Crystal and Molecular Structures of Three $M(NS)_2$ Transmetalating Agents (NS is a Monoanionic S-Methyl Hydrazinecarbodithioate Schiff Base; M = Co, Zn)

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Abstract

The crystal and molecular structures of the $M(NS)_2$ transmetalating agents bis-(S-methyl-isopropylidenehydrazinecarbodithioato)cobalt(II), its zinc analog and of bis-(S-methyl-benzylidenehydrazinecarbodithioato)zinc(II) are reported. Structural differences which may give rise to different mechanisms of transmetalation are noted.

Introduction

Direct transmetalation is the stoichiometric replacement of the metals in a polynuclear complex with core structure retention [1–4]. Complexes $M(NS)_2$, where M is Co, Ni or Zn and NS is a monoanionic S-methyl-hydrazinecarbodithioate Schiff base, are stoichiometric transmetalating agents for a variety of tetranuclear copper complexes. The driving force in these systems is the formation of very stable $Cu(NS)_2$ coproducts [1–4].

Kinetic measurements in systems of known reactant structure have been made to establish transmetalation mechanisms [4]. The reactants were excess $(\mu_4\text{-O})N_4Cu_4X_6$ (N = a monodentate pyridine, X = Cl or Br), **A** [2, 4], bis-(S-methyl-isopropylidenehydrazinecarbodithioato)nickel(II), **B** [5] and bis-(S-methyl-benzylidenehydrazinecarbodithioato) nickel(II), **C** [6] in eqn. (1).

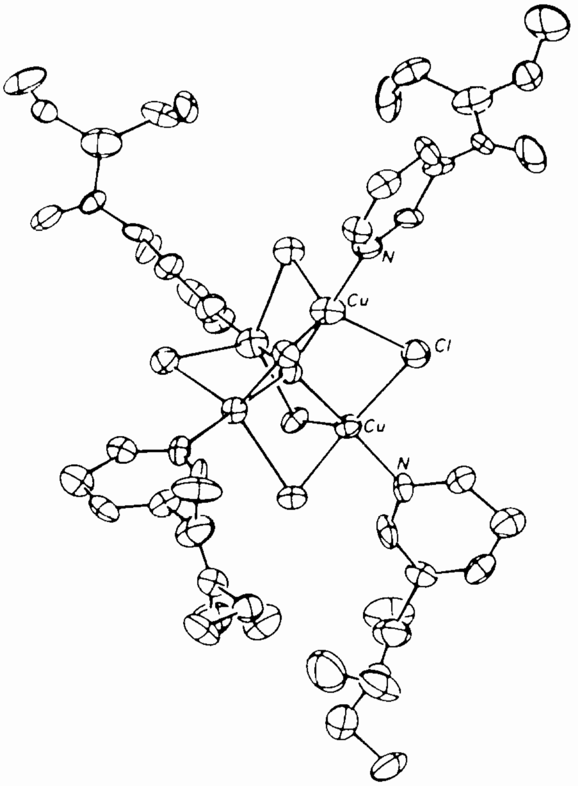
$$\mathbf{A} + \mathbf{B} \text{ or } \mathbf{C} \longrightarrow$$

$$\underset{\mathbf{D}}{(\mu_4\text{-oxo})[N_4Cu_3NiX_6]} + \mathbf{B} \text{ or } \mathbf{C}\ (M = Cu) \quad (1)$$

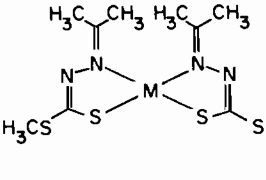
Rate laws 2 and 3 were observed for reaction 1 carried out with molecules of known structure, *cis*-**B** and *trans*-**C**, respectively. They indicate that Cu- - -S—Ni- - -X ring formation is a prerequisite for efficient transmetalation [4].

$$d[\mathbf{D}]/dt = k_{\mathbf{B}}[\mathbf{B}][\mathbf{A}]^2 \quad (2)$$

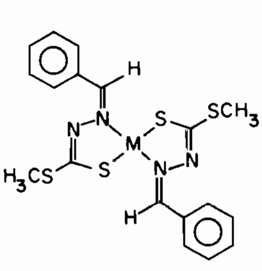
$$d[\mathbf{D}]/dt = k_{\mathbf{C}}[\mathbf{C}][\mathbf{A}] \quad (3)$$



A



B



C

A knowledge of the structures of additional $M(NS)_n$ complexes (M = Co, Zn, etc.; $n = 1–3$) will be useful in determining the mechanisms of their transmetalation reactions. This paper reports the crystal and molecular structures of the cobalt [7, 8]

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and zinc [9] analogs of **B** and of the zinc [9] analog of **C**. Attempted preparation of the cobalt analog of **C** resulted in the oxidation of cobalt to Co(III).

Experimental

Synthesis and Crystallization

The complexes bis-(S-methyl-isopropylidenehydrazinecarbodithioato)cobalt(II), **E**, its zinc analog, **F**, and bis-(S-methyl-benzylidenecarbodithioato)zinc-(II), **G**, were synthesized as described previously [7–9]. Complex **E** was prepared under dinitrogen to prevent its oxidation to $Co(NS)_3$.

Single crystals of **E** and **F** were grown as follows. A deoxygenated solution of **E** or **F** in methylene chloride (5 ml; 50–100 mM) in a 10 ml beaker was placed in a 200 ml stoppered glass jar containing 20 ml anhydrous diethylether. The jar was filled with dinitrogen, closed and then allowed to stand at room temperature for 12–24 h, whereupon single crystals formed on the sides and bottom of the beaker because of ether diffusion into the solution. Crystals of **E** and **F** proved to be isomorphous. Single crystals of **G** were obtained exactly as above but with tetrahydrofuran instead of methylene chloride and anhydrous hexane instead of diethylether (that is, by diffusion of hexane into tetrahydrofuran). Analytical and spectral data for single crystals of **E**–**G** were indistinguishable from those reported previously [7–9].

Data Collection and Structure Solution

Details of crystal data and data collection for the individual complexes are in Table I. In each experiment a crystal was attached to a glass fiber and mounted on a Syntex $P2_1$ automated diffractometer. Unit cell dimensions were obtained by a least squares fit of reflections well-separated in reciprocal space. One hemisphere of data was collected in the range $4 \leqslant 2\theta \leqslant 130°$ using $\theta/2\theta$ scans and a variable scan rate. The data were corrected for Lorentz and polarization effects; an empirical absorption correction, determined from a ψ scan, was also made. The reflections with $I \geqslant 2\sigma(I)$ were used in the structure solution and refinement.

The structures were solved via Patterson and Fourier syntheses. Full-matrix least-squares were used to refine positional and isotropic (subsequently anisotropic) thermal parameters of non-hydrogen atoms*. Hydrogen atomic positions were calculated, refined isotropically and then normalized to lie 1.04 Å from the carbon atom to which they were bonded. Convergence was reached at $R = 0.060$ (**E**), 0.045 (**F**) and 0.046 (**G**).

The atomic scattering factors for the non-hydrogen atoms were taken from ref. 11 with Zn, Co and S being corrected for anomalous scattering [12]. Scattering factors for hydrogen were taken from ref. 13.

Final atomic positional parameters for non-hydrogen atoms appear in Tables II–IV. Tables of anisotropic thermal parameters, hydrogen atom parameters, and calculated and observed structure factors are available, see 'supplementary material'.

Results and Discussion

The structures of bis-(S-methyl-isopropylidenehydrazinecarbodithioate)cobalt(II) (**E**), and its zinc analog, (**F**), proved to be isomorphous; therefore Fig. 1, which actually shows the molecular structure of the cobalt complex, represents both compounds.

TABLE I. Crystal Data and other Experimental Parameters for E, F and G

	E	F	G
Molecular formula	$CoC_{10}H_9N_4S_4$	$ZnC_{10}H_9N_4S_4$	$ZnC_{18}H_{18}N_4S_4$
Formula weight	372.40	378.84	484.01
Crystal dimensions (mm)	0.20 × .25 × 0.35	0.20 × 0.20 × 0.30	0.10 × 0.15 × 0.65
a (Å)	8.488(1)	8.471(2)	12.087(2)
b (Å)	18.112(3)	18.167(4)	14.611(2)
c (Å)	11.824(2)	11.854(2)	13.831(2)
β (deg)	109.81(1)	109.82(2)	116.40(1)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4
d_{calc} (g cm^{-3})	1.446	1.466	1.469
Minimum scan speed, 2θ (deg min^{-1})	3.0	3.0	3.0
Number of unique reflections measured	2673	2764	3486
Number of reflections with $I \geqslant 2\sigma(I)$	2081	2306	2831
R ($I \geqslant 2\sigma(I)$)	0.060	0.045	0.046

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*All crystallographic calculations were carried out on a VAX 11/780 computer. For the principal programs used see ref. 10.

TABLE II. Fractional Atomic Coordinates (×10^4) for Non-hydrogen Atoms in E[a]

Atom	*x/a*	*y/b*	*z/c*
Co	2609(1)	−43(1)	2886(1)
S(1)	1779(2)	1117(1)	3143(1)
C(2)	−202(6)	995(3)	2083(4)
N(3)	−839(5)	412(2)	1466(4)
N(4)	263(5)	−199(2)	1722(4)
S(5)	−1455(2)	1788(1)	1842(1)
C(6)	−3435(8)	1451(4)	877(6)
C(7)	−392(6)	−784(3)	1124(4)
C(8)	662(8)	−1467(3)	1303(6)
C(9)	−2118(7)	−824(4)	263(5)
S(1′)	4863(2)	−246(1)	2319(1)
C(2′)	5469(6)	−1023(3)	3218(5)
N(3′)	4879(5)	−1282(3)	4004(4)
N(4′)	3536(5)	−859(3)	4123(4)
S(5′)	7130(2)	−1489(1)	2967(1)
C(6′)	7485(8)	−2258(4)	3974(6)
C(7′)	3003(6)	−1069(3)	4969(5)
C(8′)	1573(7)	−664(4)	5133(6)
C(9′)	3696(7)	−1690(3)	5779(5)

[a]Estimated standard deviations are in parentheses.

TABLE III. Fractional Atomic Coordinates (×10^4) for Non-hydrogen Atoms in F[a]

Atom	*x/a*	*y/b*	*z/c*
Zn	2675.7(6)	−14.4(3)	2905.2(4)
S(1)	1777(1)	1132(1)	3184(1)
C(2)	−179(4)	989(2)	2092(3)
N(3)	−795(3)	410(2)	1476(3)
N(4)	301(4)	−203(2)	1726(3)
S(5)	−1464(1)	1775(1)	1837(1)
C(6)	−3448(5)	1436(3)	845(4)
C(7)	−352(4)	−785(2)	1138(3)
C(8)	716(6)	−1462(2)	1327(4)
C(9)	−2087(5)	−830(2)	262(4)
S(1′)	4903(1)	−249(1)	2293(1)
C(2′)	5472(4)	−1020(2)	3208(3)
N(3′)	4875(4)	−1268(2)	3999(3)
N(4′)	3547(4)	−844(2)	4125(3)
S(5′)	7114(1)	−1504(1)	2958(1)
C(6′)	7454(6)	−2270(3)	3951(4)
C(7′)	2990(5)	−1056(2)	4957(3)
C(8′)	1570(5)	−647(3)	5123(4)
C(9′)	3675(5)	−1698(2)	5750(3)

[a]Estimated standard deviations are in parentheses.

TABLE IV. Fractional Atomic Coordinates (×10^4) for Non-hydrogen Atoms in G[a]

Atom	*x/a*	*y/b*	*z/c*
Zn	3813.8(4)	2869.7(3)	7137.2(4)
S(1)	5010(1)	2715(1)	6266(1)
C(2)	6105(3)	3481(3)	7124(3)
N(3)	6045(2)	4035(2)	7836(2)
N(4)	4956(2)	3946(2)	7974(2)
S(5)	7454(1)	3470(1)	6958(1)
C(6)	8457(4)	4246(4)	7982(4)
C(7)	4759(3)	4630(3)	8455(3)
C(8)	3774(3)	4670(3)	8792(3)
C(9)	3356(4)	3887(3)	9098(3)
C(10)	2459(4)	3948(4)	9453(4)
C(11)	1983(4)	4776(5)	9516(4)
C(12)	2397(4)	5559(4)	9235(4)
C(13)	3300(4)	5511(3)	8889(4)
S(1′)	1736(1)	3040(1)	6345(1)
C(2′)	1577(3)	2257(3)	7230(3)
N(3′)	2380(3)	1722(2)	7922(3)
N(4′)	3597(2)	1814(2)	8042(2)
S(5′)	66(1)	2252(1)	7084(1)
C(6′)	151(4)	1473(4)	8123(4)
C(7′)	4314(3)	1177(2)	8608(3)
C(8′)	5642(3)	1112(3)	8959(3)
C(9′)	6375(3)	1860(3)	9029(3)
C(10′)	7635(4)	1750(4)	9375(3)
C(11′)	8171(4)	923(4)	9664(4)
C(12′)	7472(4)	171(3)	9618(4)
C(13′)	6198(4)	263(3)	9280(3)

[a]Estimated standard deviations are in parentheses.

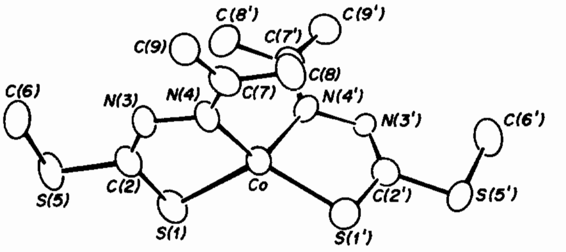

Fig. 1. Perspective view of the non-hydrogen atoms of complex E showing the numbering scheme.

The complexes exist as discrete molecular units consisting of tetrahedral $M(NS)_2$ cores. The approximately 85° angle between the S, M, N planes for these complexes attests to their tetrahedral nature (Table V). The valency angles about M range from *ca.* 87 to 129° with the smallest reflecting the bite angles of the bidentate ligands. As expected, the Zn–S and Zn–N distances are longer, respectively, than are the Co–S and Co–N distances since the ionic radius of Co^{2+} is *ca.* 0.02 Å smaller than that of Zn^{2+} [14].

The zinc analog of **C**, bis-(S-methyl-benzylidene-hydrazinecarbodithioato)zinc(II), **G**, adopts a structure which is very similar to those of **E** and **F** (Fig. 2). The $M(NS)_2$ core structure is again tetrahedral, with the angle between S, M, N planes being 89.9° and the valency angles about Zn ranging from *ca.* 87 to 126°. While the Zn–S and Zn–N distances in **G** are longer than those in **F**, they are well within accepted values. However, they are much shorter than

TABLE V. Distances (Å) of Atoms from Least-squares Planes through Various Groups of Atoms; Atoms Defining the Plane are Italicized

	E	F	G
Plane 1			
M	0.000	0.000	0.000
S(1)	0.000	0.000	0.000
C(2)	0.089	0.137	−0.285
N(3)	0.092	0.131	−0.234
N(4)	0.000	0.000	0.000
S(5)	0.196	0.290	−0.691
C(7)	−0.026	−0.055	0.382
S(1′)	1.589	1.565	1.482
N(4′)	−1.342	−1.405	−1.517
Plane 2			
M	0.000	0.000	0.000
S(1′)	0.000	0.000	0.000
C(2′)	0.244	0.204	−0.222
N(3′)	0.237	0.195	−0.174
N(4′)	0.000	0.000	0.000
S(5′)	0.533	0.454	−0.545
C(7′)	−0.120	−0.089	0.248
S(1)	−1.367	−1.280	1.434
N(4)	1.527	1.635	−1.537
Angle between planes			
1/2	84.4	85.6	89.9

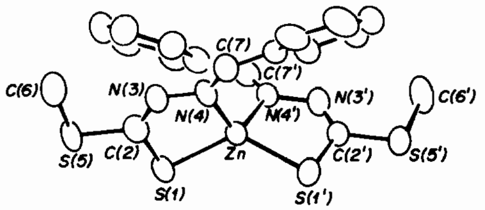

Fig. 2. Perspective view of the non-hydrogen atoms of complex **G** showing the shielding of tetrahedron faces by the benzylidene substituents.

TABLE VI. Interatomic Separations (Å) and Valency Angles (deg.) for E and F[a]

	M = Co		M = Zn	
(a) Coordination sphere				
M–S(1)	2.270(2)	2.262(2)	2.280(1)	2.280(1)
M–N(4)	2.020(4)	2.040(5)	2.052(3)	2.046(3)
S(1)–M–N(4)	86.6(1)		87.3(1)	
S(1)–M–S(1′)	121.46(7)		124.73(4)	
S(1)–M–N(4′)	129.5(1)		129.0(1)	
N(4)–M–S(1′)	120.9(1)		118.6(1)	
N(4)–M–N(4′)	116.0(2)		113.2(1)	
S(1′)–M–N(4′)	86.3(1)		87.0(1)	
(b) Ligand				
S(1)–C(2)	1.738(5)	1.734(6)	1.742(4)	1.738(4)
C(2)–N(3)	1.294(6)	1.285(7)	1.286(4)	1.289(5)
C(2)–S(5)	1.751(5)	1.753(6)	1.758(4)	1.754(4)
N(3)–N(4)	1.413(6)	1.419(6)	1.415(4)	1.412(4)
N(4)–C(7)	1.291(7)	1.288(7)	1.285(5)	1.289(5)
S(5)–C(6)	1.789(7)	1.789(7)	1.801(5)	1.783(5)
C(7)–C(8)	1.499(8)	1.486(8)	1.497(6)	1.482(6)
C(7)–C(9)	1.475(8)	1.465(8)	1.486(6)	1.487(6)
M–S(1)–C(2)	93.1(2)	93.1(2)	92.1(1)	92.1(1)
S(1)–C(2)–N(3)	128.9(4)	129.3(4)	130.1(3)	130.0(3)
S(1)–C(2)–S(5)	113.5(3)	112.1(3)	112.6(2)	111.5(2)
N(3)–C(2)–S(5)	117.6(4)	118.6(4)	117.3(3)	118.6(3)
C(2)–N(3)–N(4)	113.5(4)	113.4(4)	114.4(3)	114.2(3)
M–N(4)–N(3)	117.7(4)	116.6(3)	115.7(2)	115.9(2)
M–N(4)–C(7)	129.0(4)	128.3(4)	130.5(2)	128.5(3)
N(3)–N(4)–C(7)	113.2(4)	115.0(5)	113.8(3)	115.5(3)
C(2)–S(5)–C(6)	102.3(3)	103.1(3)	102.8(2)	103.8(2)
N(4)–C(7)–C(8)	118.3(5)	118.3(5)	117.9(3)	118.5(4)
N(4)–C(7)–C(9)	124.1(5)	124.5(5)	124.5(3)	123.5(3)
C(8)–C(7)–C(9)	117.5(5)	117.3(5)	117.6(3)	117.9(3)

[a] Estimated standard deviations are in parentheses.

analogous distances in the related, quadridentate Zn(N_2S_2) (N_2S_2 = diacetyl-bis-hydrazonato-S-methylcarbodithioate) [1].

The bond lengths and angles for **E** and **F** are compared in Table VI; Table VII shows these parameters for **G**.

All bonds in the ligands can be described as either single or double bonds; *ie.*, the double bonds are localized. For example, the mean of the C to N bonds in **E** and **F** is 1.288 Å and in **G** it is 1.286 Å. These are comparable to the C=N double bond length of 1.29 Å [15]. This type of localization has previously been observed in similar ligands [5, 6, 16–18].

The ligands in **E** and **F** are very nearly planar with the methyl group lying furthest from the S, C, N, N plane and, in each case, eclipsing the uncoordinated N atom of the ligand (C–S–C–N 7.4 and 0.7° for M = Co; 6.9 and 1.2° for M = Zn). In both **E** and **F** the M atom is slightly displaced from the S, C, N, N ligand planes (0.11 and 0.29 Å for M = Co; 0.16 and 0.24 Å for M = Zn).

In **G** the Zn atom lies 0.24 and 0.31 Å from the S, C, N, N planes and the C–S–C–N angles are small (3.9 and 4.2°). The phenyl rings show no significant deviation from planarity though the respective N(4) atoms are 0.44 and 0.35 Å from these planes. The fact that the N–N=C–C double bonds are *trans* results in the phenyl rings essentially covering two faces of the tetrahedron formed by the coordination sphere, thereby shielding the metal against nucleophilic attack from these directions. The phenyl rings are not coplanar with the S, C, N, N planes but rather form angles of 51.9 and 36.5°, respectively, with these planes.

TABLE VII. Interatomic Separations (A) and Valency Angles (deg) for G[a]

(a) Coordination sphere					
Zn–S(1)	2.267(1)		Zn–S(1′)	2.264(1)	
Zn–N(4)	2.073(3)		Zn–N(4′)	2.074(3)	
S(1)–Zn–N(4)	87.06(9)		N(4)–Zn–S(1′)	120.45(9)	
S(1)–Zn–S(1′)	125.90(5)		N(4)–Zn–N(4′)	117.30(12)	
S(1)–Zn–N(4′)	121.83(8)		S(1′)–Zn–N(4′)	87.89(8)	
(b) Ligand					
S(1)–C(2)	1.736(4)	1.748(4)	C(8)–C(9)	1.390(6)	1.382(6)
C(2)–N(3)	1.302(5)	1.282(5)	C(8)–C(13)	1.388(6)	1.387(6)
C(2)–S(5)	1.745(4)	1.746(4)	C(9)–C(10)	1.377(6)	1.388(6)
N(3)–N(4)	1.417(4)	1.412(4)	C(10)–C(11)	1.359(8)	1.344(8)
N(4)–C(7)	1.281(5)	1.277(5)	C(11)–C(12)	1.373(8)	1.371(7)
S(5)–C(6)	1.798(6)	1.800(6)	C(12)–C(13)	1.375(7)	1.402(7)
C(7)–C(8)	1.459(5)	1.459(5)			
Zn–S(1)–C(2)	92.6(1)	91.9(1)	N(4)–C(7)–C(8)	124.3(3)	126.7(3)
S(1)–C(2)–N(3)	129.5(3)	129.8(3)	C(7)–C(8)–C(9)	121.6(4)	123.2(3)
S(1)–C(2)–S(5)	112.2(2)	110.9(2)	C(7)–C(8)–C(13)	119.7(4)	117.9(3)
N(3)–C(2)–S(5)	118.4(3)	119.3(3)	C(9)–C(8)–C(13)	118.5(4)	118.8(4)
C(2)–N(3)–N(4)	114.4(3)	115.6(3)	C(8)–C(9)–C(10)	120.4(4)	120.2(4)
Zn–N(4)–N(3)	115.0(2)	113.9(2)	C(9)–C(10)–C(11)	120.2(5)	121.1(5)
Zn–N(4)–C(7)	130.6(3)	132.8(2)	C(10–C(11)–C(12)	120.4(5)	120.1(4)
N(3)–N(4)–C(7)	113.4(3)	112.9(3)	C(11)–C(12)–C(13)	120.1(5)	120.1(4)
C(2)–S(5)–C(6)	103.5(2)	103.0(2)	C(8)–C(13)–C(12)	120.3(4)	119.7(4)

[a]Estimated standard deviations are in parentheses.

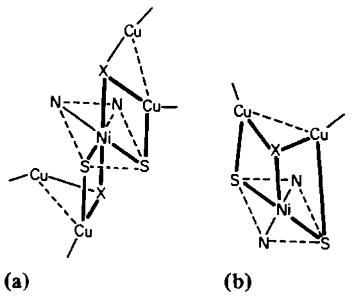

Fig. 3. Proposed intermediates in the transmetalation of A by (a) B and (b) C.

In summary, all three complexes embody a distorted tetrahedral $M(NS)_2$ core and planar ligands. In addition, by comparison of bond lengths with ionic radii it is presumed that metal bond strengths in **E** and **F** are of the same magnitude while metal bonds in **G** may be slightly weaker.

We have proposed that transmetalations of **A** by the square-planar complexes **B** and **C** proceed through structures containing the units shown in Fig. 3 [4]. The first structure is consistent with rate law 2 and the second with rate law 3. The formation of analogous structures in the transmetalation of **A** by **E**–**G** requires accessibility of M to X of the NCu–X–CuN edge of **A**. From a comparison of Figs. 1 and 2 it would appear that the formation of structure a in Fig. 3 is more likely with **E** and **F** than it is with **G** because of the relatively larger steric bulk of the benzylidene substituents. Since **E** forms stable adducts with pyridines but **F** does not [19], indicating higher Lewis acidity for **E**, we would predict transmetalation rates **E** > **F**. We are presently investigating the mechanisms of these transmetalation systems.

Supplementary Material

Tables of anisotropic thermal parameters, hydrogen atom parameters, and calculated and observed structure factors, are available from the authors on request.

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