

suggests that the metal center is more sterically constrained in **1a**, as would be expected.<sup>7</sup> However, the yttrium–C(C<sub>5</sub>Me<sub>5</sub>) average distances, 2.66 (2) Å in **1a** and 2.67 (1) Å in **1b**, are indistinguishable.

The terminal Y–Cl bond length in **1b**, 2.575 (3) Å, is very close to the terminal Y–Cl bond distances in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YCl(THF) (**2**), 2.579 (3) Å,<sup>31</sup> and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(μ-Cl)YCl(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> (**3**), 2.579 (6) Å.<sup>25</sup> The Y–(μ-Cl) distances in **1a** and **1b**, 2.650 (4) and 2.620 (3) Å, are longer than the terminal lengths, as expected. However, these distances are closer to the 2.640 (5) Å bridging bond length for the seven-coordinate metal center in **3**, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(μ-Cl)YCl(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>, than the 2.776 (5) Å length for the analogous eight-coordinate yttrium in **3**, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Y(μ-Cl)YCl(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>.

The bridging lithium–chloride bond distance in **1a**, 2.374 (16) Å, is near the normal range of 2.39–2.41 Å found in (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Yb(μ-Cl)<sub>2</sub>Li(OEt)<sub>2</sub> (**4**),<sup>7</sup> (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>Yb(μ-Cl)<sub>2</sub>Li(OEt)<sub>2</sub> (**5**),<sup>7</sup> and [C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Nd(μ-Cl)<sub>2</sub>Li(THF)<sub>2</sub> (**6**).<sup>6</sup> The 2.297 (16) Å Li–Cl distance in **1b**, in which only one anionic ligand is attached to lithium, is somewhat shorter. The average Li–O(THF) distances are not markedly different in **1a** and **1b**, 1.90 (1) and 1.91 (1) Å, respectively, and are similar to the 1.93 (3) Å distance in **6**.<sup>7</sup>

### Discussion

The cocrystallization of both disolvated and trisolvated (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YCl<sub>2</sub>Li(THF)<sub>x</sub> complexes is unusual. Generally, crystallization of a complex results in the most energetically preferred geometry available for the prevailing set of crystallization conditions. The crystallization of a complex in two different forms in the same unit cell suggests that the factors leading to the formation of these two species are very similar. A classic case of this phenomenon is the X-ray crystal structure of [Cr(H<sub>2</sub>NC–H<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>][Ni(CN)<sub>5</sub>](H<sub>2</sub>O)<sub>1.5</sub>, in which both square pyramidal and trigonal bipyramidal [Ni(CN)<sub>5</sub>]<sup>3-</sup> units are found in the

same unit cell.<sup>42</sup> The similarity in energies of these two different five-coordinate geometries is well established.<sup>43</sup>

In this case, the observation that both di- and trisolvated complexes can cocrystallize suggests that both of these forms are readily available to (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>LnZ<sub>2</sub>M(ether)<sub>x</sub> complexes. Given the differences in reactivity between terminal and bridging ligands in organolanthanide complexes,<sup>44</sup> this could have significant implications in reaction chemistry if both forms are available in solution. Specifically, the presence of a small amount of coordinating solvent, which might be expected to reduce reactivity by occupying a vacant coordination site on a lanthanide metal center, may actually enhance reactivity by generating a terminal ligand via a (C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>Ln(μ-Z)<sub>2</sub>M(ether)<sub>2</sub> to (C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>LnZ(μ-Z)M(ether)<sub>3</sub> process. In such a case, a small amount of an ether in an arene or alkane solvent could change the reactivity from that found in a rigorously ether-free solvent and could lead to variations in reactivity depending on solvent purity.

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**Supplementary Material Available:** ORTEP diagrams showing top views of **1a** and **1b**, tables of complete crystallographic data, positional parameters, bond distances and angles, and thermal parameters (18 pages); a listing of structural factor amplitudes (23 pages). Ordering information is given on any current masthead page.

(42) Raymond, K. N.; Corfield, P. W. R.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1362–1372.

(43) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; pp 471–484 and references therein.

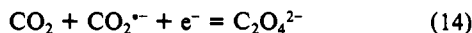
(44) (a) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263–270. (b) Evans, W. J. *Polyhedron* **1987**, *6*, 803–835.

## Additions and Corrections

1989, Volume 28

Carl R. Steffan, Andreja Bakac,\* and James H. Espenson\*: Quenching of the Doublet Excited State of Tris(polypyridine)chromium(III) Ions by Oxalate Ions: An Example of Irreversible Electron Transfer.

Page 2995. The half-reaction in eq 14, with  $E^\circ_{14} = 0.60$  V, should read



Since  $K$  for  $\text{CO}_2 + \text{CO}_2^{\cdot-} \rightleftharpoons \text{C}_2\text{O}_4^{\cdot-}$  is unknown, the value of  $E^\circ$  for  $\text{C}_2\text{O}_4^{\cdot-} + e^- = \text{C}_2\text{O}_4^{2-}$  cannot be rigorously calculated from known data, but an estimate of 1.7 V has been made (Neshvad, G.; Hoffman, M. Z. *J. Phys. Chem.* **1989**, *93*, 2445. See also: Hoffman, M. Z.; Prasad, D. R. *J. Photochem. Photobiol.*, *A* **1990**, *54*, 197).—James H. Espenson