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OXYGEN-ATOM TRANSFER FROM NITROUS OXIDE (N=N=O) TO NICKEL ALKYLS. SYNTHESES AND REACTIONS OF NICKEL(II) ALKOXIDES*

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Abstract—The dialkyl nickel complexes (bipy)Ni(R)$_2$ (**1**, R = Et; **2**, R = *iso*-Bu; bipy ≡ 2,2′-bipyridine) react with nitrous oxide (1 atm) to generate nickel(II) alkoxy alkyl complexes (bipy)Ni(OR)(R) (**3**, R = Et; **4**, R = *iso*-Bu), which in turn undergo CO-insertion followed by reductive elimination under a carbon monoxide atmosphere to afford the corresponding esters (ethyl propionate from **3**; 2-methylbutanoic acid-2-methylpropyl ester from **4**). Nitrous oxide reacts with the metallacyclopentane complex (bipy)Ni{$(CH_2)_4$} (**5**) to give the oxametallacycle (bipy)Ni{$O(CH_2)_3CH_2$} (**6**) and with (phen)Ni{$(CH_2)_4$} (**7**; phen ≡ 1,10-phenanthroline) to give (phen)Ni{$O(CH_2)_3CH_2$} (**8**). Complex **6** undergoes elimination reactions with HCl to give 1-butanol, with I_2 to give tetrahydrofuran, and with CO to give δ-valerolactone. The α-methyl substituted metallacycle (bipy)Ni{$(CH_2)_3CHCH_3$} (**9**) reacts with N_2O in a regioselective fashion (at the more highly substituted Ni—C bond) to give (bipy)Ni{$OCH(CH_3)CH_2CH_2CH_2$} (**10**) exclusively. Complex **10** undergoes elimination reactions with HCl to give 2-pentanol, with I_2 to give 2-methyltetrahydrofuran, and with CO to give δ-caprolactone. The β,β'-dimethyl substituted metallacycles, *meso*-(bipy)Ni{$CH_2CH(CH_3)CH(CH_3)CH_2$} (**11**) and *d,l*-(bipy)Ni{$CH_2CH(CH_3)CH(CH_3)CH_2$} (**12**) react with N_2O to produce the oxametallacycles (bipy)Ni{*cis*-$OCH_2CH(CH_3)CH(CH_3)CH_2$} (**13**) and (bipy)Ni{*trans*-$OCH_2CH(CH_3)CH(CH_3)CH_2$} (**14**), respectively. Complex **13** undergoes elimination reactions with HCl to give 2,3-dimethyl-1-butanol, with I_2 to give *cis*-3,4-dimethyl-tetrahydrofuran, and with CO to give tetrahydro-*cis*-4,5-dimethyl-2*H*-pyran-2-one. The metallacycles (bipy)Ni{$CH_2C(CH_2)C(CH_2)CH_2$} (**15**) and (bipy)Ni{$(CH_2)_2C_6H_4$} (**16**), both possessing sp^2-hybridized ring carbons in the β- and β'-positions, show no reactivity toward N_2O. However, **16** reacts with HCl to afford *o*-xylene, with CH_2Br_2 to afford indan, and with maleic anhydride to afford tetrahydronaphthalene anhydride.

We have been exploring the use of nitrous oxide (N=N=O) as an oxygen-atom transfer reagent toward organometallic complexes in order to introduce functionality into hydrocarbon substrates.[1] Nitrous oxide is an attractive reagent for O-transfer processes because: (i) it is a potent oxidant, comparable in oxidizing power to perbromate or hydrogen peroxide, owing to a large thermodynamic driving force for loss of N_2 (ΔG_f^o = 25 kcal mol^{-1}); (ii) its reactions hold potential for high selectivity since N_2O is kinetically inert in the absence of an appropriate activating agent (usually a metal complex or metal surface) and the sole by-product of O-transfer is the generally innocent N_2 molecule; (iii) it is an inexpensive, easy-to-handle oxidant.[2]

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*This paper is dedicated to the best organometallic chemist in the world, Professor John E. Bercaw, on the occasion of his 50th birthday.

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The reactions of N_2O with transition-metal complexes have most often led to the formation of metal oxo complexes.[3–5] The use of N_2O to directly oxidize organic substrates attached to metal centers has remained a relatively unexplored area of research. Our earlier work in this area focused on group 4 (Ti, Zr, Hf) complexes where a number of ligand transformations were examined.[1] While interesting ligand-based oxidations were discovered in these early metal systems, the oxophilicity of the group 4 metals prevented a thorough examination of the elimination chemistry of the oxidized ligands from the metal complexes since very robust M—O bonds were produced. We have therefore undertaken an examination of the reaction chemistry of N_2O with complexes of the late transition-series metals that generally form weaker bonds with hard ligands, and where elimination processes are more fully established.

Alkoxide and aryloxide complexes of Pd and Pt have been studied in some detail, but the chemistry of related Ni derivatives is not so well developed.[6] Several stable aryloxides of Ni are known,[7,11c] and a few examples of monomeric Ni alkoxides have been reported.[8–11] Recently we reported the reaction of a square-planar Ni^{II} alkyl complex with N_2O under mild conditions to effect a formal O-atom insertion into a Ni—C bond to produce a simple, stable nickel alkoxide derivative (equation 1).[12] This represented the first example of the oxidation of a saturated carbyl ligand at a metal centre using

$$(L_n)Ni{-}R + N_2O \longrightarrow (L_n)Ni{-}OR + N_2 \quad (1)$$

nitrous oxide as the oxygen-atom source, and we were curious to examine whether this N_2O protocol could provide a general synthetic route to otherwise inaccessible members of the nickel alkoxide family. The results of these studies are reported herein, some of which have been communicated in preliminary form.[12]

EXPERIMENTAL

General considerations

Reactions were carried out using standard high-vacuum and Schlenk techniques using dry, air-free solvents. Unless otherwise noted, NMR spectra were recorded in C_6D_6 solution at ambient temperature. ^1H NMR spectra were recorded at 500 MHz using a General Electric Ω-500 spectrometer; $^{13}C\{^1H\}$ NMR spectra were recorded using a GE Ω-500 or Ω-300 spectrometer operating at 125.77 or 75.5 MHz, respectively. Infrared spectra were recorded on a Nicolet 20SXB spectrometer in Nujol mull with KBr plates unless otherwise noted. Electron impact mass spectra were recorded on a VG Analytical, LTD 70-70 EQ double focusing (EB) mass spectrometer at the departmental mass spectrometry facility. Elemental analyses were performed by Desert Analytics (Tucson, AZ). 2,2′-Bipyridine (bipy), 1,10-phenanthroline (phen), 1,5-cyclooctadiene (cod) and $Ni(acac)_2$ were purchased from Aldrich Chemical Co. $(bipy)Ni(Et)_2$ (**1**),[13] $(bipy)Ni\{(CH_2)_4\}$ (**5**),[14] and (bipy)Ni(cod)[15] were prepared according to the literature procedures.

Preparation of $(bipy)Ni(OCH_2CH_3)(CH_2CH_3)$ (**3**)

A solution of **1** (0.50 g, 1.8 mmol) in THF (20 cm^3) was exposed to N_2O (1 atm) at room temperature for 12 h, during which time the color changed from green to purple. The purple solution was filtered and the insoluble materials were extracted thoroughly with THF until the filtrate was colorless. The THF solution was concentrated to 5 cm^3 and pentane (30 cm^3) was added to the solution to precipitate the product. The solid was filtered and washed with pentane (3 × 5 cm^3). Residual solvent was removed under vacuum, giving 0.35 g (1.2 mmol, 66% yield) of **3** as dark purple microcrystals. ^1H NMR: δ 1.48 (t, CH_3, 3H), 1.66 (q, CH_2, 2H), 1.81 (t, CH_3, 3H), 4.10 (q, CH_2, 2H), 6.30 (t, bipy, 1H), 6.66 (d, bipy, 1H), 6.73 (t, bipy, 1H), 6.79 (d, bipy, 1H), 6.88 (t, bipy, 1H), 6.93 (t, bipy, 1H), 8.53 (d, bipy, 1H), 9.72 (d, bipy, 1H). $^{13}C\{^1H\}$ NMR (125.77 MHz): δ 10.0, 15.8, 23.0, 60.8, 118.4, 120.8, 124.2, 125.4, 132.7, 136.0, 148.1, 149.1, 151.2, 155.8. IR: 3091 (w), 3042 (w), 3007 (m), 2675 (m), 1598 (s), 1563 (m), 1436 (vs), 1408 (s), 1358 (s), 1302 (m), 1267 (m), 1238 (w), 1161 (w), 1147 (s), 1126 (vs), 1098 (vs), 1048 (vs), 1034 (m), 992 (m), 978 (m), 893 (m), 795 (w), 767 (vs), 724 (s), 633 (m), 583 (m), 513 (w), 471 (w), 428 (m) cm^{-1}. Found: C, 57.8; H, 6.03; N, 9.26. Calc. for $C_{14}H_{18}N_2ONi$: C, 58.2; H, 6.28; N, 9.69%.

Reaction of **3** *with* CO

A solution of **3** (30 mg, 0.10 mmol) in C_6D_6 (0.5 cm^3) was exposed to CO (1 atm). After stirring at room temperature for 1 h, the volatiles were vacuum transferred to a clean flask and analysed by ^1H NMR (using ferrocene as an internal standard). The isolated yield of ethyl propionate was 0.079 mmol (76%). The product was identified by spectral comparison with an authentic sample.

Preparation of (bipy)Ni(*iso*-Bu)$_2$ (**2**)

A solution of bipy (3.65 g, 23.4 mmol) in Et_2O (50 cm^3) was added to $Ni(acac)_2$ (3.00 g, 11.7 mmol) forming a light green suspension. A toluene solution of *iso*-Bu_2AlOEt (29 mmol) was added to the suspension at −70°C. The mixture was warmed to room temperature and stirred for 1.5 days. The mixture was filtered and the insoluble materials were washed with Et_2O (2 × 10 cm^3). The solution was concentrated down to a dark oil under reduced pressure. The residue was dissolved in fresh Et_2O (20 cm^3) and the solution was cooled to −70°C for 1 h. The resulting crystalline product was filtered and washed with cold Et_2O (3 × 5 cm^3). The residual solvent was removed under reduced pressure leaving a dark green solid. The yield of **2** was 2.10 g (6.39 mmol, 55%). ^1H NMR: δ 1.63 (d, CH_3, 12H), 1.74 (d, CH_2, 4H), 2.40 (sept, CH, 2H), 6.61 (t, bipy, 2H), 6.71 (d, bipy, 2H), 7.01 (t, bipy, 2H), 9.30 (d, bipy, 2H). ^{13}C NMR (75.57 MHz): δ 28.4 (q, CH_3), 30.0 (t, CH_2), 32.2 (d, CH), 120.4 (d, bipy), 125.7 (d, bipy), 133.3 (d, bipy), 147.6 (d, bipy), 154.1 (s, bipy). IR: 3091 (w), 3070 (w), 2760 (m), 1957 (w), 1929 (w), 1901 (w), 1851 (w), 1591 (m), 1555 (w), 1443 (m), 1429 (s), 1393 (w), 1358 (m), 1344 (m), 1309 (m), 1260 (m), 1238 (w), 1196 (w), 1161 (w), 1147 (m), 1133 (m), 1055 (m), 1041 (m), 1027 (m), 992 (m), 950 (w), 872 (w), 745 (s), 717 (s), 654 (w), 640 (w), 597 (w), 576 (w), 414 (w) cm^{-1}. Found: C, 65.5; H, 7.86; N, 8.65. Calc. for $C_{18}H_{26}N_2Ni$: C, 65.7; H, 7.96; N, 8.51%.

Reaction of **2** *with* N_2O *and* CO

A stirred solution of **2** (0.20 g, 0.61 mmol) in THF (10 cm^3) was exposed to N_2O (1 atm) for 2 days at room temperature. The resulting purple solution containing **4** was degassed and the atmosphere was replaced by CO (1 atm). After stirring at room temperature for 1 h, the color had changed to pale brown. The solution was concentrated to approximately 0.5 cm^3 under reduced pressure and the remaining liquid was vacuum distilled through a short path distillation apparatus giving 63 mg (0.40 mmol, 66%) of 2-methylbutanoic acid-2-methylpropyl ester. ^1H NMR: δ 0.80 (d, CH_3, 6H), 0.85 (d, CH_2, 2H), 0.88 (d, CH_3, 3H), 1.78 (m, CH, 1H), 2.11 (m, CH, 1H), 3.84 (d, OCH_2, 2H). ^{13}C NMR (125.77 MHz): δ 19.1 (q, CH_3), 22.4 (q, CH_3), 25.9 (d, CH), 28.0 (d, CH), 43.4 (t, CH_2), 70.2 (t, OCH_2), 172.3 (s, $C{=}O$). IR (neat, KBr): 2957 (s), 2865 (m), 1732 (s), 1365 (m), 1288 (m), 1182 (m), 1161 (m), 1112 (m), 1006 (m) cm^{-1}. MS *m/z* 158 (M^+), 143 ($M^+ - CH_3$), 128 ($M^+ - 2CH_3$).

Preparation of $(bipy)Ni(OCH_2CH_2CH_2CH_2)$ (**6**)

A solution of **5** (0.400 g, 1.48 mmol) in benzene (15 cm^3) was stirred under an atmosphere of N_2O at 50 C for 48 h. The blue–purple benzene solution was worked up as described for **3**. Recrystallization by slow diffusion of pentane into a concentrated benzene solution afforded 0.235 g (0.819 mmol, 55% yield) of **8** as purple blocks. ^1H NMR: δ 1.32 (m, CH_2, 2H), 2.03 (t, $NiCH_2$, 2H), 2.10 (m, CH_2, 2H), 4.06 (t, OCH_2, 2H), 6.25 (t, bipy, 1H), 6.61 (d, bipy, 1H), 6.74 (m, bipy, 2H), 6.83 (t, bipy, 1H), 6.92 (t, bipy, 1H), 8.29 (d, bipy, 1H), 9.77 (d, bipy, 1H). ^{13}C NMR: δ 155.8 (s, bipy), 151.1 (s, bipy), 148.1 (d, bipy), 147.2 (d, bipy), 135.9 (d, bipy), 132.7 (d, bipy), 124.7 (dd, bipy), 124.2 (dt, bipy), 120.7 (dd, bipy), 118.5 (dd, bipy), 65.3 (t, OCH_2), 39.0 (t, CH_2), 26.6 (t, CH_2), 15.5 (t, CH_2). IR (Nujol, KBr): 3049 (w), 3007 (w), 2753 (m), 2661 (m), 1591 (m), 1563 (w), 1436 (s), 1400 (w), 1351 (m), 1316 (w), 1295 (m), 1260 (w), 1231 (w), 1203 (m), 1147 (m), 1105 (m), 1084 (w), 1069 (w), 1055 (w), 1048 (m), 1041 (m), 1006 (w), 992 (w), 971 (vw), 943 (w), 907 (w), 872 (vw), 823 (vw), 795 (vw), 752 (s), 717 (m), 661 (vw), 647 (vw), 626 (w), 548 (w), 485 (w), 471 (vw), 414 (m) cm^{-1}. Found: C, 58.9; H, 5.56; N, 9.52. Calc. for $C_{14}H_{16}N_2ONi$: C, 58.6; H, 5.62; N, 9.76%.

Reaction of **6** *with* HCl

A solution of **6** (20 mg, 0.070 mmol) in C_6D_6 (0.5 cm^3) was exposed to an atmosphere of anhydrous HCl gas. A pale green precipitate immediately formed. After stirring at room temperature for 10 min, the volatiles were vacuum transferred into another flask and the solution was analyzed by ^1H and ^{13}C NMR spectroscopy (using ferrocene as an internal standard). The isolated yield of 1-butanol was 0.062 mmol (88%). The product was identified by spectral comparison with an authentic sample.

Reaction of **6** *with* I_2

To a solution of **6** (50 mg, 0.17 mmol) in C_6D_6 (0.5 cm^3) was added I_2 (44 mg, 0.17 mmol). The mixture was stirred at room temperature for 2 days during which time a dark brown precipitate formed. The volatiles were vacuum transferred into another flask and the solution was analyzed by ^1H NMR (using ferrocene as an internal standard). The isolated yield of tetrahydrofuran was 0.027 mmol (16%).

Reaction of **6** *with* CO

A solution of **6** (60 mg, 0.21 mmol) in Et_2O (10 cm^3) was exposed to an atmosphere of carbon monoxide and stirred for 16 h at room temperature. The excess CO was removed and the solution was concentrated to 5 cm^3, pentane (10 cm^3) was vacuum transferred into the flask to give a red precipitate (identified by its IR spectrum as (bipy)$Ni(CO)_2$), and the solution was filtered. The more volatile solvents were removed under reduced pressure leaving a higher boiling liquid. The liquid was diluted with C_6D_6 (0.5 cm^3) and the solution was analyzed by ^1H and ^{13}C NMR spectroscopy (using ferrocene as an internal standard). The isolated yield of δ-valerolactone was 0.11 mmol (52%). The product was identified by spectral comparison with an authentic sample.

Preparation of (phen)$Ni(CH_2CH_2CH_2CH_2)$ (**7**)

A solution of 1,10-phenanthroline (0.85 g, 4.7 mmol) in THF (15 cm^3) was added by cannula to a suspension of $Ni(cod)_2$ (0.65 g, 2.4 mmol) at −70°C. The resulting solution was allowed to warm to room temperature giving a deep magenta hue. After stirring for 30 min, 1,4-dibromobutane (0.14 cm^3, 1.2 mmol) was added dropwise using a syringe at −70°C. The solution was allowed to warm to room temperature and then stirred for 6 h. The resulting deep blue solution was filtered, retaining an insoluble material that was washed with THF (3×10 cm^3). After reducing the filtrate to 15 cm^3, pentane (30 cm^3) was added to precipitate the product. The precipitate was filtered and washed with pentane (3×10 cm^3) yielding 0.12 g of dark blue crystals (0.41 mmol, 35%). ^1H NMR: δ 2.68 (m, CH_2, 4H), 2.91 (t, CH_2, 4H), 6.73 (m, phen, 2H), 6.92 (s, phen, 2H), 7.42 (d, phen, 2H), 9.25 (d, phen, 2H). ^{13}C $\{^1H\}$ NMR (125.77 MHz): δ 147.4, 131.6, 125.8, 125.3, 36.8, 29.2. IR: 2800 (w), 2758 (w), 1940 (w), 1891 (w), 1842 (w), 1624 (m), 1596 (m), 1561 (m), 1511 (m), 1406 (s), 1293 (m), 1215 (m), 1194 (s), 1159 (m), 1137 (s), 1039 (m), 1011 (m), 961 (w), 927 (w), 828 (s), 758 (s), 715 (s), 666 (m), 631 (w), 525 (w), 455 (m) cm^{-1}. Found: C, 64.8; H, 5.15; N, 9.60. Calc. for $C_{16}H_{16}N_2Ni$: C, 65.1; H, 5.47; N, 9.50%.

Preparation of (phen)$Ni(OCH_2CH_2CH_2CH_2)$ (**8**)

A navy-blue solution of **7** (0.14 g, 0.48 mmol) in benzene (20 cm^3) was exposed to N_2O (1 atm) for 36 h at 55°C. The resulting dark purple benzene solution was worked up as described for **3** to give 86 mg of **8** (0.28 mmol, 58%) as dark purple crystals. ^1H NMR: δ 1.41 (m, CH_2, 2H), 2.25 (m, CH_2, 2H), 2.77 (t, $NiCH_2$, 2H), 4.18 (t, OCH_2, 2H), 6.50 (dd, phen, 1H), 6.89 (AB q, phen, 2H), 6.97 (dd, phen, 1H), 7.31 (d, phen, 1H), 7.32 (d, phen, 1H), 8.42 (d, phen, 1H), 9.76 (dd, phen, 1H). ^{13}C $\{^1H\}$ NMR (75.57 MHz): δ 154.0, 147.7, 147.4, 146.2, 143.0, 134.0, 131.0, 125.7, 125.4, 124.2, 123.8, 120.4, 65.5, 39.4, 26.7, 15.0. IR: 2786 (w), 2730 (w), 2652 (m), 2582 (w), 1567 (w), 1406 (w), 1349 (m), 1201 (s), 1166 (m), 1152 (m), 1053 (m), 1025 (m), 941 (w), 905 (m), 821 (s), 715 (s), 553 (m), 476 (m) cm^{-1}. Found: C, 61.8; H, 4.95; N, 9.18. Calc. for $C_{16}H_{16}N_2ONi$: C, 61.8; H, 5.19; N, 9.01%.

Preparation of (bipy)$Ni(CH_2CH_2CH_2CHCH_3)$ (**9**)

The metallacycle was synthesized from $Ni(cod)_2$ (2.00 g, 7.27 mmol), bipy (2.52 g, 16.1 mmol), and 1,4-dibromopentane (0.57 cm^3, 4.2 mmol) according to the procedure described for **7** to give 0.52 g (1.8 mmol, 51%) of a dark green, microcrystalline solid. ^1H NMR: δ 1.84 (d, CH_3, 3H), 1.87 (m, CHH, 1H), 2.18 (m, CHH, 1H), 2.35 (m, CHH, 1H), 2.41 (m, CHH, 1H), 2.47 (m, CHH, 1H), 2.81 (dt, CHH, 1H), 2.92 (m, CH, 1H), 6.47 (t, bipy, 1H), 6.56 (t, bipy, 1H), 6.75 (d, bipy, 2H), 6.97 (t, bipy, 1H), 7.03 (t, bipy, 1H), 9.03 (d, bipy, 1H), 9.12 (d, bipy, 1H). ^{13}C NMR (125.77 MHz): δ 22.2 (q, CH_3), 27.5 (t, CH_2), 32.2 (t, CH_2), 37.3 (d, CH), 45.1 (t, CH_2), 120.2 (d, bipy), 120.4 (d, bipy), 125.4 (d, bipy), 126.0 (d, bipy), 133.0 (d, bipy), 133.4 (d, bipy), 148.1 (d, bipy), 148.3 (d, bipy), 154.3 (s, bipy), 154.5 (s, bipy). IR: 2823 (w), 2774 (w), 2753 (w), 1591 (m), 1555 (w), 1548 (w), 1436 (s), 1423 (m), 1302 (w), 1288 (w), 1260 (m), 1224 (w), 1203 (w), 1161 (w), 1147 (w), 1133 (w), 1091 (w), 1055 (w), 1020 (w), 1006 (w), 865 (w), 795 (w), 752 (s), 731 (w), 717 (m), 640 (w) cm^{-1}. Found: C, 62.9; H, 6.13; N, 10.1. Calc. for $C_{15}H_{18}N_2Ni$: C, 63.2; H, 6.37; N, 9.83%.

Preparation of (bipy)$Ni\{OCH(CH_3)CH_2CH_2CH_2\}$ (**10**)

A solution of **9** (0.20 g, 0.70 mmol) in C_6H_6 (15 cm^3) was exposed to N_2O (1 atm) at room temperature for 22 h. The benzene solution was worked up as described for **3**. The yield of blue microcrystals was 0.15 g (0.51 mmol, 72%). ^1H NMR: δ 1.29 (m, CHH, 1H), 1.41–1.59 (m, CH_2, 2H), 1.76 (d, CH_3, 3H), 2.14 (dd, CH_2, 2H), 2.33 (m, CHH, 1H), 4.10 (m, OCH, 1H), 6.23 (m, bipy, 1H), 6.60 (d, bipy, 1H), 6.74 (m, bipy, 2H), 6.82 (td, bipy, 1H), 6.92 (td, bipy, 1H), 8.31 (d, bipy, 1H), 9.85 (d, bipy, 1H). ^{13}C NMR (125.77 MHz): δ 17.1 (t, CH_2), 26.3 (t, CH_2), 27.6 (q, CH_3), 45.5 (t, CH_2), 67.9 (d, OCH), 118.2 (d, bipy), 120.5 (d, bipy), 124.3 (d, bipy), 124.6 (d, bipy), 132.4 (d, bipy), 135.7 (d, bipy), 147.4 (d, bipy), 148.0 (d, bipy), 151.1 (s, bipy), 155.8 (s, bipy). IR: 3056 (m), 3014 (w), 2809 (m), 2781 (m), 2739 (m), 2675 (w), 2647 (w), 2598 (m), 2563 (m), 1591 (m), 1563 (w), 1436 (s), 1400 (w), 1344 (m), 1330 (m), 1295 (m), 1260 (w), 1238 (w), 1217 (m), 1147 (w), 1126 (m), 1091 (m), 1062 (m), 1048 (m), 1034 (s), 1006 (m), 992 (w), 929 (w), 893 (w), 872 (w), 795 (w), 752 (s), 717 (s), 661 (w), 633 (w), 583 (w), 534 (w), 471 (w), 450 (w), 414 (m) cm^{-1}. Found: C, 60.2; H, 5.83; N, 9.21. Calc. for $C_{15}H_{18}N_2ONi$: C, 59.9; H, 6.03; N, 9.31%.

Reaction of **10** *with* HCl

The reaction was carried out as described for the reaction of **6** with HCl. The isolated yield of 2-pentanol was 87%. The product was identified by spectral comparison with an authentic sample.

Reaction of **10** *with* CO

A solution of **10** (20 mg, 0.066 mmol) in Et_2O (5 cm^3) was stirred at room temperature under CO (1 atm) for 30 min during which time the color changed from blue to pale pink. The Et_2O was removed under reduced pressure and the residue was extracted with $CDCl_3$ (0.5 cm^3). Analysis by ^1H NMR (using ferrocene as an internal standard) gave a yield of δ-caprolactone of 0.038 mmol (57%). The product was identified by comparison with a published spectrum.[16]

Reaction of **10** *with* I_2

The reaction was carried out as described for the reaction of **6** with I_2. The isolated yield of 2-methyltetrahydrofuran was 14%. The product was identified by spectral comparison with an authentic sample.

Preparation of meso-(bipy)Ni$\{CH_2CH(CH_3)CH(CH_3)CH_2\}$ (**11**)

The metallacycle was synthesized from (bipy) Ni(cod) (1.50 g, 4.64 mmol), bipy (0.73 g, 4.6 mmol), and *meso*-1,4-dibromo-2,3-dimethylbutane (0.35 cm^3, 2.3 mmol) according to the procedure described for **7** to give 0.54 g (1.8 mmol, 77%) of **11** as a dark green solid. The product was found to contain 92% of the *meso* isomer by ^1H NMR analysis. ^1H NMR: δ 1.52 (d, C*H*$_3$, 6H), 2.15 (dd, C*H*H, 2H), 2.51 (m, C*H*, 2H), 2.57 (m, CH*H*, 2H), 6.47 (t, bipy, 2H), 6.79 (d, bipy, 2H), 7.00 (t, bipy, 2H), 8.86 (d, bipy, 2H). ^{13}C NMR (125.77 MHz): δ 19.0 (q, CH_3), 33.5 (t, CH_2), 44.7 (d, CH), 120.3 (d, bipy), 125.6 (d, bipy), 133.4 (d, bipy), 147.7 (d, bipy), 154.0 (s, bipy). IR: 3091 (w), 3049 (w), 2999 (w), 2753 (m), 1591 (m), 1555 (w), 1548 (w), 1436 (s), 1422 (m), 1358 (w), 1351 (w), 1330 (w), 1302 (w), 1260 (m), 1161 (w), 1147 (w), 1112 (w), 1055 (w), 1020 (w), 1006 (w), 985 (w), 957 (w), 872 (w), 795 (w), 752 (s), 717 (s), 689 (w), 640 (w), 590 (w), 555 (w), 499 (w), 407 (w) cm^{-1}. Found: C, 64.0; H, 6.52; N, 9.33. Calc. for $C_{16}H_{20}N_2Ni$: C, 64.3; H, 6.74; N, 9.37%.

Preparation of d,l-(bipy)Ni$\{CH_2CH(CH_3)CH(CH_3)CH_2\}$ (**12**)

This complex was prepared from (bipy)Ni(cod), bipy, and *d,l*-1,4-dibromo-2,3-dimethylbutane in a manner identical to that used for **7**. The yield of **12** was 76%. Analysis of the ^1H NMR spectrum indicated that the product consisted of approximately 75% of the *d,l*-isomer. ^1H NMR: δ 1.49 (d, C*H*$_3$, 6H), 1.62 (m, C*H*, 2H), 2.06 (m, C*H*H, 2H), 2.26 (dd, CH*H*, 2H), 6.49 (t, bipy, 2H), 6.84 (d, bipy, 2H), 7.03 (t, bipy, 2H), 8.78 (d, bipy, 2H). ^{13}C NMR (125.77 MHz): δ 24.8 (q, CH_3), 34.5 (t, CH_2), 48.5 (d, CH), 120.4 (d, bipy), 125.5 (d, bipy), 133.4 (d, bipy), 147.4 (d, bipy), 154.0 (s, bipy).

Preparation of (bipy)Ni$\{$*cis*-$OCH_2CH(CH_3)CH(CH_3)CH_2\}$ (**13**)

A stirred solution of **11** (0.30 g, 1.0 mmol) in THF was exposed to N_2O (1 atm) at 55°C for 2 days. The THF solution was worked up as described for **3** to give 0.24 g (0.75 mmol, 75%) of **13** as a dark purple solid. ^1H NMR: δ 1.28 (d, C*H*$_3$, 3H), 1.36 (m, C*H*, 1H), 1.43 (d, C*H*$_3$, 3H), 1.69 (t, C*H*H, 1H), 2.04 (m, C*H*, 1H), 2.11 (t, CH*H*, 1H), 3.79 (t, OC*H*H, 1H), 3.90 (dd, OCH*H*, 1H), 6.34 (t, bipy, 1H), 6.70 (t, bipy, 1H), 6.85 (d, bipy, 1H), 6.98 (m, bipy, 3H), 8.22 (d, bipy, 1H), 9.58 (d, bipy, 1H). ^{13}C NMR (125.77 MHz): δ 14.0 (q, CH_3), 18.2 (q, CH_3), 23.4 (t, CH_2), 34.9 (d, CH), 45.5 (d, CH), 68.7 (t, OCH_2), 118.7 (d, bipy), 121.0 (d, bipy), 124.2 (d, bipy), 124.7 (d, bipy), 133.1 (d, bipy), 136.1 (d, bipy), 147.1 (d, bipy), 147.8 (d, bipy), 151.0 (s, bipy), 155.7 (s, bipy). IR: 3042 (w), 2774 (s), 2697 (s), 2647 (m), 2584 (w), 1591 (m), 1563 (m), 1548 (w), 1436 (s), 1408 (w), 1351 (m), 1330 (w), 1302 (m), 1260 (s), 1161 (m), 1133 (s), 1112 (s), 1084 (s), 1048 (m), 1034 (w), 1013 (w), 992 (w), 971 (w), 950 (w), 936 (w), 886 (w), 872 (w), 759 (s), 745 (s), 717 (s), 661 (w), 654 (w), 633 (w), 612 (w), 555 (m), 520 (m), 485 (m), 471 (w), 450 (w), 414 (m) cm^{-1}. Found: C, 59.5; H, 6.33; N, 8.21. Calc. for $C_{16}H_{20}N_2ONi$: C, 61.0; H, 6.40; N, 8.89%.

Reaction of **13** *with* HCl

The reaction was carried out as described for the reaction of **6** with HCl. The yield of 2,3-dimethyl-1-butanol was 51%. ^{1}H NMR : δ 0.75 (d, CH_3, 3H), 0.76 (d, CH_3, 3H), 0.82 (d, CH_3, 3H), 1.30 (m, C*H*, 1H), 1.56 (m, C*H*, 1H), 3.16 (dd, OC*H*H, 1H), 3.29 (dd, OCH*H*, 1H). ^{13}C NMR (125.77 MHz) : δ 12.8 (q, CH_3), 18.4 (q, CH_3), 20.7 (q, CH_3), 29.4 (d, *C*H), 41.9 (d, *C*H), 66.4 (t, CH_2OH). MS *m*/*z* 101 ($M^+ - H$). The characterizational data were also compared with previously published data.[17]

Reaction of **13** *with* I_2

The reaction was carried out as described for the reaction of **6** with I_2. The isolated yield of *cis*-3,4-dimethyltetrahydrofuran was 27%. ^{1}H NMR: δ 0.71 (d, CH_3, 6H), 1.93 (m, C*H*, 2H), 3.35 (dd, OCH*H*, 2H), 3.84 (t, OC*H*H, 2H). ^{13}C {^{1}H} NMR (125.77 MHz): δ 12.5 (CH_3), 36.8 (*C*H), 74.5 (OCH_2). The characterizational data were also compared with previously published data.[18]

Reaction of **13** *with* CO

A solution of **13** (30 mg, 0.095 mmol) in Et_2O (10 cm^3) was exposed to CO (1 atm). The mixture was stirred at room temperature for 1 h yielding a pale green solution. The Et_2O was removed under reduced pressure leaving a dark red residue. The volatiles were vacuum transferred into a clean flask and dissolved in C_6D_6 (0.5 cm^3). Analysis by ^{1}H NMR (using ferrocene as an internal standard) gave a yield of tetrahydro-4,5-dimethyl-2*H*-pyran-2-one of 0.083 mmol (87%). ^{1}H NMR: δ 0.39 (d, CH_3, 3H), 0.44 (d, CH_3, 3H), 1.23 (m, C*H*, 1H), 1.35 (m, C*H*, 1H), 1.93 (dd, C*H*H, 1H), 2.17 (dd, CH*H*, 1H), 3.54 (dd, OC*H*H, 1H), 3.64 (dd, OCH*H*, 1H). ^{13}C NMR (75.57 MHz): δ 11.4 (q, CH_3), 15.9 (q, CH_3), 30.2 (d, *C*H), 31.4 (d, *C*H), 36.9 (t, CH_2), 72.9 (t, OCH_2), 169.3 (s, C=O). MS *m*/*z* 128 (M^+). The characterizational data were also compared with previously published data.[19]

Preparation of (bipy)Ni{*trans*-OCH$_2$CH(CH$_3$)CH(CH$_3$)CH$_2$} (**14**)

This complex was prepared from **12** in a manner identical to that used for the preparation of **13**. The yield of **14** was 74%. ^{1}H NMR: δ 1.26 (d, CH_3, 3H), 1.40 (m, C*H*, 1H), 1.55 (d, CH_3, 3H), 1.78 (m, C*H*, 1H), 1.82 (t, C*H*H, 1H), 2.26 (dd, CH*H*, 1H), 3.70 (t, OC*H*H, 1H), 4.08 (dd, OCH*H*, 1H), 6.27 (t, bipy, 1H), 6.63 (d, bipy, 1H), 6.72 (t, bipy, 1H), 6.77 (d, bipy, 1H), 6.85 (t, bipy, 1H), 6.91 (t, bipy, 1H), 8.45 (d, bipy, 1H), 9.70 (d, bipy, 1H). ^{13}C NMR (125.77 MHz): δ 17.3 (q, CH_3), 22.6 (q, CH_3), 25.8 (t, CH_2), 37.5 (d, *C*H), 48.2 (d, *C*H), 71.5 (t, OCH_2), 118.4 (d, bipy), 120.7 (d, bipy), 124.3 (d, bipy), 124.7 (d, bipy), 132.7 (d, bipy), 135.8 (d, bipy), 147.7 (d, bipy), 148.1 (d, bipy), 151.2 (s, bipy), 155.8 (s, bipy).

Preparation of (bipy)Ni{CH$_2$C(CH$_2$)C(CH$_2$)CH$_2$} (**15**)

A solution of (bipy)Ni(cod) (1.01 g, 3.13 mmol) in THF (25 cm^3) was cooled to 0°C and exposed to allene (1 atm). The mixture turned blue–green immediately. After warming to room temperature, the mixture was stirred for 1 h. The resulting solid was filtered and washed with THF (5×10 cm^3). The residual solvent was removed under reduced pressure leaving a blue–green solid. Additional product was isolated by concentrating the mother liquor to give a total yield of 0.85 g (2.9 mmol, 92%). ^{1}H NMR: δ 2.88 (s, CH_2, 4H), 5.23 (d, C*H*H, 2H), 5.41 (d, CH*H*, 2H), 6.38 (td, bipy, 2H), 6.67 (d, bipy, 2H), 6.87 (td, bipy, 2H), 8.56 (d, bipy, 2H). ^{13}C {^{1}H} NMR (75.57 MHz): δ 27.1, 94.7, 119.9, 125.6, 131.5, 134.1, 148.0, 151.8. IR: 3049 (m), 1612 (m), 1591 (s), 1555 (w), 1506 (w), 1422 (s), 1415 (m), 1330 (w), 1302 (w), 1288 (w), 1260 (m), 1238 (w), 1189 (w), 1147 (m), 1098 (w), 1055 (w), 1013 (w), 985 (m), 929 (w), 872 (m), 823 (s), 745 (s), 717 (s), 689 (m), 647 (m), 597 (m), 506 (w), 414 (m) cm^{-1}. Found: C, 65.4; H, 5.38; N, 9.30. Calc. for $C_{16}H_{16}N_2Ni$: C, 65.1; H, 5.47; N, 9.50%.

Preparation of (bipy)Ni{(CH$_2$)$_2$C$_6$H$_4$} (**16**)

The metallacycle was synthesized from (bipy) Ni(cod) (2.00 g, 6.19 mmol), bipy (0.97 g, 6.2 mmol), and α,α'-dibromo-*o*-xylene (1.00 g, 3.79 mmol) according to the procedure described for **7** to give 0.41 g (1.3 mmol, 42%) of **16** as blue–green microcrystals. ^{1}H NMR : δ 3.41 (s, CH_2, 4H), 6.44 (td, bipy, 2H), 6.68 (d, bipy, 2H), 6.88 (td, bipy, 2H), 7.33 (dd, aryl, 2H), 7.65 (dd, aryl, 2H), 8.73 (d, bipy, 2H). ^{13}C {^{1}H} NMR (125.77 MHz): δ 26.5, 120.0, 123.9, 125.6, 134.2, 148.0, 154.3, 154.7, 163.2. IR : 3056 (w), 3035 (w), 2999 (w), 2802 (w), 2746 (m), 1591 (m), 1570 (m), 1471 (s), 1436 (s), 1422 (s), 1302 (m), 1267 (m), 1238 (w), 1175 (w), 1161 (w), 1147 (m), 1112 (w), 1055 (m), 1041 (m), 1013 (m), 950 (w), 922 (w), 879 (w), 844 (w), 752 (s), 738 (s), 717 (m), 562 (w), 527 (w), 414 (m) cm^{-1}. Found: C, 68.0; H, 4.94; N, 8.58. Calc. for $C_{18}H_{16}N_2Ni$: C, 67.8; H, 5.06; N, 8.78%.

Reaction of **16** *with* HCl

The reaction was carried out as described for the reaction of **6** with HCl. The isolated yield of *o*-xylene was 68%. The product was identified by spectral comparison with an authentic sample.

Reaction of **16** *with* CH_2Br_2

To a solution of **16** (52 mg, 0.16 mmol) in C_6D_6 (0.5 cm^3) was added CH_2Br_2 (11 μL, 0.16 mmol) using a syringe. The mixture was stirred at room temperature for 2 h during which time a light green precipitate formed. The volatiles were vacuum transferred to a clean flask and analyzed by ^1H NMR (using ferrocene as an internal standard). The isolated yield of indan was 0.043 mmol (27%). The product was identified by spectral comparison with an authentic sample.

Reaction of **16** *with maleic anhydride*

A Schlenk tube was charged with **16** (0.15 g, 0.47 mmol) and maleic anhydride (92 mg, 0.94 mmol). Et_2O (10 cm^3) was added and the mixture was stirred at room temperature for 2 h during which time the solution changed from blue–green to brick red. The resulting red precipitate was filtered and washed with Et_2O (2×30 cm^3). The combined Et_2O solutions were concentrated to 10 cm^3 and cooled to -30°C. A mass of colorless needles was isolated and the mother liquor was concentrated further to obtain two additional crops. The total yield of tetrahydronaphthalene anhydride was 60 mg (0.30 mmol, 63%). ^1H NMR: δ 2.09 (m, C*H*H, 2H), 2.38 (t, CH*H*, 2H), 2.66 (dd, C*H*, 2H), 6.76 (dd, aryl, 2H), 6.87 (dd, aryl, 2H). ^{13}C NMR (CD_2Cl_2, 75.57 MHz): δ 29.8 (t, CH_2), 41.1 (d, CH), 128.0 (dd, aryl), 128.3 (dt, aryl), 134.8 (s, aryl), 174.1 (s, *C*=O). IR ($CHCl_3$, KBr): 1852 (m), 1773 (s), 1706 (w), 1597 (w), 1488 (w), 1312 (w), 1112 (w) cm^{-1}. MS *m/z* 202 (M^+). Found: C, 71.3; H, 5.05. Calc. for $C_{12}H_{10}O_3$: C, 71.3; H, 4.98%.

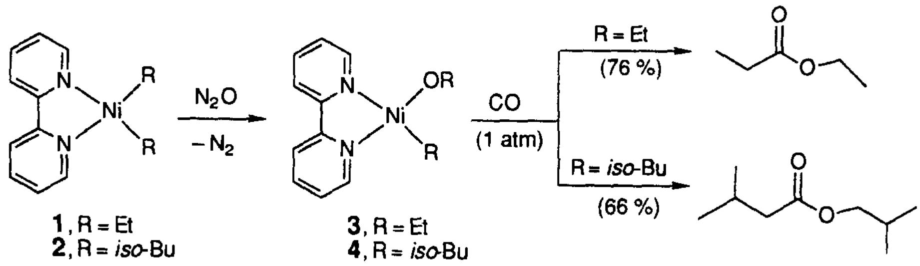
RESULTS AND DISCUSSION

The green, square-planar complex (bipy)Ni($Et)_2$ (**1**) reacts under an atmosphere of nitrous oxide (THF solution, 20°C, 12 h) to extrude dinitrogen and produce the purple Ni^{II} ethoxy complex (bipy) Ni(OEt)(Et) (**3**) in 66% yield, as shown in Scheme 1. These conditions are roughly optimized and are somewhat critical; longer reaction times or higher temperatures result in diminished isolated yields due to a competing secondary reaction of **3** with N_2O to yield a brown precipitate, N_2, and free bipyridine. Complex **3** has been characterized by its ^1H and ^{13}C NMR spectra, IR, elemental analysis and by its reaction chemistry (see below). It is significant to note that previous studies have shown that reactions of aliphatic alcohols with **1** do not lead to isolable nickel alkoxides.[7a] Only the fluorinated alcohols $(CF_3)_2CHOH$ and $Ph(CF_3)$ CHOH have led to stable nickel alkoxides by this route.[11b,c] Despite the presence of β-H atoms in both the ethoxide and ethyl ligands of **3**, the complex is quite stable in the solid state and can be stored for extended periods at ambient temperature under an inert atmosphere.

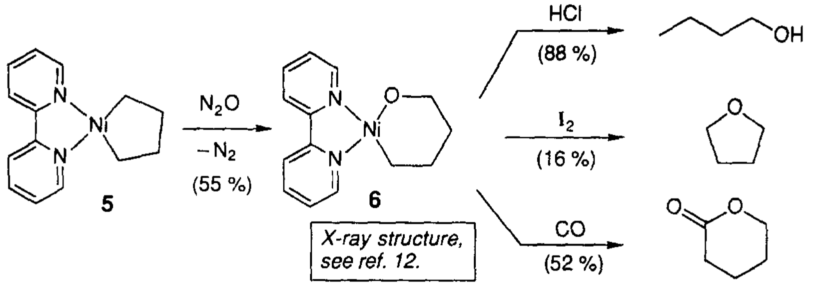
Carbon monoxide (1 atm) reacts with **3** to effect CO-insertion (into either the Ni—C or Ni—O bond) followed by reductive elimination to give ethyl propionate in 76% yield. Although we observe no intermediates in the formation of the ester, Yamamoto has described analogous formation of esters in related Ni^{II} and Pd^{II} alkoxide and aryloxide systems, and suggests that the insertion of CO occurs at the Ni—C bond (not the Ni—O bond) based on observation of an acyl intermediate, (bipy) Ni{C(O)Me}(O-*p*-C_6H_4-CN), in one case.[11b,20] It should be noted, however, that Bryndza *et al.*, observe preferential CO-insertion into the Pd—O bonds (not Pd—C) in mixed alkoxy alkyl complexes of that metal.[6]

Reaction of (bipy)Ni(*iso*-$Bu)_2$ (**2**) with N_2O proceeds to give the isobutoxide derivative (bipy)Ni(O-*iso*-Bu)(*iso*-Bu) (**4**) which is significantly less thermally stable than **3**. Because of this thermal instability, **4** was not isolated in pure form. However, as shown in Scheme 1, exposure of the reaction mixture containing **4** to CO (1 atm) prior to work-up affords 2-methylbutanoic acid-2-methylpropyl ester in 66% yield (Scheme 1).

Related cyclic dialkylnickel complexes (e.g. metallacyclopentanes)[21] react with N_2O to give oxametallacycles. Thus, N_2O oxidation of (bipy) Ni{$(CH_2)_4$} (**5**) (50°C, 48 h) gives (bipy) Ni{$O(CH_2)_3CH_2$} (**6**) in good yield, and (phen) Ni{$(CH_2)_4$} (**7**) reacts with N_2O to afford (phen) Ni{$O(CH_2)_3CH_2$} (**8**). As shown in Scheme 2, **6** undergoes elimination reactions with HCl to give 1-butanol, with I_2 to give tetrahydrofuran, and with CO to give δ-valerolactone. The reaction of **6** with iodine to give tetrahydrofuran (although in only 16% yield) is a particularly intriguing one since it represents a formal reductive elimination from nickel with formation of a new O—C bond. Oxi-



Scheme 1.

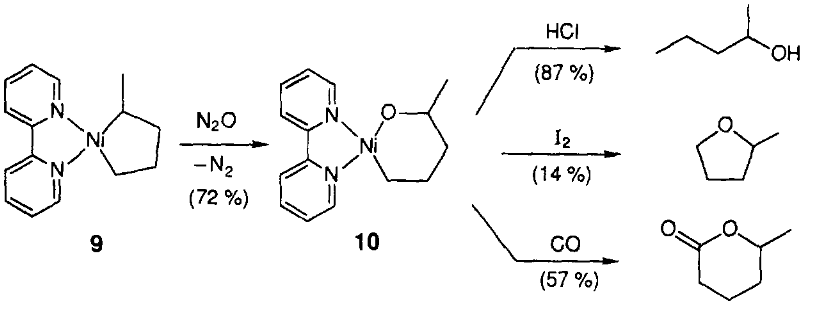


Scheme 2.

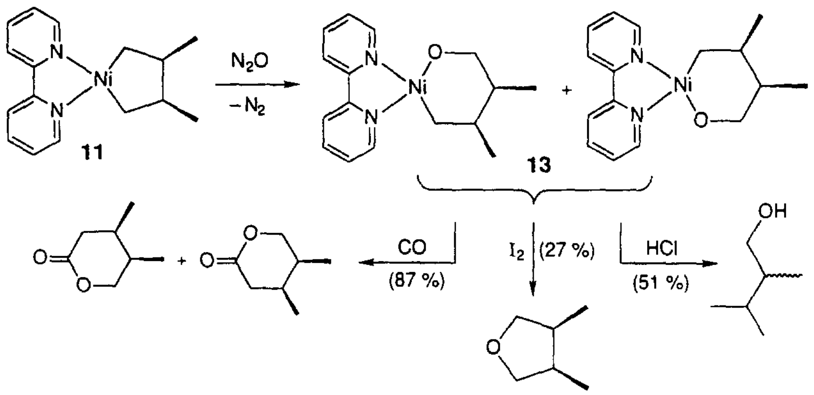
datively induced reductive eliminations are common, but not those involving heteroatoms.[22] Substituted oxametallacycles in this system also undergo a similar reaction with I_2 to give substituted tetrahydrofurans (in 14–27% yields), but the "untethered" alkyl alkoxides do not yield acyclic ethers (i.e. **3** does not react with I_2 to give significant amounts of diethyl ether). We are currently investigating the scope and mechanistic aspects of this O—C elimination reaction.

The reactivity of N_2O with other (bipy)Ni metallacycles has been probed in order to assess the tolerance of the O-transfer reaction to ring substitution. Introduction of a single methyl group at an α-carbon position of the metallacycle was effected by reaction of 1,4-dibromopentane with $Ni(cod)_2$ and bipy, giving $(bipy)Ni(CH_2CH_2CH_2CHCH_3)$ (**9**). As shown in Scheme 3, **9** reacts with N_2O (20°C, 22 h) to form the corresponding alkoxide $(bipy)Ni\{OCH(CH_3)CH_2CH_2CH_2\}$ (**10**) in 72% isolated yield. The assignment of **10** follows directly from its spectroscopic and analytical data, as well as from an analysis of its elimination products (Scheme 3): **10** reacts with (i) HCl to give exclusively 2-pentanol, and (ii) CO (1 atm) to give δ-caprolactone as the sole organic product. As with the parent oxametallacycle **5**, a small amount of the ring closure product 2-methyltetrahydrofuran was obtained upon reaction of **10** with I_2.

The reaction of **9** with N_2O to give **10** has two notable features. First, the reaction conditions represent a significantly reduced reaction time at a significantly lower temperature than those for the unsubstituted metallacycle (20°C, 22 h *vs* 55°C, 48 h). Second, the O-atom insertion occurs *regioselectively* at the more highly substituted Ni—C bond.



Scheme 3.



Scheme 4.

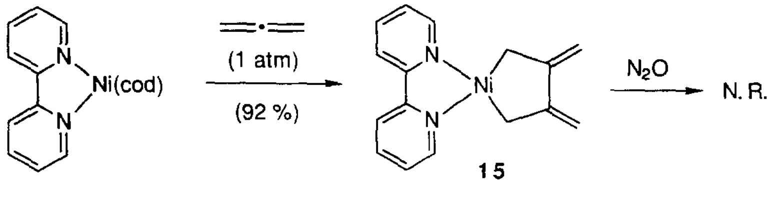
These observations might reflect steric weakening of the Ni—C bond at the α-substituted site, making this position more susceptible to the insertion reaction. The overall reaction sequence of **9** with N_2O and CO to produce the substituted lactone demonstrates the same regiochemical preference as is observed in the Baeyer–Villager oxidation of aldehydes or ketones to form esters.[23] Moreover, $(PR_3)_2Ni$ complexes containing both alkyl and aryl ligands have been recently found to display similar Baeyer–Villager selectivity by preferentially producing the aryl ester upon sequential reaction with N_2O and CO.[24]

Substitution at the β-carbon positions of the metallacycle does not interfere in its reactivity toward N_2O, as demonstrated for the isomers of the β,β′-dimethylmetallacyclopentane complexes *meso*-(bipy)Ni{$CH_2CH(CH_3)CH(CH_3)CH_2$} (**11**) and *d*, *l*-(bipy)Ni{$CH_2CH(CH_3)CH(CH_3)CH_2$} (**12**). The *meso*- (or *cis*-) and *d,l*-(or *trans*-) isomers **11** and **12** can be made from the *meso*- and *d,l*-diastereomers of 1,4-dibromo-2,3-dimethylbutane,[25] respectively, using standard methodology (*vide supra*). However, because of difficulties in separating the *meso*- and *d,l*-diastereomers of the organic dibromide, **11** was isolated in 92% isomeric purity while **12** was obtained in 75% isomeric purity.

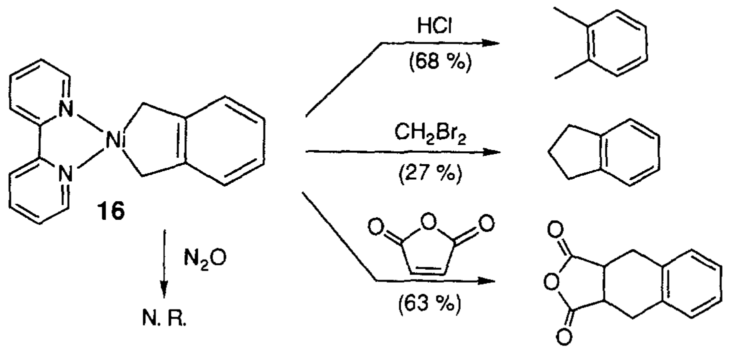
Both **11** and **12** show identical reactivity toward N_2O (55°C, 2 d) to afford the oxametallacycles (bipy)Ni{*cis*-$OCH_2CH(CH_3)CH(CH_3)CH_2$} (**13**) and (bipy)Ni{*trans*-$OCH_2CH(CH_3)CH(CH_3)CH_2$} (**14**), respectively. The robust reaction conditions are similar to those required for the parent metallacycle **5**, and are necessitated because of the absence of substitution at the α-carbon positions. Because of the lower isomeric purities of **12** and **14**, subsequent reactions have only been examined for the isomerically purer (92%) *cis*-dimethyloxametallacycle **13**. As indicated in Scheme 4, **13** undergoes elimination reactions with anhydrous HCl to afford 2,3-dimethyl-1-butanol, with I_2 to give *cis*-3,4-dimethyltetrahydrofuran, and with CO (1 atm) to produce tetrahydro-*cis*-4,5-dimethyl-2*H*-pyran-2-one.

One class of (bipy)Ni metallacyclopentane derivatives shows no reactivity toward N_2O even over extended periods at elevated temperatures: those possessing sp^2-hybridized carbon atoms in the β-positions of the metallacycle. As shown in Scheme 5, the Ni^0 complex (bipy)Ni(cod) reacts with two equivalents of allene to undergo a cyclization reaction, forming the bis(methylene) substituted metallacycle (bipy)Ni{$CH_2C(CH_2)C(CH_2)CH_2$} (**15**); an analogous bis(phosphine) complex of nickel has been previously synthesized by a similar route.[26] Below its decomposition temperature, **15** is unaffected by nitrous oxide.

A metallacycle incorporating an aryl ring in its backbone, (bipy)Ni{$(CH_2)_2C_6H_4$} (**16**), can be prepared by reaction of (bipy)Ni(cod) with α,α′-dibromo-*o*-xylene. Like **15**, **16** is unreactive toward N_2O (see Scheme 6). The absence of reactivity of



Scheme 5.



Scheme 6.

these two complexes with N_2O might be due to an increase in the rigidity of the metallacycles imposed by the presence of the two sp^2-hybridized carbons in the ring. Flexibility in the metallacycle could be critical in allowing distortions required to accommodate the incoming N_2O substrate (perhaps including an intermediate N_2O-coordination complex) prior to O-transfer.[27,28]

Several substrates do react with **16** in transformations that result in elimination chemistry (Scheme 6). Thus, **16** reacts with anhydrous HCl to produce *o*-xylene, and with dibromomethane to generate indan. Interestingly, **16** reacts with an excess of the strained olefin maleic anhydride to effect cycloaddition of the olefin and the dimethylenebenzene fragment to give tetrahydronaphthalene anhydride in good yield.

CONCLUSIONS

Nitrous oxide reacts with both cyclic and acyclic nickel alkyls to produce rare examples of stable nickel alkoxide complexes. Variations in the ligand environment around nickel have a dramatic effect on the reactivity toward N_2O: (i) acyclic dialkyls show both faster reaction rates and lower solution stability than cyclic alkyls, (ii) substitution at the α-position of the metallacycle ring can introduce regioselectivity into the oxygen insertion process, (iii) sp^2-hybridized carbons in the metallacycle backbone shut down the reactivity toward N_2O, and (iv) stereocenters can be introduced into the metallacycle ring to generate organic products containing chiral centers. The oxygen insertion methodology using N_2O has provided a new route to previously inaccessible nickel alkoxide complexes, thus allowing a study of their chemistry. Further work will explore in detail the elimination chemistry of these complexes.

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