Sulfur-Atom Transfer from Elemental Sulfur to Nickel−Carbon Bonds as a New Route to Reactive Nickel(II) Thiolates

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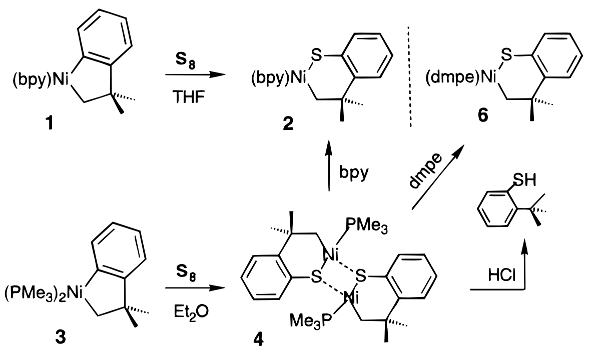
Transition-metal complexes containing thiolate (RS^-) ligands have been widely studied by inorganic chemists, in large part because of the ubiquitous occurrence of S-donor ligands in biologically relevant metal complexes and proteins. The principal synthetic route to these complexes involves metathesis of a thiolate salt with a metal halide or pseudohalide derivative.[1,2] Additionally, thiol and thiolate displacement of neutral ligands (like CO) and oxidative addition of S−S bonds (of disulfides) and S−C bonds (of cyclic thioethers) to lower valent metals comprise a class of viable, but less-generally applicable, synthetic approaches to M−SR moieties.[2,3]

We are especially interested in accessing new routes to thiolate complexes of nickel because such compounds are useful models for intermediates in Ni-mediated biological processes.[4] For example, in the pathway of CO_2 fixation in anaerobic bacteria, nickel is believed to play a key role in the synthesis of acetyl-CoA by the metalloenzyme carbon monoxide dehydrogenase.[5] EPR data indicate that Ni is involved in the binding of CO, which forms the C-1 carbon of acetyl-CoA, and EXAFS data suggest that the Ni atom is four-coordinate with S- and N- (or O-) donor ligands in the coordination sphere. In the course of studying atom- and group-transfer reactions involving the late transition metals, we have successfully effected oxygen-atom transfer from nitrous oxide to nickel alkyls to give simple nickel alkoxides ($Ni{-}R + N_2O \rightarrow N_2 + Ni{-}OR$),[6] and have shown that aryl azides can serve as "NR" sources to transform nickel alkyls into simple nickel amides ($Ni{-}R + N_3R' \rightarrow N_2 + Ni{-}NRR'$).[7] Herein we describe the use of elemental sulfur in the first examples of sulfur-atom-transfer reactions with late-metal carbyls that result in the formation of the corresponding thiolates (e.g., $Ni{-}R + S_8 \rightarrow Ni{-}SR$).[8]

Scheme 1



Solutions of $(bpy)\overline{Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)}$ (**1**; bpy = 2,2′-bipyridine)[9] react stoichiometrically with elemental sulfur (THF, 23 °C, 40 min) to undergo a color change from green to dark purple. Treatment of the solution with cold pentane gives a precipitate which upon recrystallization affords analytically pure dark-purple microcrystals of $(bpy)\overline{Ni(S\text{-}o\text{-}C_6H_4CMe_2CH_2)}$ (**2**) in 43% isolated yield (Scheme 1). Sulfur reacts analogously with the trimethylphosphine nickelacycle $(PMe_3)_2\overline{Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)}$ (**3**)[10] to give dimeric $[(PMe_3)\overline{Ni(S\text{-}o\text{-}C_6H_4CMe_2CH_2)}]_2$ (**4**, 25% yield, Scheme 1). In this latter reaction, $S{=}PMe_3$ and the heterocycle 2,3-dihydro-3,3-dimethylbenzo⟨*b*⟩thiophene, $\overline{S\text{-}o\text{-}C_6H_4CMe_2CH_2}$ (**5**), were isolated as byproducts (vide infra). Dimeric **4** reacts with the chelating ligands bpy and dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) to afford the monomeric complexes **2** and $(dmpe)\overline{Ni(S\text{-}o\text{-}C_6H_4CMe_2CH_2)}$ (**6**), respectively, in high yields (Scheme 1). Complexes **2**, **4**, and **6** were characterized by ^1H and ^{13}C NMR spectroscopies, elemental analyses, and chemical reactivity. The site of S-atom insertion, at the Ni-aryl bond and not at the Ni-alkyl bond,[11] was determined by spectroscopic comparison of **2**, **4**, and **6** with the related oxygenates $(bpy)\overline{Ni(O\text{-}o\text{-}C_6H_4CMe_2CH_2)}$,[6c] $[(PMe_3)\overline{Ni(O\text{-}o\text{-}C_6H_4CMe_2CH_2)}]_2$,[6c] and $(dmpe)\overline{Ni(O\text{-}o\text{-}C_6H_4CMe_2CH_2)}$,[6c] and by the reaction of **4** with HCl to give 2-*tert*-butylbenzenethiol (88% yield). In a related S-atom-transfer reaction, the saturated nickelacyclobutane complex $(bpy)\overline{Ni(CH_2CH_2CH_2CH_2)}$ (**7**)[12] reacts rapidly with sulfur (23 °C, 15 min), but the resulting thianickelacycle is unstable under the reaction conditions with respect to reductive elimination and formation of tetrahydrothiophene (**8**, 30%), as determined by ^1H NMR spectroscopy. Reactions of sulfur with metal−carbon bonds that yield metal−thiolate derivatives are unusual, but have been previously observed in the transformations of $(\eta\text{-}C_5H_5)_2Zr(Me)_2$ to $(\eta\text{-}C_5H_5)_2Zr(SMe)_2$,[13] and $(\eta\text{-}C_5H_5)W(NO)(Me)_2$ to $(\eta\text{-}C_5H_5)W(NO)(SMe)(Me)$ and $(\eta\text{-}C_5H_5)W(NO)(SMe)_2$.[14]

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[11] While the isolated complexes suggest exclusive S-insertion into the Ni-aryl bond, it is possible that S-insertion into the Ni-alkyl bond results in an unstable compound that undergoes spontaneous reductive elimination to give **5**, as observed in the reaction of **7** with S_8 to give **8**.

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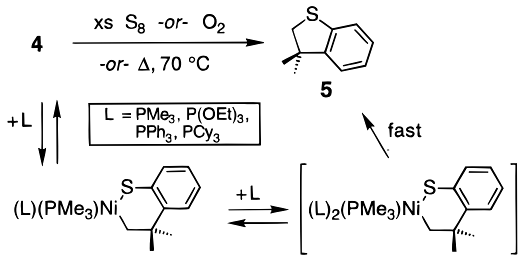
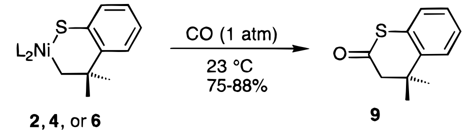
Scheme 2



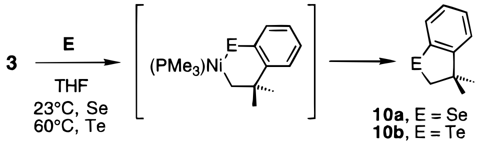
The thiametallacycles (**2**, **4**, **6**) are subject to C,S-reductive elimination reactions under a variety of conditions. As shown in Scheme 2, heating THF solutions of **4** (70 °C, 24 h) results in *thermally*-induced reductive elimination with formation of **5** in 75% isolated yield upon chromatographic workup. Complexes **2** and **6** are more thermally robust, but heating solutions for 24 h at 100 °C also results in formation of **5** in high yields (82% and 75%, respectively). As shown in Scheme 2, an excess of sulfur reacts with THF solutions of **4** at ambient temperature over a 30 min period to give **5** in 77% yield, along with S═PMe$_3$ and NiS (as a black precipitate). This accounts for the relatively low isolated yields of **4** in the reaction of **3** with S$_8$ since sulfur-induced reductive elimination from **4** is competitive with its formation under the reaction conditions (vide supra). In a reaction similar to that observed for the O- and RN- analogues,[6,7,15] oxygen reacts rapidly (23 °C, 10 min) with **4** to trigger *oxidatively*-induced reductive elimination, giving **5** in 86% yield (Scheme 2). Complexes **2** and **6** likewise undergo reaction with O$_2$ (23 °C, 30 min) to give **5** (88% and 86% yields, respectively). The formation of **5** is noteworthy since reductive-elimination reactions that form C−S bonds of thioethers are rare; examples of such reactions with Pd complexes have recently been reported,[16] and are implicated in other systems.[17]

It is appreciated that C,C-reductive elimination from square-planar *cis*-dialkyl Ni(II) complexes is accelerated by coordination of a fifth ligand ("ligand-induced reductive elimination").[18] In this light, we have observed that addition of phosphines (PMe$_3$, PPh$_3$, PCy$_3$) or triethyl phosphite to solutions of **4** at ambient temperature results in significantly accelerated reductive elimination and production of **5** in high yields (see Scheme 2). When PMe$_3$ (2 equiv) is added to solutions of **4**, an intermediate immediately forms for which NMR data are consistent with a four-coordinate monomer, $(\mathrm{PMe_3})_2\overline{\mathrm{Ni(S}\text{-}o\text{-}\mathrm{C_6H_4CMe_2C}}\mathrm{H_2)}$; attempts to isolate the monomer resulted in loss of PMe$_3$ and recovery of **4**. Additional trimethylphosphine gives rise to **5**. In the presence of a 10-fold excess of PMe$_3$, the rate of reductive elimination exhibits a pseudo-first-order dependence on the concentration of the intermediate ($k_{\mathrm{obs}} = 9.0 \times 10^{-4}$ s^{-1}; $t_{1/2} \sim 13$ min; 23 °C). Similar intermediates were also observed in the presence of PPh$_3$, PCy$_3$, and P(OEt)$_3$, with corresponding $t_{1/2}$'s of 300, 30, and 6 min, respectively. Since the four-coordinate monomers **2** and **6** are stable at room temperature and undergo C,S-reductive elimination only at ~100 °C, an associative mechanism involving a five-coordinate intermediate seems likely for this ligand-induced elimination. Addition of PR$_3$ ligands does not show a significant accelerating effect for C,S-elimination from **2** or **6**. In fact, **6** is quite stable at room temperature even in the presence of a large excess of PMe$_3$. However, addition of excess PMe$_3$ to a solution of **2** results in the displacement of bipyridine and generation of $(\mathrm{PMe_3})_2\overline{\mathrm{Ni(S}\text{-}o\text{-}\mathrm{C_6H_4CMe_2C}}\mathrm{H_2)}$ followed by formation of **5**. The lack of influence of added PR$_3$ on C,S-reductive elimination from **2** and **6** (which possess *two* bidentate ligands) might be a consequence of these relatively rigid structures being unable to undergo a requisite pseudorotation (to a TBP structure), as suggested for ligand-induced C,C-reductive elimination from *cis*-(PR$_3$)$_2$NiR$_2$.[19]

Scheme 3



Scheme 4



Reaction of the thiametallacycles **2** or **6** with CO (1 atm, 23 °C) results in the formation of 4,4-dimethylthiochroman-2-one, $\overline{\mathrm{CH_2CMe_2}\text{-}o\text{-}\mathrm{C_6H_4SC}}\mathrm{(O)}$ (**9**), (quantitatively by ^{1}H NMR), which was isolated in high yields (88%) upon chromatographic workup (Scheme 3). Interestingly, dimeric **4** also reacts with CO to give **9** (75% yield), but a significant amount of **5** (13%) was obtained in addition to the carbonylation product, a result of CO-induced C,S-reductive elimination similar to that observed in reactions with PR$_3$. These results serve to further confirm that the formation of thioesters by reductive elimination of thiolate and acyl groups from nickel centers is general.[3a,4a,5c]

Finally, we have observed that elemental selenium and tellurium undergo reactions with **3** to afford excellent yields of the seleno- and telluroheterocycles $\overline{\mathrm{E}\text{-}o\text{-}\mathrm{C_6H_4CMe_2C}}\mathrm{H_2}$ (**10a**, E = Se, 77%; **10b**, E = Te, 74%), but the organometallic selenate and tellurate intermediates were not observed (Scheme 4). Presumably, these reactions proceed by a similar insertion/elimination mechanism as osberved for sulfur (Scheme 1). Such atom-insertion reactions for the heavier chalcogenides have substantial literature precedent in organotransition-metal systems as well as in main-group organometallic systems.[12,20] We are currently exploring the synthetic scope of these S, Se, and Te transfer reactions toward other organonickel(II) complexes.

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Supporting Information Available: Experimental, spectroscopic, and analytical details (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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