

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

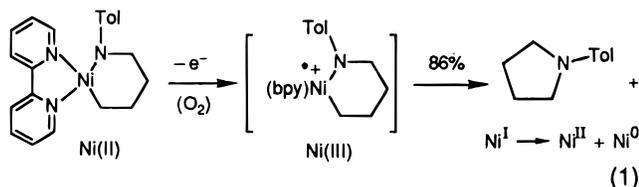
Runyu Han and Gregory L. Hillhouse*

Searle Chemistry Laboratory, Department of Chemistry
The University of Chicago, Chicago, Illinois 60637

Received May 9, 1997

Reductive-elimination reactions from transition-metal complexes comprise one of the most ubiquitous and synthetically useful families of organometallic reactions.¹ 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.^{2,3} Of particular note are processes catalyzed by Pd phosphine systems that afford arylamines via key C–N reductive-elimination steps.⁴ Recently, this chemistry has been elaborated to provide new synthetic routes to arylethers via C–O elimination.⁵

We are actively investigating reductive-elimination reactions in nickel(II) systems that form new C–N and C–O bonds.³ 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).^{3d} In contrast, C–O



eliminations from related Ni(II) complexes are not very efficient and are limited to cyclic derivatives.^{3a,b} 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 $(PMe_3)_2Ni(CH_2CMe_2-$

(1) 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) (a) Hoberg, H.; Schaefer, D.; Burkhart, G.; Kruger, C.; Romao, M. *J. J. Organomet. Chem.* **1984**, *266*, 203. (b) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3921. (c) Baranano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937.

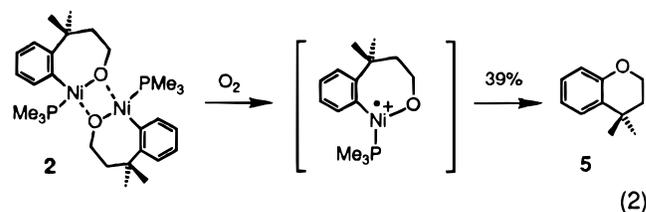
(3) (a) Matsunaga; Hillhouse, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 2075. (b) Matsunaga, P. T.; Mavropoulos, J. C.; Hillhouse, G. L. *Polyhedron* **1995**, *14*, 175. (c) Koo, K.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 456. (d) Koo, K.; Hillhouse, G. L. *Organometallics* **1995**, *14*, 4421. (e) Koo, K.; Hillhouse, G. L. *Organometallics* **1996**, *15*, 2669.

(4) (a) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901. (b) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 5969. (c) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348. (d) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708. (e) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609. (f) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. (g) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217.

(5) (a) Palucki, M.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 10333. (b) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109. (c) Palucki, M.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 3395.

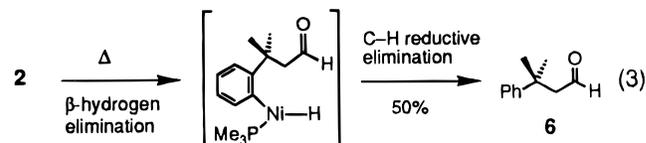
$-o-C_6H_4$) (**1**) with paraformaldehyde.⁶ Monomeric analogues of **2** containing bidentate ligands were prepared by stirring THF or ether solutions of **2** with 1,2-bis(dimethylphosphino)ethane (dmpe) or 2,2'-bipyridine (bpy), giving high yields of (dmpe)- $NiOCH_2CH_2CMe_2-o-C_6H_4$ (**3**)⁶ and (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).⁷ 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),^{3d} a transformation that can also be effected by use of the one-electron oxidant (1,1'-diacetylferrocenium)silver tetrafluoroborate, $(AcC_5H_4)_2Fe \cdot AgBF_4$.⁸ 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 β -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 β -H elimination from oxametallacycles to give aldehydes, analogous β -hydrogen elimination is a common pathway for the decomposition of acyclic alkoxide complexes.⁹ 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

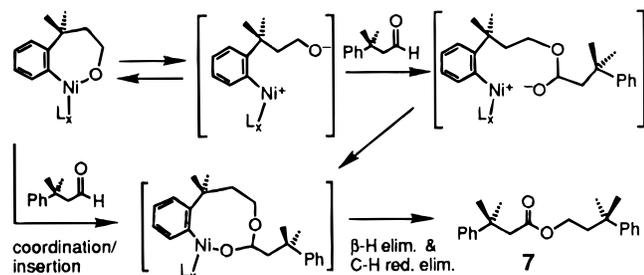
(6) Carmona, E.; Gutierrez-Puebla, E.; Martin, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883.

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

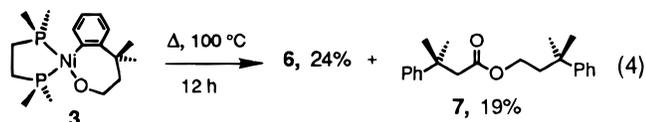
(8) Carty, P.; Dove, M. F. *J. Organomet. Chem.* **1971**, *28*, 125.

(9) Brynza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

Scheme 1

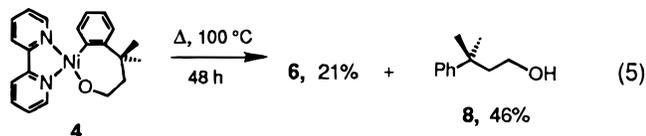


of **6** and **7** are dependent on the initial concentration of the oxametallacycle **3**, with the partition favoring **7** with increasing initial [**3**].



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 β -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).¹⁰ 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

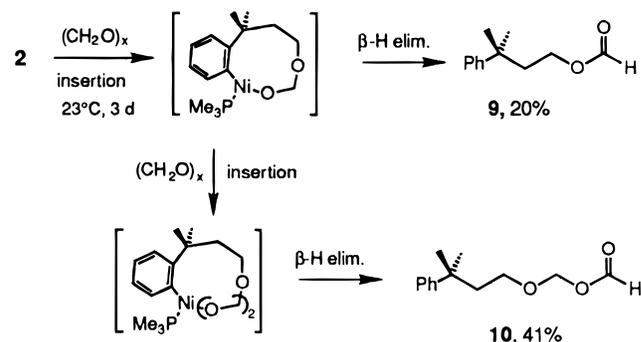


thermally robust than either **2** or **3** is probably a consequence of the greater ease in forming three-coordinate Ni complexes that are subject to elimination or insertion reactions (see above) for these phosphine-containing compounds than for the more rigid and less labile bpy derivative. Although 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 CH₂O into

(10) (a) Villani, F. J.; Nord, F. F. *J. Am. Chem. Soc.* **1947**, *69*, 2605. (b) Tsuda, T.; Habu, H.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1974**, 620. (c) Stapp, P. R. *J. Org. Chem.* **1973**, *38*, 1433. (d) Murahashi, S.-I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem.* **1987**, *52*, 4319.

Scheme 2



M–H, M–C, and M–O bonds have been reported,¹¹ and sequential insertions of CH₂O in Cu–C and Cu–O bonds were suggested for the formation of (2,4,6-trimethylbenzyl)formate from the reaction of Cu(PPh₃)(2,4,6-Me₃C₆H₂) with paraformaldehyde.^{11b} As reported by Carmona and co-workers, reaction of solutions of **1** stirred over paraformaldehyde results in initial insertion of OCH₂ into the Ni–C(alkyl) bond to give good yields of **2**.⁶ However, as shown in Scheme 2, solutions of **2** are unstable in the presence of paraformaldehyde. Formal sequential CH₂O 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, PhCMe₂CH₂CH₂OC(O)H (**9**), which incorporates two CH₂O units, and formic acid (3-methyl-3-phenylbutoxy)methyl ester, PhCMe₂CH₂CH₂OC(O)H (**10**), which incorporates three CH₂O 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 β -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 β -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 CH₂O 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.

JA9714999

(11) (a) Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634. (b) Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1983**, *255*, C31. (c) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576. (d) Tikkanen, W. R.; Petersen, J. L. *Organometallics* **1984**, *3*, 1651. (e) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354. (f) Wei, M.; Wayland, B. B. *Organometallics* **1996**, *15*, 4681.