Group-Transfer Reactions of Nickel−Carbene and −Nitrene Complexes with Organoazides and Nitrous Oxide that Form New C=N, C=O, and N=N Bonds

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Nitrous oxide (N_2O) and organoazides (N_3R') are energy-rich molecules that undergo a variety of reactions with group 10 transition metal complexes resulting in transfer of an "O" or "NR" moiety to the metal with loss of dinitrogen. Complexes of the type L_2NiR_2 ($L = PMe_3$; L_2 = bipyridine, phenanthroline; R = alkyl, aryl) undergo quite general insertion reactions with nitrous oxide to afford alkoxide or aryloxide products $L_2NiR(OR)$[1] and with organoazides to yield amide derivatives $L_2NiR(NR'R)$ upon N_2 extrusion.[2] Organoazides have also been shown to react directly with unsaturated group 10 metal fragments to give imido complexes like $(Ph_2MeP)_2M=NCF_2CFHCF_3$ (M = Pd, Pt),[3] $[Me_2C_3H\{(2,6-Me_2C_6H_3)N\}_2]Ni=NAd$,[4] and $(dtbpe)Ni=NMes$ (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane).[5] In the course of investigating group-transfer reactions of ligands involved in multiple-bonding to three-coordinate nickel,[6] we encountered facile reactions of nitrous oxide and organoazides with Ni−carbene and −imido complexes that generate new C=N, C=O, and N=N double bonds. Herein we report the results of these studies, including experimental and computational data that give insight into the mechanism of these unusual heteroatom-coupling reactions.

Reaction of cold diethylether solutions of the green diphenyl-carbene complex $(dtbpe)Ni=CPh_2$ (**1**)[7] with 2 equiv of mesitylazide (N_3Mes) or 1-adamantylazide (N_3Ad) results in elimination of N_2 and formal "carbene−nitrene" coupling to give the corresponding ketimines $RN=CPh_2$ (**2a**, R = Mes; **2b**, R = Ad) in 76% and 72% isolated yields, respectively (Scheme 1). The resulting "(dtbpe)Ni⁰" fragment is trapped by a second equivalent of N_3R to give the known organoazide complexes $(dtbpe)Ni(\eta^2-N_3R)$ (**3a**, R = Mes; **3b**, R = Ad) as kinetic products that undergo subsequent thermal N_2 elimination to afford the Ni(II) imido complexes $(dtbpe)Ni=NR$ (**4a**, R = Mes; **4b**, R = Ad) as the ultimate nickel-containing products.[5] Such transition metal mediated carbene−nitrene coupling reactions are unusual, but not unprecedented. Fischer has shown that $(CO)_5M=CPh_2$ reacts with N_3R to give $(CO)_5M(\kappa^1-NR=CPh_2)$ (M = Cr, W),[8] and Grubbs has reported that N_3R reacts with $(N(2-P-i-Pr_2-4-Me-C_6H_3)_2)Ir=CH(O-t-Bu)$ to afford $RN=CH(O-t-Bu)$ and $(N(2-P-i-Pr_2-4-Me-C_6H_3)_2)Ir(N_2)$.[9] A novel *intramolecular* imido−carbene coupling reaction has been observed by Meyer in a (trisNHC)Co=NR complex (NHC = *N*-heterocyclic carbene).[10]

A kinetic study of the reaction of **1** with N_3Ad was carried out to gain mechanistic insight into ketimine (**2b**) formation. (The reaction of N_3Mes with **1** was too fast to conveniently be monitored by NMR, even at low temperature.) Disappearance of **1** and formation of **2b** were followed by ¹H NMR spectroscopy over a temperature range of 35−65 °C (C_7D_8 solution). The reaction is

Scheme 1
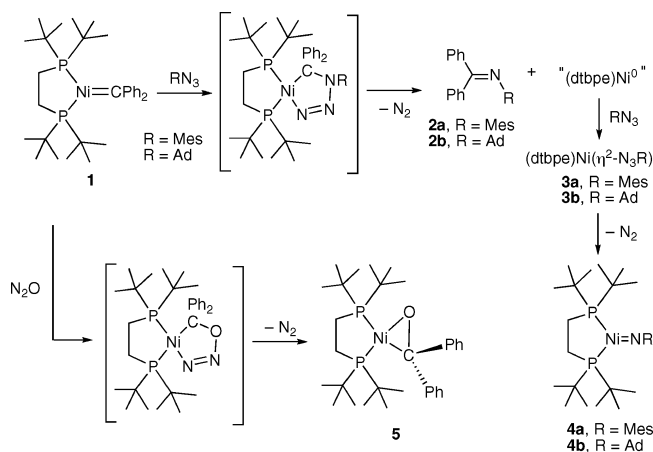
first-order in both [**1**] and [N_3Ad] with a second-order rate constant of 1.7×10^{-3} (± 0.2) M^{-1} s^{-1} at 35 °C. No intermediates were observed when the reaction was followed by ³¹P or ¹H NMR. An Eyring analysis of the kinetic data reveals the reaction to have a small activation enthalpy ($\Delta H^{\ddagger} = 8$ (± 1) kcal/mol) and a large activation entropy ($\Delta S^{\ddagger} = -44$ (± 3) cal/(mol·K)), suggestive of a highly ordered transition state.

Net "carbene−oxygen" coupling with formation of the red benzophenone adduct $(dtbpe)Ni(\eta^2-OCPh_2)$ (**5**; 65% isolated yield) occurs upon addition of a controlled excess (∼2 equiv) of nitrous oxide to a −78 °C toluene solution of **1**, followed by slow warming to ambient temperature (Scheme 1). Complex **5** was characterized by comparison to an authentic sample prepared by literature methods.[11] The reaction conditions were optimized for the production of **5**, and use of a larger excess of N_2O in the reaction results in oxidation of the dtbpe ligand, formation of free benzophenone, and precipitation of Ni(0).

Treatment of ether solutions of the imido complex **4a** with 2 equiv of N_3Mes results in formal "nitrene−nitrene" coupling to give 1,2-dimesityldiazene (**6a**, MesN=NMes; 78% yield) along with **4a**. **4b** reacts similarly with N_3Ad to afford 1,2-bis(1-adamantyl)-diazene (**6b**, AdN=NAd; 64% yield) and **4b** (Scheme 2). **4a** reacts with N_3Ad to give the mixed diazene MesN=NAd (**6c**), demonstrating that the diazenes do not form by bimolecular decomposition of **4a,b** under these conditions. Azo-coupling is not catalytic with excess N_3R because the diazene products compete with N_3R as Ni(0) traps. Reaction of the Ni(0) benzene complex $\{(dtbpe)Ni\}_2(C_6H_6)$[12] with **6a** gives $(dtbpe)Ni(MesN=NMes)$ (**7**) in high yield. The diazene products **6a−c** are unusual in that 1,4-tetrazenes are the usual organoazide coupling products with transition metal imides,[13] exemplified by the reactions of N_3R

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Scheme 2
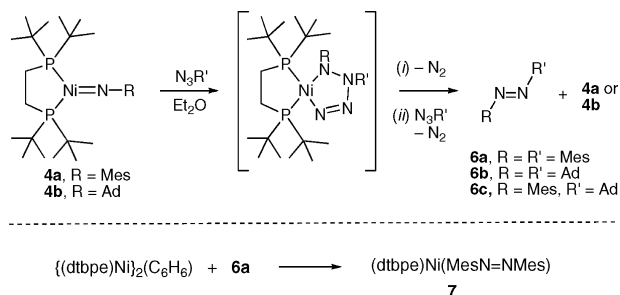
with Cp$_2$Zr(=N-t-Bu)(THF) to form Cp$_2$Zr(κ^2-RN$_4$-t-Bu) or (cymene)Os=N-t-Bu to yield (cymene)Os(κ^2-RN$_4$-t-Bu).[14]

B3LYP/6-311+G(d) computations were carried out to explore the notion that the reactions of **1** and **4** with N$_3$R and N$_2$O, classic 1,3-dipolar reagents, proceeded by a cycloaddition pathway with five-membered ring (i.e., Huisgen) intermediates. A summary of the calculated results based on the model complexes (dhpe)Ni=E (E = CH$_2$, NMe) with N$_2$X (dhpe = 1,2-bis(dihydridophosphino)-ethane; X = O, NMe) is shown in Figure 1 and provides a consistent picture for all three reactions modeled. The reactions proceed via initial 1,3-dipolar cycloaddition of (dhpe)Ni=E with N$_2$X to give a five-membered transition state (Figure 2), which is evocative of transition states calculated by Houk et al. for organic 1,3-dipolar cycloadditions.[15] Enthalpic barriers for 1,3-dipolar cycloadditions are reasonable and consistent with the exothermicity of the reactions to form Huisgen intermediates.
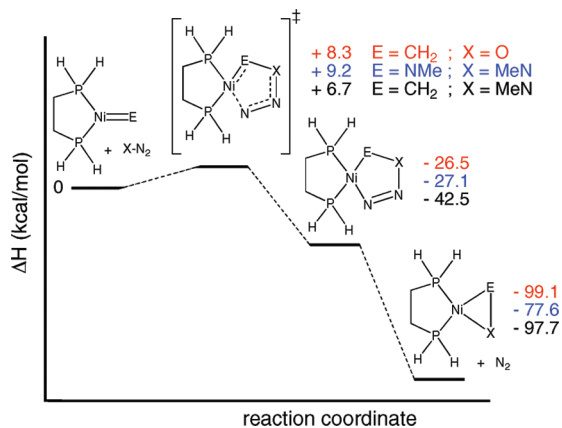

Figure 1. B3LYP/6-311+G(d)-calculated enthalpies (1 atm, 298.15 K) for model 1,3-dipolar cycloaddition mechanisms.
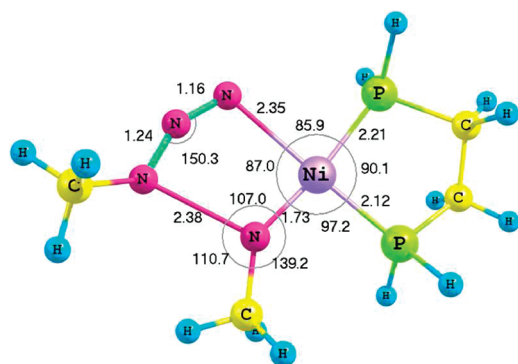

Figure 2. Calculated transition state for the 1,3-dipolar cycloaddition of N$_3$Me to (dhpe)Ni=NMe in forming a 1,2-tetrazene intermediate.

Transition state geometries for [(dhpe)Ni=NMe + N$_3$Me] and [N$_2$O + (dhpe)Ni=CH$_2$] are planar at Ni, while that for [N$_3$Me + (dhpe)Ni=CH$_2$] is tetrahedrally distorted. Calculated activation parameters for the reaction of (dhpe)Ni=CH$_2$ + N$_3$Me are $\Delta H^{\ddagger} = +6.7$ kcal/mol and $\Delta S^{\ddagger} = -40.7$ cal/(mol·K), giving a $\Delta G^{\ddagger}$ of +18.8 kcal/mol (at 298.15 K). These values compare well with the experimentally obtained values ($\Delta H^{\ddagger} = 8$ (±1) kcal/mol; $\Delta S^{\ddagger} = -44$ (±3) cal/(mol·K)) for the reaction of **1** with N$_3$Ad. No evidence for a precursor adduct between (dtbpe)Ni=E and N$_2$X was found, so the calculated barriers are relative to separated reactants. The transition state structures collapsed to stable Huisgen intermediates, but these were considerably higher in energy than the eventual products, which result after N$_2$ elimination to give (dtbpe)Ni(η^2-EX). Experimentally, in the reaction of **1** with N$_2$O this is the observed product (i.e., **5**), but the reactions of **1** and **4a,b** with N$_3$R give imido complexes in which a second equivalent of N$_3$R replaces the bulky E=X ligand and N$_2$ is extruded.

In summary, we have shown that the nickel carbene complex **1** and the imido complexes **4a** and **4b** readily react with N$_2$X substrates via net "CR$_2$", "NR", or "O" transfer to form multiply bonded organic products. Experimental, kinetic, and computational results all support a mechanism involving 1,3-dipolar cycloaddition of N$_2$X to (dtbpe)Ni=CPh$_2$ or (dtbpe)Ni=NR to give five-membered Huisgen-type intermediates. Product formation results on elimination of N$_2$.

Supporting Information Available: Experimental and computational procedures with characterization data and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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