

**Supplementary Material Available:** Tables of positional and thermal parameters and interatomic distances and angles (14 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

**Organolanthanide and Organoactinide Oxidative Additions Exhibiting Enhanced Reactivity. 4. Products, Stoichiometry, and Preliminary Kinetic Studies of the Reaction of  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  and  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$  with Alkyl and Aryl Halides. Evidence for the Importance of Electron Transfer in Atom-Abstraction Oxidative Additions**

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**Summary:**  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  exhibits oxidative addition reactions with alkyl and aryl halides faster than any f-block organometallic compound studied to date. The generalized stoichiometry displayed is  $(a + b)(C_5Me_5)_2Sm^{II}\cdot OEt_2 + (a + c)RX \rightarrow (a - 2c)(C_5Me_5)_2Sm^{III}X + (b)(C_5Me_5)_2Sm^{III}R + (c)/z - [(C_5Me_5)_3Sm_2^{III}X_3]_z + (c)C_5Me_5R + (a + b)Et_2O + (a - b)R\cdot$  products. On the other hand,  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$  undergoes a nonredox reaction with alkyl and aryl halides, acting only as a "Eu<sup>II</sup>-Grignard" reagent according to the stoichiometry:  $1.0(C_5Me_5)_2Eu^{II}\cdot OEt_2 + 2.0RX \rightarrow 1.0EuX_2 + 2.0C_5Me_5R$ . Comparisons of the relative rates of reaction between  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ ,  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$ ,  $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ , and  $(C_5Me_5)_2U^{III}(Cl)(THF)$  reveals the series  $Sm \gg U > Yb \gg Eu$  and supports the proposal that the transition state for these inner-sphere "atom-abstraction" oxidative addition reactions contains the anticipated contribution from electron transfer.

We report herein the results of product, stoichiometry, and preliminary kinetic and mechanistic investigations of the alkyl halide oxidative addition reactions of  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  and  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$ . The only other detailed studies of organolanthanide and organoactinide oxidative additions are our recent report<sup>1a-c</sup> on

$(C_5Me_5)_2Yb^{II}\cdot OEt_2$  and our earlier report<sup>1d,e</sup> on  $(C_5Me_5)_2U^{III}(Cl)(THF)$ .

Green/black crystalline  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  was prepared at Du Pont<sup>2</sup> from  $SmBr_2$  and  $KC_5Me_5$  by using methods analogous to the synthesis of  $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ .<sup>3</sup> The complex was pure as judged by <sup>1</sup>H NMR, elemental analysis, and IR.

Benzyl chloride emerged as a typical and convenient substrate for <sup>1</sup>H NMR product and stoichiometry studies following an examination of 15 alkyl and aryl halide oxidative additions to  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ . The product assignments provided below were made by comparison to authentic bibenzyl,  $C_5Me_5CH_2Ph$ ,<sup>4</sup>  $(C_5Me_5)_2Sm^{III}(Cl)(OEt_2)$ ,<sup>5</sup> and a product or products of net composition  $[(C_5Me_5)_3Sm_2^{III}Cl_3]_z$ .<sup>6</sup>

In a typical reaction,  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  (22 mg, 0.044 mmol), hexamethylbenzene (2 mg, 0.02 mmol) as an internal standard, benzene-*d*<sub>6</sub> (0.4 mL), and benzyl chloride were combined in an NMR tube. The  $PhCH_2Cl$  was added (0.25 equiv at a time) via gas-tight syringe until it was no longer consumed and the excess was observable by <sup>1</sup>H NMR. During addition of the first 1.0 equiv of  $PhCH_2Cl$ , the <sup>1</sup>H NMR  $C_5Me_5$  resonance of the green/black  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  solution shifts upfield from its initial  $\delta$  2.9 position to a broadened singlet at  $\delta$  0.9 (b s, 30 H,  $lw_{1/2}$  = 30 Hz) characteristic of  $(C_5Me_5)_2Sm^{III}Cl$ .<sup>5</sup> Concomitantly, the solution becomes orange, confirming the formation of  $(C_5Me_5)_2Sm^{III}(Cl)(OEt_2)$ .<sup>5</sup> Further addition of 0.5 equiv of  $PhCH_2Cl$  (0.25 equiv at a time, 1.5 equiv total)

(2) Green/black  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  shows  $\lambda_{max}$  = 680 nm and obeys Beer's law over the concentration range examined,  $(1.26-6.03) \times 10^{-3} M$  ( $\epsilon_{680} 260 \pm 8 M^{-1} cm^{-1}$ ). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  2.85 (s, 30 H,  $lw_{1/2}$  = 14 Hz), -4.88 (b s, 4 H,  $lw_{1/2}$  = 16 Hz), 20.88 (b s, 6 H,  $lw_{1/2}$  = 16 Hz).

(3) (a) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (b) Watson, P. L.; Roe, D. C. *Ibid.* **1982**, *104*, 6471. (c) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (d) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (e) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652.

(4)  $C_5Me_5CH_2Ph$  was identified by its characteristic <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>):<sup>1b,c</sup>  $\delta$  2.65 (s, 2 H), 1.77 (s, 6 H), 1.57 (s, 6 H), 0.98 (s, 3 H), 7.03 (m, 5 H).

(5) Orange  $(C_5Me_5)_2Sm^{III}(Cl)(OEt_2)$  was prepared independently by reaction of  $CHCl_3$  with  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  in  $Et_2O$ . The composition of this well-established type of lanthanide complex,<sup>8,8,10,11</sup> while fixed with certainty by the reaction stoichiometries with good mass balance, was confirmed by elemental analysis on a crystalline sample prepared at Du Pont. Calcd for  $(C_5Me_5)_2Sm^{III}(Cl)(OEt_2)$ : C, 54.35; H, 7.60; Cl, 6.68; Sm, 28.35. Found: C, 54.25; H, 7.56; Cl, 6.49; Sm, 29.5% (repeat Sm analysis, 28.1%). The UV/visible spectrum displays a  $\lambda_{max}$  at 426 nm. The <sup>1</sup>H NMR spectrum is somewhat variable depending upon the amount of  $Et_2O$  (or other ligands), the amount of  $Sm^{II}$ , and the amount of  $Sm^{III}$  species present, suggesting that aggregates form in solution.<sup>7c</sup>  $(C_5Me_5)_2Sm^{III}(Cl)(OEt_2)$  alone shows (benzene-*d*<sub>6</sub>):  $\delta$  0.88 (s, 30 H,  $lw_{1/2}$  = 10 Hz), 1.06 (b q, 4 H), 0.14 (b t, 6 H). The THF analogue exhibits its <sup>1</sup>H NMR  $C_5Me_5$  resonance at  $\delta$  1.28 (s, 30 H). The resonances due to bound THF were not observable under the conditions used.

(6) The composition  $[(C_5Me_5)_3Sm_2Cl_3]_z$  in solution following oxidative addition, the conditions relevant to this work, is solidly based upon the 14 reaction stoichiometries in Table I (supplementary material), the application of mass balance, and NMR data showing the presence of three (different) types of  $C_5Me_5$  groups. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  1.15 (s, 15 H,  $lw_{1/2}$  = 6 Hz), 0.32 (s, 15 H,  $lw_{1/2}$  = 6 Hz), -0.99 (s, 15 H,  $lw_{1/2}$  = 6 Hz). However, the molecular weight and thus *z* value are not yet known. On the basis of the observation that ligands, L, such as pyridine or THF cleave the aggregate to yield  $(C_5Me_5)_2SmCl(L)$  (by <sup>1</sup>H NMR,<sup>1c</sup> one is led to think of *z* = 1 and a  $(C_5Me_5)_2SmCl(C_5Me_5)SmCl_2$  formulation.<sup>1c</sup> (However, the  $(C_5Me_5)SmCl_2$  half of this aggregate is not detected (may not be detectable) by <sup>1</sup>H NMR in the L = py or THF cleavage experiments.) Note that *z* = 2 leads to possibilities such as  $[(C_5Me_5)_2SmCl]_3\cdot SmCl_3$  and that equilibria which are possible under the reaction conditions, such as  $(C_5Me_5)_2SmCl + SmCl_3 = 2(C_5Me_5)SmCl_2$ , and which we have demonstrated in the analogous Yb compounds (see p 169, ref 1c), have yet to be ruled out. The independent synthesis of  $[(C_5Me_5)_3Sm_2Cl_3]_z$  (red,  $\lambda_{max}$  = 451 nm) from  $(C_5Me_5)_2Sm^{III}(Cl)(OEt_2)$  plus 0.5 equiv of  $PhCH_2Cl$  does give the same <sup>1</sup>H NMR  $C_5Me_5$  resonances listed above, but the high solubility of the product even in pentane has frustrated isolation attempts (see p 229, ref 1c). Recent isolation attempts at Du Pont produce an orange powder (possibly  $SmCl_3$ )<sup>12</sup> and red crystals; efforts at single-crystal X-ray diffraction structural analysis are in progress.

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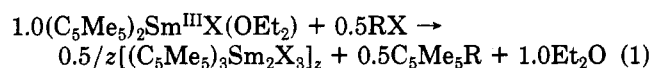
† Contribution No. 4203.

(1) (a) Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1986**, *5*, 598. (b) Finke, R. G.; Keenan, S. R.; Watson, P. L.; Schiraldi, D. A., manuscript in preparation. (c) Keenan, S. R. Ph.D. Dissertation, University of Oregon, Eugene, OR, 1986. It should be noted that a value of *z* = 1 (in (c)/*z*, eq 2, and in  $[(C_5Me_5)_3Sm_2Cl_3]_z$ ) is assumed therein; i.e., the possibility that *z* may be >1 is not treated in this thesis. (d) Finke, R. G.; Schiraldi, D. A.; Hirose, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1875. (e) Schiraldi, D. A. Ph.D. Dissertation, University of Oregon, Eugene, OR, 1982.

causes the intensity of the  $\delta$  0.9 resonance to decrease while the resonances characteristic of the composition<sup>6</sup>  $[(C_5Me_5)_3Sm_2^{III}Cl_3]_z$  increase by an equivalent amount. The solution is now red, characteristic of the latter poly-metallic samarium composition.<sup>6,7</sup> Bibenzyl and  $C_5Me_5CH_2Ph^4$  are the only other products detected by  $^1H$  NMR, and the above reaction accounts for all of the starting  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ .

The reaction of  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  with  $PhCH_2Cl$  differs from the analogous  $(C_5Me_5)_2Yb^{II}\cdot OEt_2$  reaction<sup>1a,c</sup> in that there is no evidence for the formation of a transient  $(C_5Me_5)_2Sm^{III}CH_2Ph$  species, either by  $^1H$  NMR or by GLC. Moreover, experiments designed to maximize the formation of  $(C_5Me_5)_2Sm^{III}CH_2Ph$  (and successful in the case of  $(C_5Me_5)_2Yb^{II}\cdot OEt_2$  plus  $PhCH_2Cl$ )<sup>1a</sup> show no toluene by GLC after a methanol quench. [A 12-fold excess of  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  and slow  $PhCH_2Cl$  addition ( $8.7 \times 10^{-3}$  M total) followed by MeOH addition were used for this experiment.] However, reactive alkyl complexes were observed by NMR as expected based on the literature<sup>8</sup> in the case of  $RX = PhCl, PhBr,$  and  $PhI$  [ $(C_5Me_5)_2Sm^{III}Ph(THF)$ :  $^1H$  NMR  $\delta$  1.49 (s, 30 H) in the presence of THF<sup>9</sup>]. Evidence for an initial  $(C_5Me_5)_2Sm$ - (neopentyl) product was also obtained when  $RX =$  neopentyl chloride. In both the  $R = Ph$  and  $R =$  neopentyl cases, the presence of the expected quantity of RH following a MeOH quench was demonstrated by GLC. The details of these experiments are available for the interested reader as supplementary material.

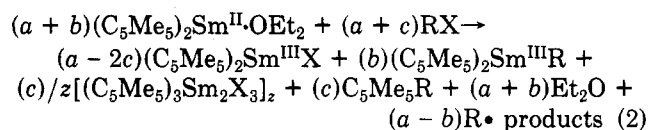
The observed products include those probably formed from followup, "Sm<sup>III</sup>-Grignard" reactions of the initial oxidative addition product  $(C_5Me_5)_2SmCl(OEt_2)$  (eq 1),



analogous to the "Yb<sup>III</sup>-Grignard" reactions we recently reported.<sup>1a</sup> This "Sm<sup>III</sup>-Grignard" reaction was independently verified; it occurs immediately upon mixing of  $(C_5Me_5)_2Sm^{III}X(OEt_2)$  with 0.5 equiv of  $PhCH_2X$  or  $CH_3I$ , for example, and obeys the stoichiometry shown in eq 1. When the alkyl halide is  $t$ -BuCl, pentamethylcyclopentadiene ( $C_5Me_5R, R = H$ ; eq 1) is observed. We have not ruled out possible contributions from  $(C_5Me_5)_2Sm^{III}-R$  or  $(C_5Me_5)_2Sm^{II}$  "Sm-Grignard" reactions; evidence for the former in the case of  $(C_5Me_5)_2Yb^{III}-R$  is available.<sup>1a-c</sup> Some evidence has been obtained that the  $[(C_5Me_5)_3Sm_2Cl_3]_z$  product may be  $(C_5Me_5)_2SmCl \cdot (C_5Me_5)SmCl_2$  ( $z = 1$ ) or, perhaps more consistent with the data,  $\{[(C_5Me_5)_2SmCl_3] \cdot SmCl_3\}$  ( $z = 2$ ).<sup>6</sup> Precedent for several types of Ln ( $Ln = Sm, Yb$ ) aggregates and/or different Ln coordination environments is also available.<sup>7,10,11</sup> An ad-

ditional, slow reaction to form  $SmX_3^{12}$  and more  $C_5Me_5R$  occurs when  $RX$  is present in large excess.

The final stoichiometry resulting from the initial oxidative addition pathway and the followup reactions is given in generalized form in eq 2. A table of the stoichiometry coefficients  $a, b,$  and  $c$  (eq 2) for 14  $RX$  and  $ArX$  are available as supplementary material.



Preliminary kinetic studies have been performed by monitoring the loss of  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  at  $\lambda_{max} = 680$  nm. The key results are (a) that the reactions of  $Sm^{II}$  are at least  $10^2$  times faster than the corresponding reactions of  $Yb^{II}$  and (b) that ligand ( $Et_2O$ ) loss as found for  $Yb(II)^{1a,c}$  and  $U(III)^{1d,e}$  appears to be necessary to achieve the enhanced rates observed, suggesting an inner-sphere pathway as documented earlier for  $Yb(II)^{1a,c}$  and  $U(III)^{1d,e}$ . A table of comparative  $Sm^{II}, Yb^{II},$  and  $U^{III}$  rates documenting the relative rates  $Sm \gg U > Yb$  and the details of the preliminary kinetic studies are also available as supplementary material.

$(C_5Me_5)_2Eu^{II}\cdot OEt_2$  reactions with  $RX$  provide an interesting comparison in that they differ from the other lanthanides and actinides examined to date. Of particular interest is that no oxidative addition,  $Eu(III)$  products are observed. The starting europium complex  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$  was prepared as a dark red solid<sup>13</sup> in a manner completely analogous to that used for the  $(C_5Me_5)_2Yb^{II}\cdot OEt_2$  and  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  complexes.<sup>3</sup> Reactions of  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$  with  $RX = PhCH_2Cl$  and  $t$ -BuCl monitored by  $^1H$  NMR yield solids and  $C_5Me_5R$  ( $R = CH_2Ph$  and  $H$ , respectively) as the only organic products. No organic products indicative of a  $Eu(II/III)$  redox reaction<sup>14</sup> were found for any substrate. Elemental analysis of the solid isolated from a reaction of  $PhCH_2Cl$  with  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$  suggests the empirical formula  $Eu^{II}Cl_2 \cdot 0.5Et_2O$ .<sup>15</sup>  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$  appears, therefore, to act solely as an "Eu<sup>II</sup>-Grignard" reagent (eq 3).

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(12) Orange  $SmCl_3$  was synthesized from  $(C_5Me_5)_2Sm^{II}\cdot OEt_2$  (103 mg, 0.208 mmol) and 0.5-mL each of  $t$ -BuCl (4.6 mmol) and  $PhCH_2Cl$  (4.3 mmol) in 1.0 mL of toluene.<sup>1c</sup> Elemental analysis shows that the material is impure and contains variable amounts of  $Et_2O$ . Calcd for  $SmCl_3 \cdot 0.5Et_2O$ : Sm, 45.45; Cl, 32.14; C, 14.52; H, 3.05. Found: Sm, 40.02; Cl, 32.63; C, 19.03; H, 2.75. Calcd ratios:  $Sm_1Cl_3C_4H_{10}O$ . Obsd ratios:  $Sm_1Cl_{3.5}C_{5.9}H_{10.2}O_{1.3}$ .

(13) Dark red  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$  shows no detectable resonances in the  $^1H$  NMR under the reaction conditions. A typical sample for a  $^1H$  NMR monitored reaction consisted of  $(C_5Me_5)_2Eu^{II}\cdot OEt_2$  (20 mg, 0.040 mmol), hexamethylbenzene (2 mg, 0.012 mmol), and 0.5 mL of benzene- $d_6$ .

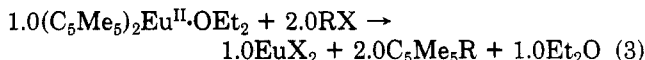
(14) Interestingly,  $Eu^{III}$  ions have been found to accept a single electron from 2-hydroxy-2-propyl radicals to give  $Eu^{II}$ , again showing the stability of  $Eu(II)$ . Muralidharan, S.; Espenson, J. H. *Inorg. Chem.* **1984**, *23*, 636.

(15) Anal. (after drying in vacuo for 15 min) Calcd for  $EuCl_2 \cdot 0.5Et_2O$ : Eu, 51.17; Cl, 23.88. Found: Eu, 51.14; Cl, 24.11. A second sample, submitted for analysis after being subjected to additional drying ( $\approx 2$  h) in vacuo, best fits a  $0.5Et_2O$  complex: Eu, 58.51; Cl, 27.44; C, 8.21; H, 1.55. Calcd for  $EuCl_2 \cdot 0.5Et_2O$ : Eu, 58.46; Cl, 27.28; C, 9.24; H, 1.94.

(7) (a) Although the precise components of  $[(C_5Me_5)_3Sm_2Cl_3]_z$  and their structures must await further data, the larger<sup>7b</sup> early lanthanides are known<sup>7a,c</sup> to form multiple metal aggregates. (b) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751. (c) Desolvated  $(C_5Me_5)_2SmCl$  has been crystallized and structurally characterized as the cyclic, Cl-bridged trimer  $[(C_5Me_5)_2SmCl]_3$ . This is one of four different, crystallographically determined coordination environments for  $(C_5Me_5)_2SmCl(L)_x$  species: Evans, W. J., private communication. We thank Professor Evans for making this information available to us prior to publication: Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.*, in press.

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(9) Stronger binding ligands, such as THF, were added to separate overlapping  $(C_5Me_5)_2Sm$  resonances and to render homogeneous product solutions containing the slightly soluble  $(C_5Me_5)_2Sm^{III}X(OEt_2)$  ( $X = Br, I$ ).



These results and the decreasing rates of oxidative addition  $\text{Sm}^{\text{II}} \gg \text{U}^{\text{III}} > \text{Yb}^{\text{II}} \gg \text{Eu}^{\text{II}}$ , which mirror their decreasing reduction potentials,<sup>16,17</sup>  $\approx -2.0$ ,<sup>17a</sup>  $-1.3$ ,<sup>17c</sup>  $\approx -1.4$ ,<sup>17a,d</sup> and  $\approx -0.8$ <sup>17a</sup> (V vs. SCE), respectively, must be reconciled with any intimate mechanism proposed for these "atom-abstraction" oxidative additions. The presence of a single electron transfer component in these "atom abstractions" as well as in others<sup>18</sup> is strongly implied.<sup>19</sup>

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**Registry No.**  $(\text{C}_5\text{Me}_5)_2\text{Sm}^{\text{II}}\cdot\text{OEt}_2$ , 85962-90-9;  $(\text{C}_5\text{Me}_5)_2\text{Eu}^{\text{II}}\cdot\text{OEt}_2$ , 84254-55-7;  $\text{SmBr}_2$ , 50801-97-3;  $\text{KC}_5\text{Me}_5$ , 94348-92-2;  $\text{PhCH}_2\text{Cl}$ , 100-44-7;  $\text{C}_5\text{Me}_5\text{CH}_2\text{Ph}$ , 100692-30-6;  $(\text{C}_5\text{Me}_5)_2\text{Sm}^{\text{III}}(\text{Cl})(\text{OEt}_2)$ , 107846-38-8;  $\text{CHCl}_3$ , 67-66-3;  $\text{SmCl}_3$ , 10361-82-7;  $t\text{-BuCl}$ , 507-20-0;  $\text{Eu}^{\text{II}}\text{Cl}_2 \cdot 0.5 \text{Et}_2\text{O}$ , 107799-45-1.

**Supplementary Material Available:** Summary of products and stoichiometries for 15 RX and ArX; details of GLC studies and NMR studies; summary of attempted independent syntheses of  $(\text{C}_5\text{Me}_5)_2\text{Sm}^{\text{III}}\text{R}$  complexes; details of the preliminary kinetic studies; a table of Sm(II), U(III), and Yb(II) absolute rate constants for *n*-octyl fluoride and phenyl chloride reactions (7 pages). Ordering information is given on any current masthead page.

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## Spectroscopic Identification of the Nickel Acylate Complex

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**Summary:** NMR and IR spectral data of the pentanoyl nickelate complex are presented and are consistent with a mononuclear nickel complex. This nickel acylate complex is thermally stable in THF at ambient temperature (+20 °C) for prolonged periods (24 h) but decomposes rapidly in air.

The nickel acylate complex formed from the reaction of nickel tetracarbonyl with an organolithium reagent has

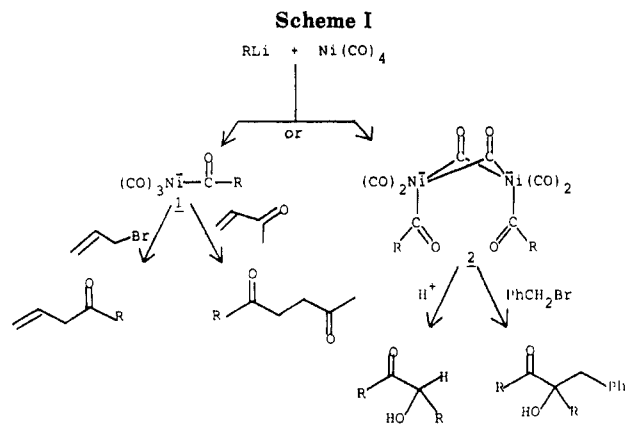


Table I. Spectral Data for the Pentanoyl Nickelate Complex

$(\text{CO})_3\text{Ni}=\text{C} \begin{matrix} \text{O-Li} \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{matrix}$	
Carbon Number	2      1    3    4    5    6
<sup>1</sup> H NMR $\delta^{a,b}$	IR $\nu(\text{CO})^{c,d}$ cm <sup>-1</sup>
2.555 (t, <i>J</i> = 7.50, 2 H, H <sub>C3</sub> )	317.018 (C1)    1980 (w)
1.625 (m, <i>J</i> = 7.50, 2 H, H <sub>C4</sub> )	205.296 (C2)    1935 (s)
1.356 (m, <i>J</i> = 7.35, 2 H, H <sub>C5</sub> )	66.476 (C3)    1535 (m)
0.973 (t, <i>J</i> = 7.20, 3 H, H <sub>C6</sub> )	27.752 (C4)
	24.012 (C5)
	15.013 (C6)

\* Solvent: THF-*d*<sub>8</sub>. Reference: residual proton on  $\alpha$ -carbon of THF at +3.700 ppm. *J* values in Hz. <sup>1</sup>H chemical shifts of 10.6 M BuLi in THF are +1.576, +1.362, +0.975, and -0.891 ppm. <sup>c</sup> Solvent: THF. Reference:  $\alpha$ -carbon of THF at +68.600 ppm. <sup>d</sup> Chemical shift of Ni(CO)<sub>4</sub> in THF is +192.964 ppm; chemical shifts of 10.6 M BuLi in THF are +159.367, 82.201, 26.032, and 14.405 ppm. <sup>e</sup> Solvent: THF. Range of scan: 2500-1500 cm<sup>-1</sup>. <sup>f</sup> CO stretch for Ni(CO)<sub>4</sub> in THF is 2050 cm<sup>-1</sup>; in this spectrum, there is a weak peak at 2025 cm<sup>-1</sup> which corresponds to Ni(CO)<sub>4</sub> in THF with added LiOTf.

not been structurally well-characterized.<sup>1</sup> This lack of characterization may be due, in part, to the instability of this complex in the presence of oxygen.<sup>2</sup> In addition, temperatures greater than 0 °C have been reported<sup>1</sup> to cause decomposition of the nickel acylate complex in ether, while temperatures greater than -20 °C and prolonged reaction times have been reported<sup>3</sup> to produce undesirable side reactions in tetrahydrofuran (THF).

Attempts to determine the structure of the nickel acylate complex based on the products isolated from the reaction of the complex with an electrophile have resulted in controversy. As shown in Scheme I, when the nickel acylate complex is allowed to react, in ether, with an allylic halide or a conjugated enone,<sup>3,4</sup> one acyl group is transferred to the final product, thus suggesting a monomeric structure, such as 1, for this complex. Similar results have also been observed from the reaction of the nickel acylate with quinone ketals in THF.<sup>2</sup> However, when the nickel acylate complex is allowed to react with a proton source, such as

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