ORGANOMETALLICS

Volume 17, Number 2, January 19, 1998

Communications

Oxidative Addition of Dimesitylphosphine to Platinum(0): P−H vs P−C Activation

Igor V. Kourkine, Matthew D. Sargent, and David S. Glueck*

6128 Burke Laboratory, Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Received August 21, 1997[⊗]

*Summary: Reaction of Pt(dppe)(trans-stilbene) (**1**) with dimesitylphosphine initially gives, in equilibrium with **1**, $PHMes_2$, and trans-stilbene, the kinetic product of P−H activation, $Pt(dppe)(PMes_2)(H)$ (**2**, dppe = $Ph_2PCH_2CH_2PPh_2$, Mes = 2,4,6-$Me_3C_6H_2$). Further reaction of this mixture gives the thermodynamic product of P−C activation, Pt(dppe)(PHMes)(Mes) (**3**), plus the disproportionation products $Pt(dppe)_2$ (**4**) and Pt(0).*

Oxidative addition of element−hydrogen (E−H) and E−C bonds is a fundamental reaction in organometallic chemistry and homogeneous catalysis.[1] For E = P, these steps are important in catalytic addition of the P−H group to unsaturated substrates[2] and deactivation of phosphine-containing metal catalysts, respectively.[3] We report here the observation of both P−H and P−C oxidative addition of dimesitylphosphine ($PHMes_2$, Mes = 2,4,6-$Me_3C_6H_2$) to the Pt(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) fragment, which provides a rare opportunity to compare oxidative additions of two different bonds in a single substrate to a metal center.[4] Mechanistic studies suggest that both reactions proceed via a common intermediate, three-coordinate $Pt(dppe)(PHMes_2)$.

As previously reported, treatment of Pt(dppe)(*trans*-stilbene) (**1**) with $PHMes_2$ in THF or benzene at room temperature generates, in minutes, the phosphido hydride $Pt(dppe)(PMes_2)(H)$ (**2**, Scheme 1).[2,5] Complex **2** appears to exist in an equilibrium mixture with **1**, stilbene, and $PHMes_2$. On standing, however, **1** and **2** are slowly consumed and Pt(dppe)(PHMes)(Mes) (**3**) is formed in ~70% yield (^{31}P NMR integration) after several days at room temperature in THF (Scheme 1). Some $Pt(dppe)_2$ (**4**, 15%) is also produced;[6] the other products of this disproportionation, Pt(0) and $PHMes_2$, were observed as a black precipitate and by ^{31}P NMR, respectively. Although still slow, the reaction proceeds somewhat more quickly on heating and requires 2 days at 55 °C in THF for complete conversion; in this case, the yields of **3** and **4** are 60% and 20%, respectively.

Complex **3** was prepared independently (Scheme 1). Displacement of COD from Pt(COD)(Mes)(Br)[7] yields Pt(dppe)(Mes)(Br) (**5**).[8] Treatment of **5** with NaOMe in toluene/methanol gave a yellow solution, presumably

---

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1997.

(1) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley: New York, 1992. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

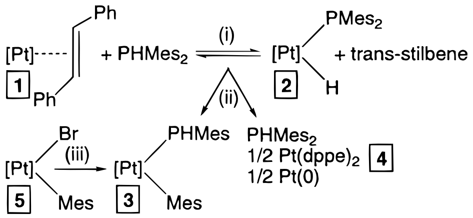
(2) See Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039−5040 and ref 1 therein for examples.

(3) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171−185.

(4) For related observations, see: (a) C−H vs C−Si addition Hofmann, P.; Heiss, H.; Neiteler, P.; Muller, G.; Lachmann, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880−882. Hofmann, P. In *Organosilicon Chemistry: From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1994; pp 231−250. (b) N−H vs N−C addition Bonanno, J. B.; Henry, T. P.; Neithamer, D. R.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1996**, *118*, 5132−5133. (c) C−H vs C−C addition Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406−12415.

S0276-7333(97)00754-1 CCC: $15.00 © 1998 American Chemical Society
Publication on Web 01/19/1998

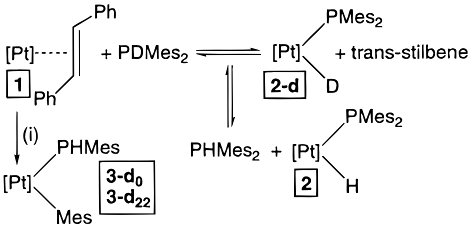
Scheme 1[a]



[a] [Pt] = Pt(dppe). Conditions: (i) 23 °C, minutes; (ii) 23 °C, days (iii) NaOMe then PH_2Mes.

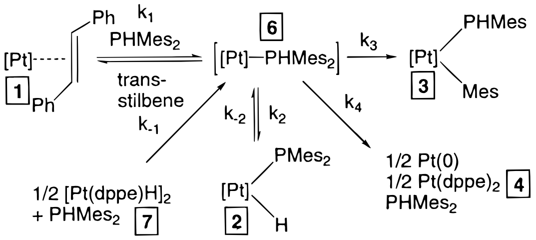
containing the methoxide complex Pt(dppe)(Mes)(OMe),[9] which reacted with PH_2Mes to give **3** as a yellow solid in 78% recrystallized yield.[10] The primary phosphido ligand was identified by ^{31}P NMR (C_6D_6, δ −97.4, $^2J_{PPtrans} = 127$, $^1J_{Pt-P} = 726$, $^1J_{PH} = 198$), ^1H NMR (δ 3.80, ddd, $J_{PH} = 198, 21, 6$; $^2J_{Pt-H} = 66$, PH), and IR (2283 cm^{-1}, KBr).

Scheme 2[a]



[a] [Pt] = Pt(dppe). Reagents: (i) $^1/_2$ $PHMes_2$, $^1/_2$ $PHMes_2$-d_{22}, 55 °C.

Scheme 3[a]



[a] [Pt] = Pt(dppe).

Reaction of $PDMes_2$ with Pt(dppe)(*trans*-stilbene) initially gave, as expected, Pt(dppe)($PMes_2$)(D) (**2**-*d*).[8] However, this was accompanied by label scrambling to afford $PHMes_2$ and, later, Pt(dppe)($PMes_2$)(H) (Scheme 2). This exchange could be reduced, but not stopped, by rigorous measures to exclude water, such as using THF stored over Na and employing a Teflon insert (Wilmad) in a glass NMR tube. In a more informative crossover experiment,[11] **1** was treated with a 1:1 mixture of $PHMes_2$ and PH(Mes-d_{11})$_2$ to give **3** as a mixture of d_0 and d_{22} products; mass spectroscopic analysis showed that no crossover to d_{11} species occurred (Scheme 2). This observation is consistent with *intramolecular* P−C bond cleavage.

We have not yet performed a full kinetic analysis, but the observations described above are consistent with the mechanism shown in Scheme 3. The proposed three-coordinate intermediate Pt(dppe)($PHMes_2$) (**6**), formed reversibly by displacement of stilbene from **1** by dimesitylphosphine and not observed under the reaction conditions, could undergo reversible P−H oxidative

---

(5) **Reaction of 1 with PHMes$_2$.** To a slurry of **1** (50 mg, 0.06 mmol) in THF (1 mL) was added a solution of $PHMes_2$ (30 mg, 0.11 mmol) in THF (1 mL) to afford a yellow solution. The solvent was removed, and the residue was washed with petroleum ether (3 × 2 mL) and dried in vacuo. The solid residue, which contained a mixture of **1**, **2**, and some $PHMes_2$ and *trans*-stilbene, was dissolved in C_6D_6 for NMR: ^1H NMR (C_6D_6) δ 7.22−7.00 (24H, m, Ar), 2.79 (12H, *o*-Me), 2.50−1.60 (4H, br, CH_2), 2.17 (6H, *p*-Me), −2.13 (1H, ddd, $^2J_{PH_{trans}} = 187$, $^2J_{PH_{cis}} = 13.5$, $^2J_{PH_{cis}} = 13.5$, $^1J_{Pt-H} = 1107$, Pt−H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 53.3 (d, $^2J_{PP_{trans}} = 156$, $^1J_{Pt-P} = 2011$), 44.9 ($^1J_{Pt-P} = 1906$), −59.0 (d, $^2J_{PP_{trans}} = 156$, $^1J_{Pt-P} = 1212$). In the ^1H-coupled ^{31}P NMR spectrum, the δ 44.9 peak shows $^1J_{PH} = 187$. IR (KBr): 2033 cm^{-1} (Pt−H). In a related experiment, a mixture of **1** (40 mg, 0.05 mmol), $PHMes_2$ (14 mg, 0.05 mmol), and Ph_3PO (ca. 5 mg, internal standard) was dissolved in THF (0.65 mL) and transferred into an NMR tube, which was kept at 23 °C. The reaction was monitored by ^{31}P NMR spectroscopy over ∼ 3 half-lives. During the first 2 h, the only signals observed in the $^{31}P\{^1H\}$ NMR spectra of the reaction mixture were those of **1**, **2**, and $PHMes_2$; after 2 h, additional peaks due to **3** and **4** appear; these grow over the next 170 h, while those due to **1** and **2** decrease. Extrapolation of the changes of the concentrations of products with time, determined by integration of the $^{31}P\{^1H\}$ NMR spectra, shows that the reaction should be complete in ca. 450 h, for this 1:1 stoichiometry, with yields of 70% for **3** and 15% for **4**. Related reactions with 2 equiv of $PHMes_2$ per 1 equiv of **1** are complete in ∼250 h, with similar yields.

(6) Complex **4** was identified by ^{31}P NMR in comparison to an authentic sample, see: Clark, H. C.; Kapoor, P. N.; McMahon, I. J. *J. Organomet. Chem.* **1984**, *265*, 107−115.

(7) COD = 1,5-cyclooctadiene. Fallis, K. A.; Anderson, G. K.; Rath, N. P. *Organometallics* **1993**, *12*, 2435−2439.

(8) For experimental details and characterization data, see the Supporting Information.

(9) The $^{31}P\{^1H\}$ NMR spectrum of this intermediate (THF, δ 34.8 ($^1J_{Pt-P} = 1770$), 27.4 ($^1J_{Pt-P} = 3362$)) is similar to that reported for Pt(dppe)(Me)(OMe) (THF-d_8, δ 37.35 ($^1J_{Pt-P} = 1852$), 36.00 ($^1J_{Pt-P} = 3356$)). See: Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805−4813.

(10) **Pt(dppe)(PHMes)(Mes) (3).** To a slurry of **5** (800 mg, 1.0 mmol) in toluene (20 mL) was added a solution of NaOMe (prepared from Na (400 mg, 17.4 mmol) and MeOH (100 mL)), and the resulting mixture was stirred overnight, during which time it turned yellow. The solvent was removed, and the residue was dissolved in THF (20 mL). A solution of PH_2Mes (170 mg, 1.1 mmol) in THF (3 mL) was added, and the resulting mixture was stirred for 2 days. The solvent was removed, and the residue was extracted with toluene (3 × 3 mL) and concentrated. By layering petroleum ether, 670 mg (78% yield) of the product was obtained at −20 °C. ^1H NMR (C_6D_6): δ 8.07 (2H, Ar), 7.52 (2H, br, Ar), 7.12 (8H, br, Ar), 7.00−6.79 (8H, br, Ar), 6.71 (2H, Ar), 6.59 (2H, Ar), 3.85 (1H, ddd, $^3J_{PH} = 6$, $^3J_{PH} = 21$, $^1J_{PH} = 198$, $^2J_{PtH} = 66$, PH), 2.50 (4H, br, CH_2), 2.26 (6H, *o*-Me), 2.20 (9H, *o*-Me + *p*-Me), 2.13 (3H, *p*-Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 47.0 ($^1J_{Pt-P} = 1728$), 43.8 (d, $^2J_{PP} = 127$, $^1J_{PtP} = 1929$), −97.4 (d, $^2J_{PP} = 127$, $^1J_{Pt-P} = 726$). In the ^{31}P NMR spectrum, the δ −97.4 peak shows $^1J_{PH} = 198$. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.4 (dd, $J = 12, 92$, Pt−C), 144.0 (m, Ar), 139.8 (Ar), 139.4 (Ar), 135.8 (br, Ar), 134.8 (m, Ar), 133.6 (Ar), 133.3 (Ar), 131.9 (Ar), 131.4 (br m, Ar), 130.3 (br m, Ar), 129.0 (m, Ar), 127.9 (Ar), 28.0 (m, CH_2), 26.8 (m, CH_2), 24.6 (d, $J_{PC} = 11$, *o*-Me), 23.1 (d, $J_{PC} = 2$, *o*-Me), 21.4 (*p*-Me), 20.0 (*p*-Me). IR: 3051, 2913, 2283, 1435, 1185, 1098, 1027, 878, 846, 744, 694, 529, 488. High-resolution FAB MS (Magic Bullet): 863.2514 (Found); 863.2538 (Calcd for $C_{44}H_{47}P_3{}^{195}Pt$). Low-resolution FAB MS (Magic Bullet): 864.1 [$(M)^+$], 712.1 [$(M - PHMes)^+$], 592.0 [$(M - PHMes - Mes)^+$]. Anal. Calcd for $C_{44}H_{47}P_3Pt$: C, 61.18; H, 5.48. Found: C, 60.95; H, 5.34.

(11) **Crossover experiment.** PH(Mes-d_{11})$_2$ was prepared from commercially available mesitylene-d_{12}. As a control, reaction of **1** with PH(Mes-d_{11})$_2$ at 55 °C in THF gave Pt(dppe)(PHMes-d_{11})(Mes-d_{11}) (**3**-d_{22}). Low-resolution FAB MS (3-NBA): 885.4 [$(M)^+$], 723.3 [(M − PHMes-d_{11})$^+$], 593.1 [(M − PHMes-d_{11} − Mes-d_{11})$^+$]. Then, to **1** (50 mg, 0.06 mmol) was added a mixture of $PHMes_2$ (9 mg, 0.03 mmol) and PH(Mes-d$_{11}$)$_2$ (10 mg, 0.03 mmol) in THF (2 mL) to afford a red-yellow solution, which was heated at 55 °C for 6 h. The solvent was removed, and the residue was washed with petroleum ether (3 × 3 mL) and dried in vacuo. $^{31}P\{^1H\}$ NMR (THF): δ 46.0 ($^1J_{Pt-P} = 1743$), 42.3 (d, $^2J_{PP} = 128$, $^1J_{Pt-P} = 1949$), 31.7 ($^1J_{Pt-P} = 3734$, Pt(dppe)$_2$), −100.2 (d, $^2J_{PP} = 128$, $^1J_{Pt-P} = 726$), −100.3 (d, $^2J_{PP} = 128$, $^1J_{Pt-P} = 726$), plus peaks due to traces of **1** and the phosphines. Low-resolution FAB MS (3-NBA): 885.4 [$(M)^+$, **3**-d_{22}], 863.3 [$(M)^+$, **3**], 723.3 [(M − PHMes-d_{11})$^+$, **3**-d_{22}], 712.2 [$(M - PHMes)^+$, **3**], 593.1 [$(M - PHMes - Mes)^+$ or (M − PHMes-d_{11} − Mes-d_{11})$^+$, **3** or **3**-d_{22}]. No peaks due to Pt(dppe)(Mes)(PHMes-d_{11}) or Pt(dppe)(Mes-d_{11})(PHMes) were observed.

addition to afford **2** or, irreversibly, form **3** by P−C oxidative addition and **4** by disproportionation.[12,13]

The proposed mechanism is supported by several qualitative observations. Sizable concentrations of **1** persist through much of the reaction, and the H−D exchange observed with PDMes$_2$ could occur via reversible stilbene substitution and P−H oxidative addition.[14] Consistent with this hypothesis, adding stilbene to a mixture of **1** and PHMes$_2$ greatly slows the formation of **2**, **3**, and **4**, and adding PHMes$_2$ speeds it up. Moreover, an alternative source of Pt(0), the dimer [Pt(dppe)H]$_2$ (**7**, Scheme 3),[15] is consumed in hours on reaction with PHMes$_2$; apparently, loss of H$_2$ from **7** is irreversible.[8] In contrast, Pt(dppe)(CH$_2$CHCN)[2] does not react with PHMes$_2$, presumably since acrylonitrile binds more tightly to Pt than does stilbene.

Analysis of the conversion of phosphido hydride **2** to phosphido aryl **3** (eq 1) provides thermodynamic information. Assuming that entropic effects are minimal,[16]

$$\mathrm{Pt(dppe)(PMes_2)(H)} \rightarrow \mathrm{Pt(dppe)(PHMes)(Mes)} \quad (1)$$

then bond dissociation energies may be used to approximate the free energy of reaction (eq 2).

$$\Delta G \approx \Delta H = D(\mathrm{Pt{-}H}) + D(\mathrm{Pt{-}PMes_2}) + D(\mathrm{Mes{-}PMes}) - D(\mathrm{Pt{-}Mes}) - D(\mathrm{Pt{-}PHMes}) - D(\mathrm{H{-}PMes}) \quad (2)$$

Some related thermochemical data is available. D(Pt−H) in *trans*-Pt(PPh$_3$)$_2$(H)(Cl) is 73.4 ± 8.8 kcal/mol, and D(Pt−Ar) in *cis*-Pt(PEt$_3$)$_2$(o-Tol)(Cl) and *cis*-Pt(PEt$_3$)$_2$(*o*-Tol)$_2$ are 71.2 ± 4.3 and 71.7 ± 8.1 kcal/mol, respectively.[17] The average P−C bond energy in PPh$_3$ is 77.9 ± 1.5 kcal/mol,[18] and the P−H bond strength in PHMe$_2$ is 77.3 kcal/mol.[19] Although these are not ideal models, substitution into eq 2 gives $\Delta G \approx \Delta H = 2.5$ kcal/mol + $D(\mathrm{Pt{-}PMes_2}) - D(\mathrm{Pt{-}PHMes}) < 0$.[20]

This suggests that formation of the Pt−PHMes bond at the expense of the Pt−PMes$_2$ bond is thermodynamically favorable. Consistent with this idea, Pt(dppe)(Me)(PMes$_2$)[2] reacts quantitatively with PH$_2$Mes to give Pt(dppe)(Me)(PHMes) and PHMes$_2$ (eq 3).[8] Since form-

$$\mathrm{Pt(dppe)(Me)(PMes_2)} \xrightarrow[-\mathrm{PHMes_2}]{\mathrm{PH_2Mes}} \mathrm{Pt(dppe)(Me)(PHMes)} \quad (3)$$

ing the secondary P−H bond in PHMes$_2$ while breaking the primary one in PH$_2$Mes is likely to be uphill (by ~2 kcal/mol, if PH$_2$Me and PHMe$_2$ are reasonable models)[19] and given the assumptions above, this reaction must be driven by the relative Pt−P bond strengths.[21]

Conclusion. We have observed a direct competition between kinetic P−H and thermodynamic P−C oxidative addition of dimesitylphosphine at a Pt(0) center. P−C cleavage appears to be possible because P−H activation is reversible, and relative Pt−P bond strengths in the phosphido ligands contribute to the thermodynamic product control. These results suggest further rational development of reactions involving P−H and P−C oxidative addition is possible, and we are continuing the study of phosphido complexes along these lines, in addition to more detailed kinetic and mechanistic studies of the title reaction.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Exxon Education Foundation, DuPont, the NSF CAREER program, and Dartmouth College for partial support. We also thank Johnson-Matthey/Alfa/Aesar for the loan of the Pt salts.

Supporting Information Available: Text giving further experimental details and characterization data (6 pages). Ordering information is given on any current masthead page.

OM970754V

---

[12] For related examples of disproportionation of Pt(0) species, see ref 6 and (a) Bennett, M. A.; Chiraratvatana, C. *J. Organomet. Chem.* **1985**, *296*, 255−267. (b) Davies, J. A.; Eagle, C. T.; Otis, D. E.; Venkataraman, U. *Organometallics* **1989**, *8*, 1080−1088. (c) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915−2916. Control experiments show that under the reaction conditions, **1** is stable and that only traces of **4** are formed by decomposition of **3**.[8]

[13] This mechanism is closely related to one suggested for reaction of the isoelectronic Pt(dtbpm) (dtbpm = (t-Bu)$_2$PCH$_2$P(t-Bu)$_2$) fragment with SiMe$_4$,[4a] which includes the intermediate Pt(dtbpm)(SiMe$_4$) and competitive C−H and C−Si oxidative addition and disproportionation steps.

[14] For examples of reversible P−H activation, see: (a) Baker, R. T.; Calabrese, J. C.; Glassman, T. E. *Organometallics* **1988**, *7*, 1889−1891. (b) Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Organometallics* **1993**, *12*, 830−841. See also: Schunn, R. A. *Inorg. Chem.* **1973**, *12*, 1573−1579.

[15] Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1988**, 1554−1556. This paper states that **7** is a good source of the Pt(dppe) fragment in reactions with Lewis bases, without further details.

[16] As pointed out by a referee, the definition of the bond strengths incorporates any changes in the properties of the ancillary ligand bonds during this transformation. For further discussion of this point, see: Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *10*, 1875−1887. For similar thermodynamic analyses of proton transfers in the Pt(dppe)(Me)(X) system, see: (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444−1456. (b) Bryndza, H. E.; Domaille, P. J.; Tam, W.; Fong, L. K.; Paciello, R. A.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 1441−1452.

[17] Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629−688. Because dppe has a greater trans influence than Cl, the Pt−H bond strength in **2** is likely to be lower than this estimated value.

[18] Pilcher, G. In *The Chemistry of Organophosphorus Compounds*; F. R. Hartley, Ed.; John Wiley and Sons: New York, 1990; Vol. 1, pp 127−136.

[19] McKean, D. C.; Torto, I.; Morrisson, A. R. *J. Phys. Chem.* **1982**, *86*, 307−309.

[20] See ref 17. A referee also made the reasonable comment that there are significant steric and electronic differences between PHMes$_2$ and the model compounds; this reflects the limited data available in organophosphorus thermochemistry (see ref 18). Because of the relatively crude nature of these approximations, the main value of this analysis is its prediction about relative Pt−P bond strengths.

[21] Related studies designed to provide an ordering of relative Pt−phosphido bond strengths and to probe the importance of steric and electronic effects are in progress (Wicht, D. K.; Paisner, S. N.; Lew, B. M.; Glueck, D. S.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L.; Haar, C. M.; Nolan, S. P. Submitted for publication).