Ligand exchange in mixed organocuprate(I) π-complexes.

Steven H. Bertz,* Kelsey L. Browder, Richard A. Hardin, Michael D. Murphy, Craig A. Ogle,* and Andy A. Thomas[†]

Department of Chemistry, University of North Carolina–Charlotte, Charlotte, NC 28223

Supporting Information

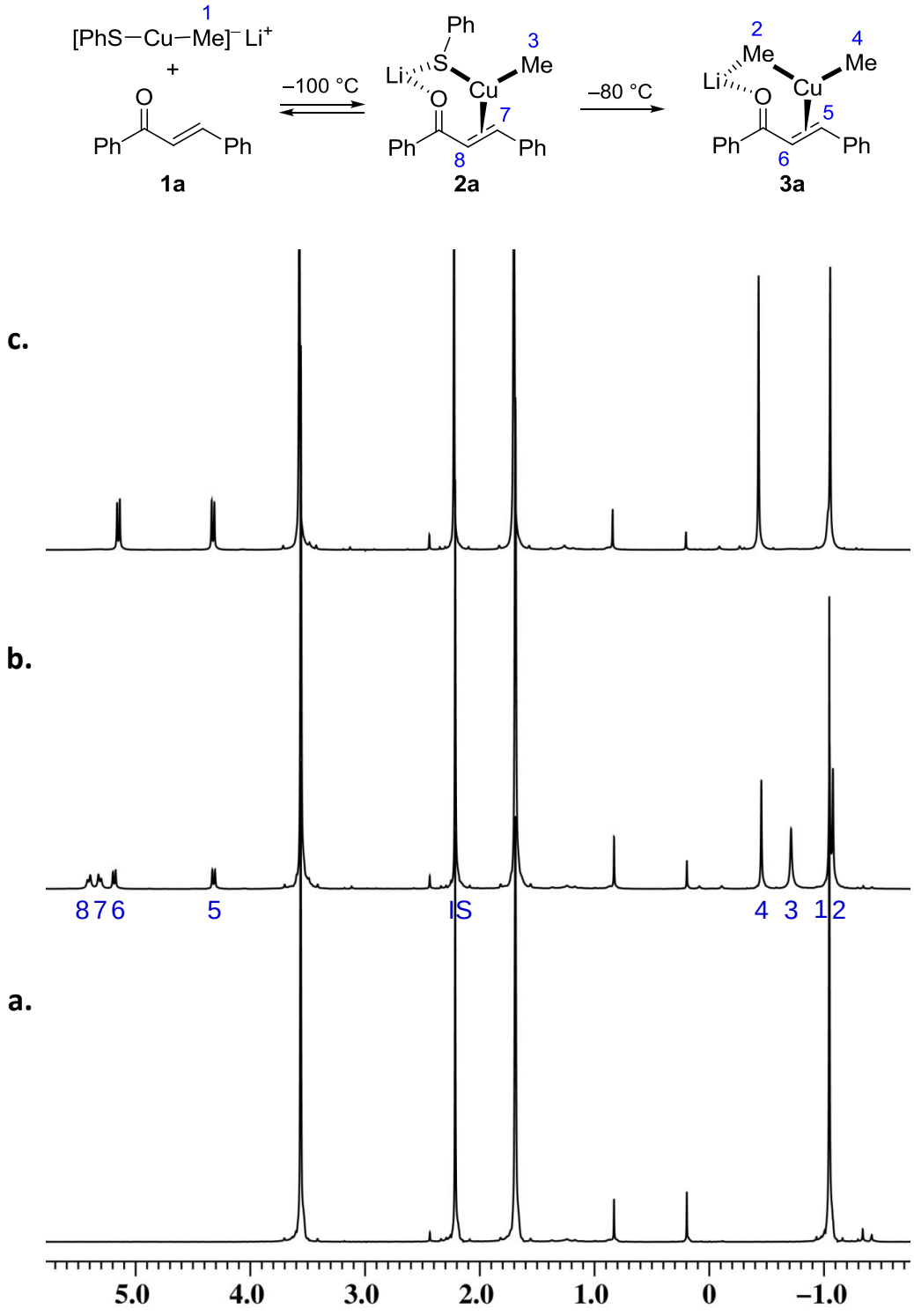


Fig. SI-1. ^{1}H spectra recorded during the conversion of Me(PhS)CuLi-chalcone.
a. [PhS–Cu–Me]$^{-}$Li^{+} at –100 ^{o}C. **b.** After rapid injection of chalcone at –100 ^{o}C.
c. 134 minutes after warming to –80 ^{o}C. The internal standard is mesitylene.

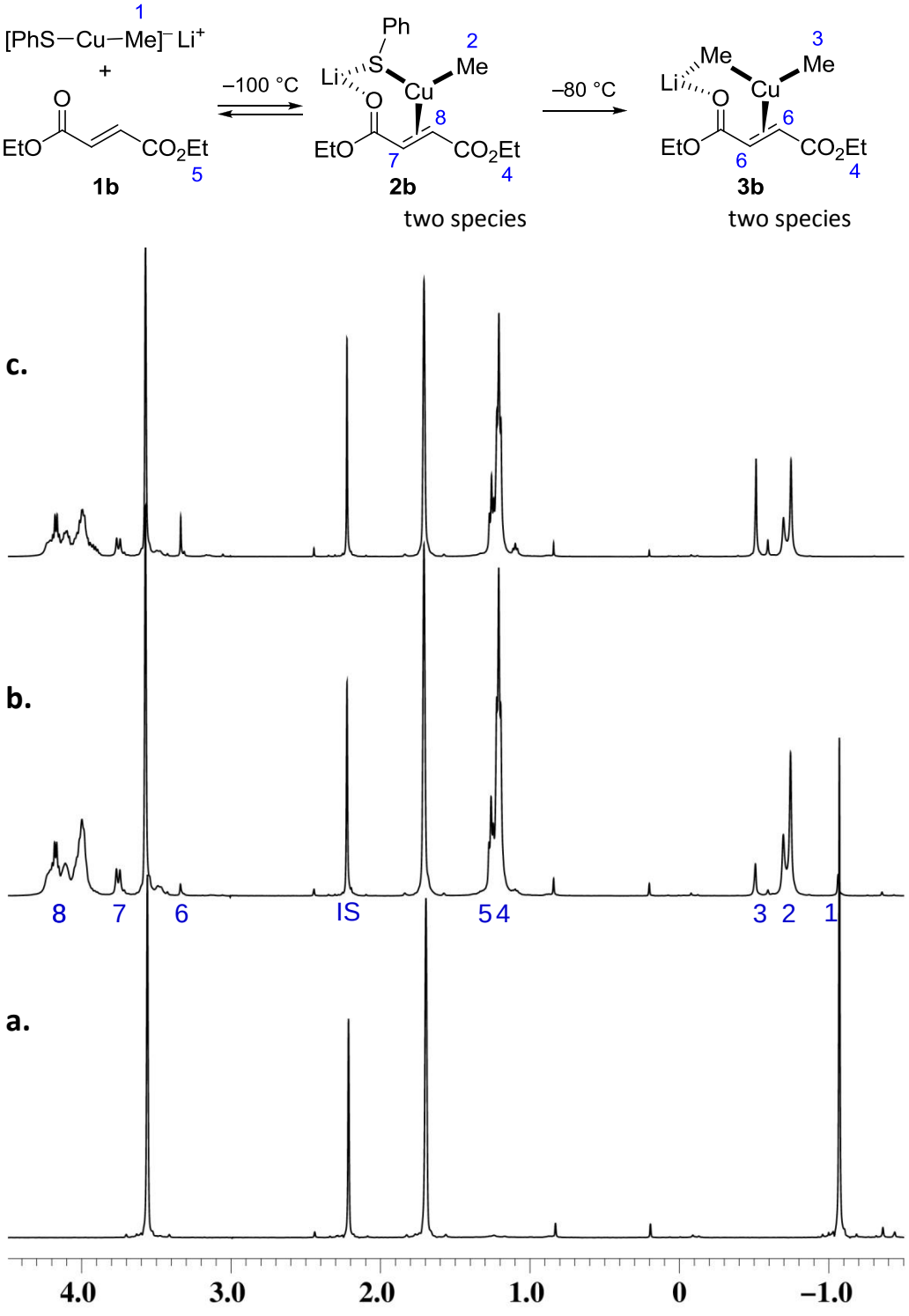


Fig. SI-2. ^{1}H spectra recorded during the conversion of Me(PhS)CuLi-DEF. **a.** [PhS–Cu–Me]$^{-}$Li^{+} at –100 °C. **b.** After rapid injection of DEF and warming to –80 °C. **c.** 240 minutes later. The internal standard is mesitylene.

Table SI-1. Example of the MathCad™ worksheet used to determine the rate constants in the ligand exchange mechanism of Chart 1 .

Import text file containing data using an Input table.

data :=

	t	Sub	HC-Sub	MC-Sub	MC
	1	2	3	4	5
1	0	24.26	12.96	7.64	33.29
2	0.5	24.12	13.02	6.14	32.74
3	1	24.61	13.37	5.14	33.46
4	1.5	23.81	13.88	4.93	33.37
5	2	22.61	14.1	5.03	32.43
6	3	22.62	14.43	4.65	31.45
7	4	22.08	15.16	4.45	30.86
8	5	21.35	15.39	4.24	29.66
9	6	22.12	16.16	4.08	29.21
10	7	21.55	16.44	3.81	28.88

Count data points:

$rows := rows(data)$

Create vectors for time and concentrations:

$time := data^{\langle 1 \rangle}$ $sub := data^{\langle 2 \rangle}$ $HPsub := data^{\langle 3 \rangle}$ $MPsub := data^{\langle 4 \rangle}$ $MC := data^{\langle 5 \rangle}$

Enter rate constants, initial concentrations, and vector of first derivatives

$k_f := 0.016$ $k_r := 3.0$ $k_2 := 0.0035$ $Y0 := \begin{pmatrix} 15 \\ 13 \\ 13 \\ 25 \end{pmatrix}$ $Q(t, Y) := \begin{pmatrix} -k_f \cdot Y_1 \cdot Y_4 + k_r \cdot Y_2 \\ k_f \cdot Y_1 \cdot Y_4 - k_r \cdot Y_2 - k_2 \cdot Y_2 \cdot Y_4 \\ k_2 \cdot Y_2 \cdot Y_4 \\ -k_f \cdot Y_1 \cdot Y_4 + k_r \cdot Y_2 - k_2 \cdot Y_2 \cdot Y_4 \end{pmatrix}$

Enter range and number of increments:

$t0 := 0$ $tmax := 150$ $ncalc := 1000$

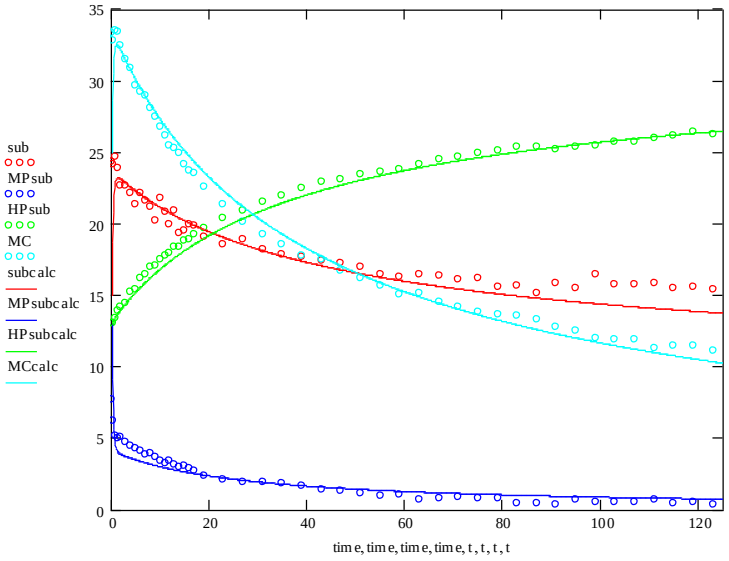
Solve differential equations using Runge-Kutta method with adaptive step size

$R := Rkadapt(Y0, t0, tmax, ncalc, Q)$

Extract vectors for time and calculated concentrations

$t := R^{\langle 1 \rangle}$ $subcalc := R^{\langle 2 \rangle}$ $MPsubcalc := R^{\langle 3 \rangle}$ $HPsubcalc := R^{\langle 4 \rangle}$ $MCcalc := R^{\langle 5 \rangle}$

Plot data and calculated concentrations



Convert calculated concentrations to spline functions

$fa(x) := linterp(R^{\langle 1 \rangle}, R^{\langle 2 \rangle}, x)$ $fb(x) := linterp(R^{\langle 1 \rangle}, R^{\langle 3 \rangle}, x)$ $fc(x) := linterp(R^{\langle 1 \rangle}, R^{\langle 4 \rangle}, x)$ $fd(x) := linterp(R^{\langle 1 \rangle}, R^{\langle 5 \rangle}, x)$

$i := 1 .. rows - 1$

Calculate residuals squared and $\chi 2$

$da_i := |fa(time_i) - sub_i|^2$ $db_i := |fb(time_i) - MPsub_i|^2$ $dc_i := |fc(time_i) - sub_i|^2$ $dd_i := |fd(time_i) - MC_i|^2$

$chisq := \sum_i (da_i + db_i + dc_i + dd_i)$ $chisq =$

Write concentration matrix to text file

$WRITEPRN("c:\kinetics\run2\_fit.txt") := R$