the reaction of excess **C** with $\mathbf{A}_1$ in methylene chloride at the following temperatures (°C): 10.0, ●; 17.0, ▼; 22.0, ○; 27.0, △; 29.0, □. See text for definition of C.

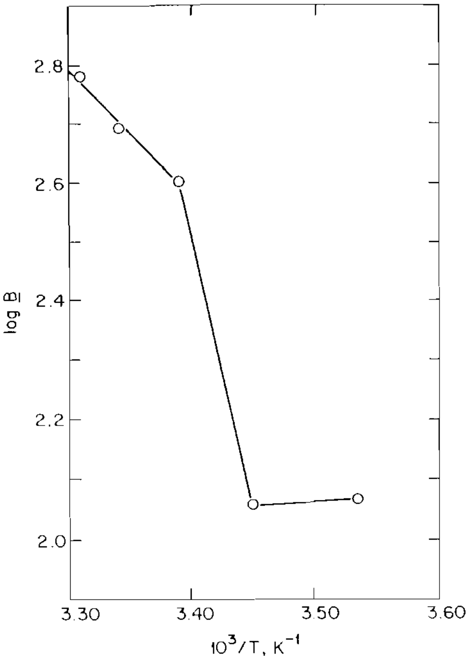


Fig. 5. Plot of log B vs. $1/T$ for the reaction of excess **C** with $\mathbf{A}_1$ in methylene chloride. See text for definition of B.

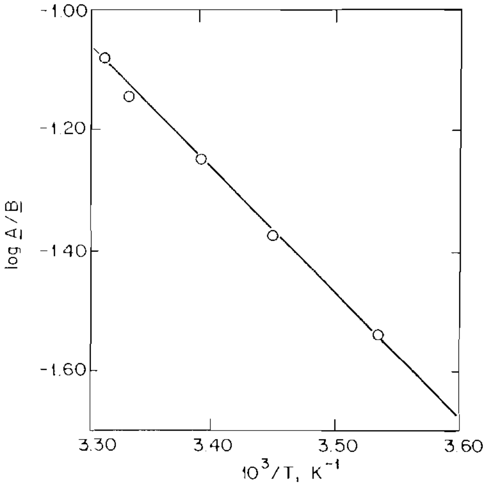


Fig. 6. Plot of log A/B vis. $1/T$ for the reaction **C** with $\mathbf{A}_1$ in methylene chloride. See text for definitions of A and B.

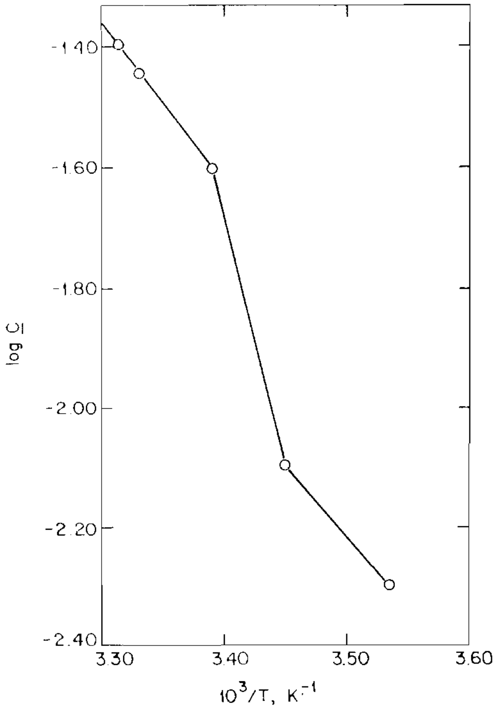


Fig. 7. Plot of log C vs. $1/T$ for the reaction of **C** with $\mathbf{A}_1$ in methylene chloride. See text for definition of C.

Figure 9 correlates equilibrium data for seven different copper targets reacting reversibly with five different reagents **A** or **B** in two different aprotic solvents. All the reactants are neutral. The linear plot (slope 310 ± 20 K) indicates that all equilibrium interactions between these reactants give rise to closely compensated heat and entropy changes. However, there is no discernable relationship between the relative stability of the $M(NS)_2$ reagents [11] and their heats and entropies of interaction with any fixed target. Because of this compensation of enthalpy and entropy changes, it is difficult to identify primary reactant properties that are responsible for the observed variations in the equilibrium parameters.

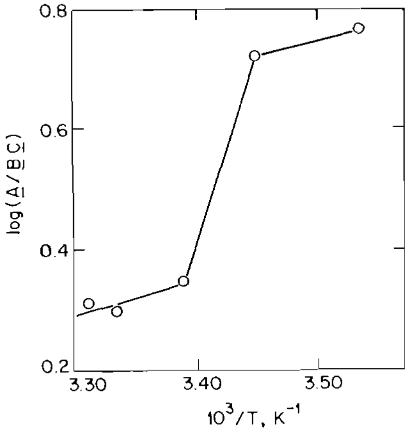


Fig. 8. Plot of log A/BC vis. $1/T$ for the reaction of **C** with $\mathbf{A}_1$ in methylene chloride. See text for definitions of A, B and C.

TABLE 2. Measured and derived parameters for the reaction of excess **C** with $\mathbf{A}_1$ in methylene chloride (Scheme 2)

Parameter	M^a	ΔH_i^b	ΔS_i^c
(a) Equilibrium parameters			
β_4	490 ± 15	10.3 ± 0.6	47 ± 5
β_4'	110 ± 10	−1.0 ± 0.5	6 ± 4
β_p	4.5	11.4 ± 0.6	41 ± 5
K_4	2	−2.0 ± 0.6	−10 ± 5
K_4'	4.6	−2.0 ± 0.6	−3 ± 5
β_s	2	11.4 ± 0.6	34 ± 5
Parameter	M^a	$\Delta H_i^{\neq b}$	$\Delta S_i^{\neq c}$
(b) Kinetic parameters			
k_4	0.068	9.3 ± 0.6	−33 ± 5
k_4'	0.068	9.3 ± 0.6	−33 ± 5)^d
k_{-4}	0.032	11.8 ± 0.5	−24 ± 5
k_{-4}'	0.014	10.8 ± 0.5	−31 ± 5

[a] Magnitude of the cited parameter at 23 °C in methylene chloride. [b] Units are kcal mol^{-1}. [c] Units are cal deg^{-1} mol^{-1} at 25 °C. [d] Quantities in parentheses are assumed on the basis of considerations in the text.

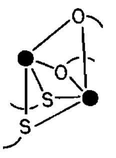
We note, however, that the majority of precursors and successor complexes are formed with little net heat or entropy change. The exceptions are (i) points 1, 2 and 8–10, which apparently refer to the formation of species with incomplete four-membered rings between the reactants and exhibit relatively large heats and entropies of formation (e.g. β_p and β_s in Scheme 2, see below) and (ii) one precursor (point 5) and one complex (point 15) that are formed exothermically with markedly negative formation entropies.

Figure 10 shows the heat and entropy changes for four of the equilibria and the two rate-determining processes in Scheme 2 as a function of reaction coordinate. The data are taken from Table 2. Formation of successor complex S_{Ni} from **C** and $\mathbf{A}_1$ is endothermic and results in an entropy increase, while formation of the other successor complex S_{Ni}' is almost thermoneutral and results in little entropy change.

The remarkable feature of Fig. 10 is an almost constant enthalpy difference between P_{Ni} and P_{Ni}', their respective activated complexes and between the successor complexes S_{Ni} and S_{Ni}'. Parallel and compensating trends of the respective entropy differences also are evident in the lower section of Fig. 10. These features suggest that the formation of P_{Ni} from P_{Ni}', their conversion to the respective activated complexes and the conversion of S_{Ni}' to S_{Ni} all involve breaking the same kind of bond. We propose that this bond completes the four-membered rings of species P_{Ni}' and S_{Ni}' in Scheme 2. Breaking this bond results in an entropy increase of *c*. 50 cal deg^{-1} mol^{-1} at 25 °C in methylene chloride (Fig. 10).

Linkage of the reactants in four-membered rings has previously been suggested to facilitate metal exchange in transmetalation reactions [13–20]. According to Fig. 10 and proposed Scheme 2, such four-membered rings already exist in P_{Ni}' and S_{Ni}'. We feel that some chelate rings are already opened on precursor formation in light of the associated entropy changes. For example, assembly of precursor P_{Ni} from **C** and $\mathbf{A}_1$ would be expected to result in an entropy decrease [18, 19, 24], but the measured value is 47 ± 5 cal deg^{-1} mol^{-1} (Table 2). The disposition of open chelate rings in Scheme 2 has been arbitrarily assigned to account in a consistent manner for the observed entropy differences between the various proposed species.

Our view of the activated complexes for rate-determining interconversion of the precursors and successor complexes in Scheme 2 is as follows. The activated complex for interconversion of P_{Ni} and S_{Ni} contains no complete four-membered ring, while that for interconversion of P_{Ni}' and S_{Ni}' contains such a ring. The observed negative entropy of activation in both metal exchange pathways makes it reasonable to assume that copper and nickel are both at least weakly bonded to one donor atom of exchanging ligands NS and acac. This would link each metal to two S and two O atoms in symmetrical activated complexes, as suggested below. Such interactions are necessary to explain the absence of mixed ligand products M(acac)NS in the reaction of C with A_1.



Reaction of excess C with Cu(NS)$_2$ (A$_2$)

Mixing an excess of dimeric copper target E with nickel reagent A_1 results in a first-order absorbance increase followed by a first-order absorbance decrease at 600 nm (see Fig. 3 of ref. 20). These events have been associated with (i) metal exchange through a weak precursor (Fig. 3b and eqn. (11)) and (ii) irreversible relaxation to a successor complex, respectively [20]. Mixing M(NS)$_2$ reactants A (M = Co, Cu or Zn) with excess E results in a kinetically measurable absorbance decrease at 600 nm. This was accounted for [20] by immeasurably faster metal exchange with the much less thermodynamically stable cobalt and zinc reactants [11] and measurable, irreversible formation of the same sort of successor complex as with copper reactant A_2.

The first-order absorbance decrease at 600 nm observed in the reaction of excess C with A_2 (Fig. 2 and eqn. (6)) indicates successor complex formation, as supported by the activation parameter correlation in Fig. 11. All the events that are correlated in Fig. 11 evidently proceed through especially stable precursors (to account for their observed first-order rate law (6)) and have negative entropies of activation. In the rightmost column of Scheme 2 we suggest that the reaction of C with A_2 proceeds via precursor P_{Cu} to give successor complex S_{Cu}'. Precursor P_{Cu} is evidently much more stable (larger β_4) than P_{Ni} and P_{Ni}' in the C/A_1 system.

Conclusions

Evidence is mounting that all transmetalation reactions proceed through precursors to give successor complexes that dissociate when subjected to silica gel or gel permeation chromatography. There are particular interactions in these associated forms that are responsible for specific metal exchange. We are actively pursuing these matters and will report our results in subsequent papers.

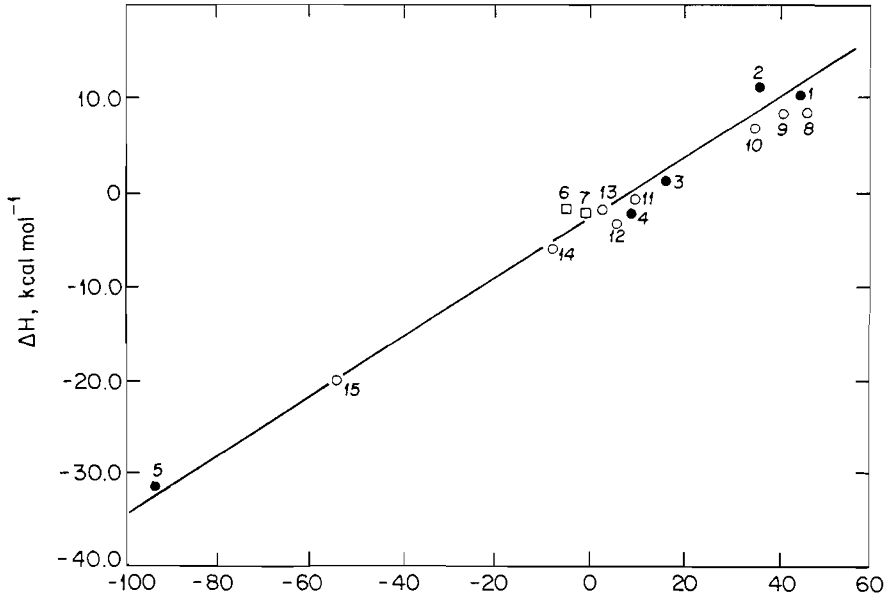


Fig. 9. Plot of enthalpy vs. entropy changes for precursor (β_4, β_4', β_p, β_s: filled circles and squares) and overall successor complex formation (β_4K_4, β_4K_4': open circles). The data are taken from Table 2 of this paper (target C), Table V of ref. 16 (targets $L_2Cu_2X_2$), Table IV of ref. 18 (targets μ_4-O)$N_4Cu_{4-x}(Ni(H_2O))_xCl_6$) and Table III ($k_{obs}(1)$ data only) of ref. 20 (target E). The parameters refer to eqns. (10) or (11) (where observed) and to Schemes 1 and 2. The transmetalators are particular reagents A or B, the solvent is either methylene chloride or nitrobenzene and the temperature is 25 °C.

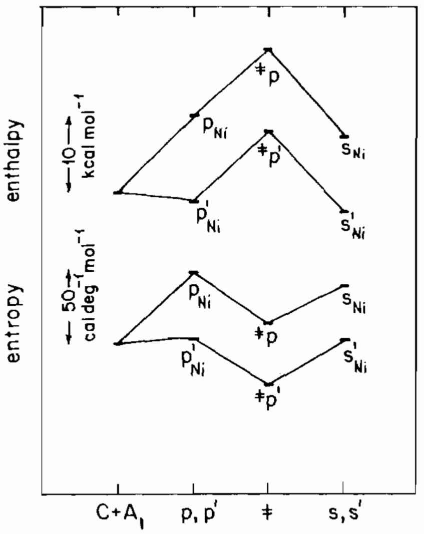


Fig. 10. Enthalpy and entropy profiles for the reaction of excess C with A_1 via precursors P_{Ni}, P'_{Ni} and respective activated complexes $\neq_p$ and $\neq_p{}'$ to respective successor complexes S_{Ni} and S'_{Ni}. The data are taken from Table 2.

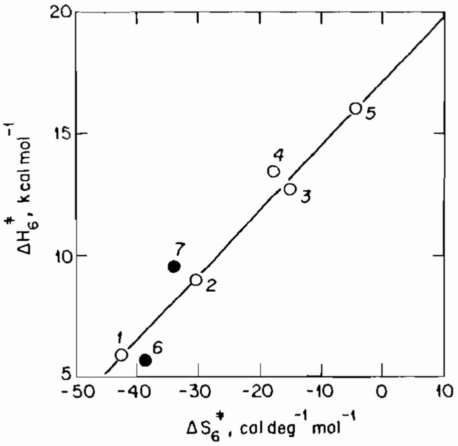


Fig. 11. Plot of $\Delta H_6^{\neq}$ vs $\Delta S_6^{\neq}$ for successor complex formation. Figure 6 of ref. 20 has been augmented by addition of data for the reaction of excess C with A_2 (k_6, Table 1, point 6) and k_4 for the rate-determining step in the reaction of excess C with A_1 (Table 2, point 7).

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