

## Carbon–Oxygen Reductive-Elimination from Nickel(II) Oxametallacycles and Factors That Control Formation of Ether, Aldehyde, Alcohol, or Ester Products

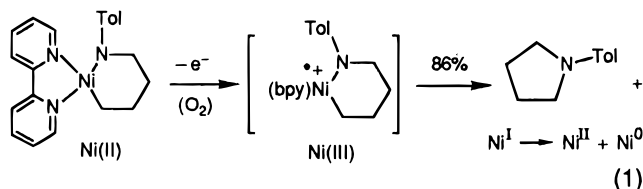
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Reductive-elimination reactions from transition-metal complexes comprise one of the most ubiquitous and synthetically useful families of organometallic reactions.<sup>1</sup> Recent research aimed at extending reductive-elimination reactions from the common classes that form new C–H and C–C bonds to include those that form C–X bonds (where X = O, S, N, halide, etc.) has been intense.<sup>2,3</sup> Of particular note are processes catalyzed by Pd phosphine systems that afford arylamines via key C–N reductive-elimination steps.<sup>4</sup> Recently, this chemistry has been elaborated to provide new synthetic routes to arylethers via C–O elimination.<sup>5</sup>

We are actively investigating reductive-elimination reactions in nickel(II) systems that form new C–N and C–O bonds.<sup>3</sup> Alkylnickel(II) amides {i.e.,  $L_nNi(R)(NR_2)$ } were shown to react with oxidants in a one-electron process to give high yields of C,N-reductive-elimination products, especially when the alkyl and amido moieties are tethered together in the form of an azametallacycle (as shown in eq 1).<sup>3d</sup> In contrast, C–O



eliminations from related Ni(II) complexes are not very efficient and are limited to cyclic derivatives.<sup>3a,b</sup> Herein we report on our studies of the (i) thermal and (ii) oxidatively-induced reaction chemistries of the dimeric seven-membered nickel(II) oxametallacycle  $[(PMe_3)NiOCH_2CH_2CMe_2-o-C_6H_4]_2$  and its related monomeric Ni derivatives.

Dimeric  $[(PMe_3)NiOCH_2CH_2CMe_2-o-C_6H_4]_2$  (**2**) was synthesized according to the method of Carmona by the room-temperature reaction of THF solutions of  $(PMe_3)_2Ni(CH_2CMe_2-$

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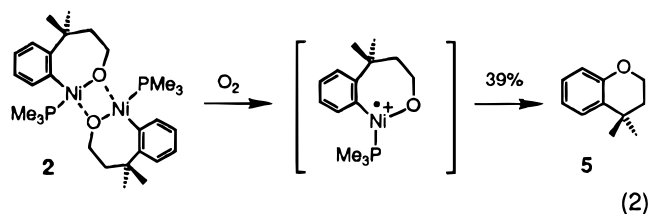
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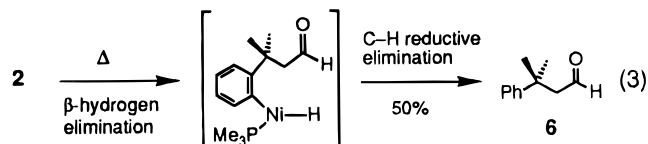
$o-C_6H_4$ ) (**1**) with paraformaldehyde.<sup>6</sup> Monomeric analogues of **2** containing bidentate ligands were prepared by stirring THF or ether solutions of **2** with 1,2-bis(dimethylphosphino)ethane (dmpe) or 2,2'-bipyridine (bpy), giving high yields of (dmpe)- $NiOCH_2CH_2CMe_2-o-C_6H_4$  (**3**)<sup>6</sup> and (bpy) $NiOCH_2CH_2CMe_2-o-C_6H_4$  (**4**), respectively.

When benzene solutions of **2** are stirred under dry  $O_2$  (1 atm), a slow reaction ensues over the course of 72 h at ambient temperature resulting in formation of a new C–O bond via oxidatively-induced reductive-elimination to give 4,4-dimethylchroman,  $o-C_6H_4CMe_2CH_2CH_2O$  (**5**), in 39% isolated yield (eq 2).<sup>7</sup> Under these conditions the  $PMe_3$  ligands of **2** are



oxidized to  $O=PMe_3$ , and an intractable black precipitate is formed that contains the Ni. As for C–N elimination upon oxidation of Ni(II) amido alkyl complexes, the role of  $O_2$  is probably to carry out oxidation of Ni(II) to Ni(III) (eq 2),<sup>3d</sup> a transformation that can also be effected by use of the one-electron oxidant (1,1'-diacetylferrocenium)silver tetrafluoroborate,  $(AcC_5H_4)_2Fe \cdot AgBF_4$ .<sup>8</sup> The monomeric oxametallacycles **3** and **4** react in a similar fashion with  $O_2$ , giving **5** in ~40% isolated yields, although the reaction of **3** with  $O_2$  is significantly faster than those of  $O_2$  with **2** or **4**.

The reactivity of **2** with oxygen differs dramatically from its thermal reactivity in the absence of an oxidant. Heating a benzene solution of **2** at 100 °C for 12 h causes a color change from canary yellow to dark yellow. Removal of the solvent under vacuum and extraction of the residue with hexanes followed by chromatographic workup allows for isolation of 3-methyl-3-phenylbutyraldehyde,  $PhCMe_2CH_2CHO$  (**6**), in 50% yield, with no formation of the chroman **5** (confirmed by  $^1H$  NMR). Thus, thermolysis of **2** favors  $\beta$ -hydrogen elimination from the seven-membered oxametallacycle followed by C–H reductive-elimination to give **6** as shown in eq 3. While there



is little precedent for  $\beta$ -H elimination from oxametallacycles to give aldehydes, analogous  $\beta$ -hydrogen elimination is a common pathway for the decomposition of acyclic alkoxide complexes.<sup>9</sup> Heating solutions of the dmpe and bpy complexes **3** and **4** at 100 °C likewise gives aldehyde **6** in lower yields, with varying relative rates for the eliminations and with formation of two significant coproducts. As shown in eq 4, thermolysis of **3** results in competitive formation of aldehyde **6** along with significant amounts of ester **7**. The relative yields

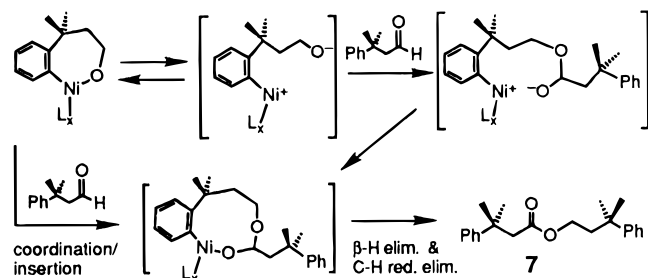
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(7) Experimental, spectral, and analytical details are given in the Supporting Information.

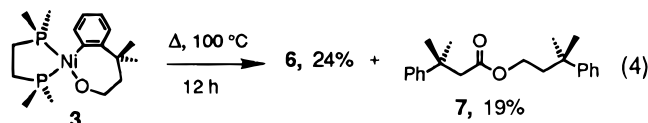
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## Scheme 1

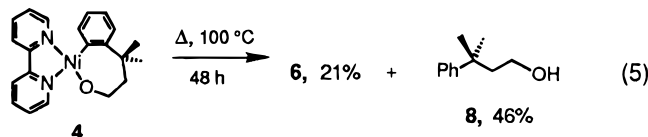


of **6** and **7** are dependent on the initial concentration of the oxametallacycle **3**, with the partition favoring **7** with increasing initial [**3**].



A reasonable reaction sequence accounting for the formation of **7** is shown in Scheme 1. The overall transformation leading to production of **7** is a formal insertion of **6** into the Ni–O bond of **3** followed by  $\beta$ -H elimination and C,H-reductive-elimination to give the ester. This is effectively a type of Ni-mediated Tishchenko reaction (which typically gives esters from coupling of aldehydes or primary alcohols).<sup>10</sup> Aldehyde couplings related to that in eq 4 are addressed subsequently with regard to reactions of formaldehyde.

Prolonged thermolysis of the bpy derivative **4** yields aldehyde **6** along with a significant amount of the primary alcohol 3-methyl-3-phenylbutanol (**8**), as shown in eq 5. That **4** is more

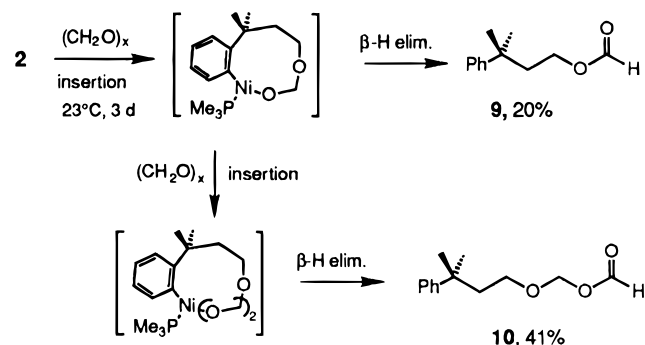


thermally robust than either **2** or **3** is probably a consequence of the greater ease in forming three-coordinate Ni complexes that are subject to elimination or insertion reactions (see above) for these phosphine-containing compounds than for the more rigid and less labile bpy derivative. Although the source of the protons in the formation of **8** has not been established, the alcohol possibly derives from homolytic Ni–O bond-breaking followed by H-abstraction. In this reaction, only traces of **7** are observed.

The observation of aldehyde (**6**) insertion into the Ni–O bond of **3** to give, ultimately, an ester led us to reinvestigate the reactivity of **1** with formaldehyde. Insertions of CH<sub>2</sub>O into

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## Scheme 2



M–H, M–C, and M–O bonds have been reported,<sup>11</sup> and sequential insertions of CH<sub>2</sub>O in Cu–C and Cu–O bonds were suggested for the formation of (2,4,6-trimethylbenzyl)formate from the reaction of Cu(PPh<sub>3</sub>)(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) with paraformaldehyde.<sup>11b</sup> As reported by Carmona and co-workers, reaction of solutions of **1** stirred over paraformaldehyde results in initial insertion of OCH<sub>2</sub> into the Ni–C(alkyl) bond to give good yields of **2**.<sup>6</sup> However, as shown in Scheme 2, solutions of **2** are unstable in the presence of paraformaldehyde. Formal sequential CH<sub>2</sub>O insertion into Ni–O bonds occurs slowly when **2** is stirred (23 °C, 3 days) with a suspension of paraformaldehyde, giving formic acid 3-methyl-3-phenylbutyl ester, PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)H (**9**), which incorporates two CH<sub>2</sub>O units, and formic acid (3-methyl-3-phenylbutoxy)methyl ester, PhCMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OC(O)H (**10**), which incorporates three CH<sub>2</sub>O units, in 20 and 41% yields, respectively. Products incorporating more than 3 equiv of formaldehyde were not detected, consistent with slow insertion steps and increasingly faster rates of  $\beta$ -H elimination as the size of the metallacycle increases (a seven-membered ring for **2** and nine- and eleven-membered rings for the parents of **9** and **10**, respectively). The instability of the oxametallacycle intermediates might also be a consequence of the large ring sizes prohibiting dimerization analogous to **2**.

In summary, the seven-membered Ni(II) oxametallacycles **2–4** undergo oxidatively-induced C,O-reductive-eliminations to give 4,4-dimethylchroman, whereas thermolysis of these complexes results in  $\beta$ -H elimination with formation of 3-methyl-3-phenylbutyraldehyde. Examples of aldehyde insertion into the Ni–O bonds of these complexes were observed, including insertion of 2 equiv of CH<sub>2</sub>O with **2**.

**Acknowledgment.** We are grateful to the National Science Foundation (CHE-9505692) for financial support of this research.

**Supporting Information Available:** Synthetic, spectroscopic, and analytical data (5 pages). See any current masthead page for ordering and Internet access information.

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