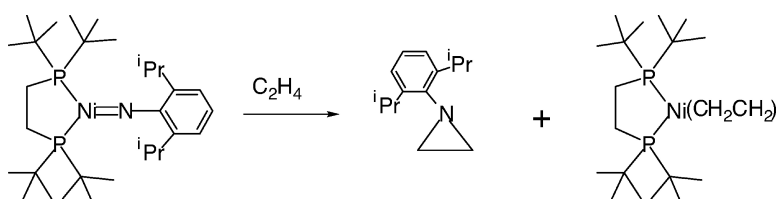## Communication

Group Transfer from Nickel Imido, Phosphinidene, and Carbene Complexes to Ethylene with Formation of Aziridine, Phosphirane, and Cyclopropane Products

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Group Transfer from Nickel Imido, Phosphinidene, and Carbene Complexes to Ethylene with Formation of Aziridine, Phosphirane, and Cyclopropane Products

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Formation of carbon−carbon and carbon−heteroatom bonds is a fundamental objective in synthetic chemistry.[1] Toward this end, we have had a longstanding interest in atom- and group-transfer reactions as a route to carbon−heteroatom bond formation.[2] Our recent preparations of stable imido ((dtbpe)Ni=NAr, **1**),[3] phosphinidene ((dtbpe)Ni=P(dmp), **2**),[4] and carbene ((dtbpe)Ni=CPh$_2$, **3**)[5] complexes (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane, Ar = 2,6-di-isopropylphenyl, dmp = 2,6-dimesitylphenyl) have allowed the reactivity of late-transition-metal multiply bonded complexes to be assessed. Late-transition-series elements are active catalysts in synthetically important reactions such as aziridination[6] and cyclopropanation,[7] where imido[6b] and carbene[7] complexes are often postulated as key intermediates. Herein, we report the stoichiometric transfer of the nitrene, phosphinidene, and carbene fragments from complexes **1**−**3** to ethylene with formation of the corresponding three-membered aziridine, phosphirane, and cyclopropane rings.

Treating toluene solutions of **1** with ethylene (1 atm, 70 °C, 8 days) forms (dtbpe)Ni(CH$_2$CH$_2$) (**4**)[9] and 2,6-di-isopropylphenylaziridine (**5**) in 58% isolated yield (eq 1).[8] This is, to the best of our knowledge, the first example of an isolated imido complex undergoing aziridination, although Groves has reported stoichiometric aziridination of cyclo-octene with a Mn-imdo generated in situ.[10] No intermediates are observed when the reaction is monitored by NMR spectroscopy (¹H, ³¹P; C$_6$D$_6$). Under the reaction conditions, **1** partially decomposes to insoluble nickel-containing products, free dtbpe, and paramagnetic (dtbpe)Ni(NHAr) as observed by ¹H and ³¹P NMR spectroscopy.[3] The identity of **5** was confirmed by an independent synthesis adapted from literature routes to aryl aziridines.[8]
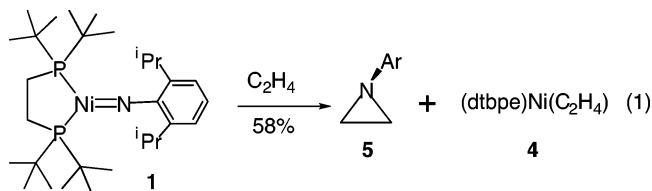

Initial [2+2] cycloaddition to afford a nickel(II) azametallacyclobutane intermediate which then undergoes thermal or ligand-induced reductive elimination to give **5** is a reasonable mechanism for the nitrene-group transfer in eq 1. The related Ni(II) azametallacyclobutane complexes (2,2′-bipyridine)Ni(NTsCHRCH$_2$) are known to undergo oxidatively induced reductive elimination (to form tosyl aziridines) on exposure to O$_2$.[11] Complex **1** reacts with *trans*-ethylene-d_2 to give the dideuterio aziridine (**5-d_2**) having exclusively anti geometry ($^3J_{HH}$ = 3.6 Hz, eq 2, single enantiomer of **5-d_2** shown for clarity) as determined by ¹H NMR.[8] The net retention of stereochemistry in this reaction is consistent with copper-catalyzed olefin aziridinations.[6] Interestingly, the oxidatively

induced reductive elimination from (2,2′-bipyridine)Ni(NTsCHRCH$_2$) has been shown to proceed with inversion of relative stereochemistry at the methylene carbon.[11]
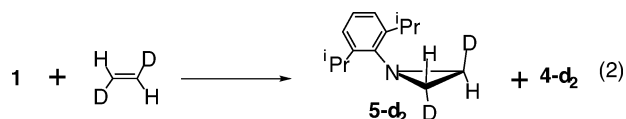

The phosphinidene complex **2** reacts rapidly with ethylene at ambient temperature over the course of 1 h to give 2,6-dimesitylphenylphosphirane (**7**) and **4** (eq 3).[8] The reaction appears to proceed quantitatively as determined by ¹H NMR (**7** exhibits a distinctive AA′BB′X pattern for its methylene resonances centered at δ 0.46), but due to its high solubility, **7** was isolated in 73% yield.[12] If the reaction is monitored by ¹H and ³¹P NMR at low temperature (−28 °C, C$_7$D$_8$), an intermediate consistent with the [2+2] cycloadduct (dtbpe)Ni{*P,C*:CH$_2$CH$_2$P(dmp)} (**6**) is observed. The unique phosphorus of **6** resonates as a doublet-of-doublets at δ −42 (³¹P{¹H}), similar to other four-membered cycloadducts of **2**.[8,13] In the ¹H NMR spectrum, the two methylene groups of the
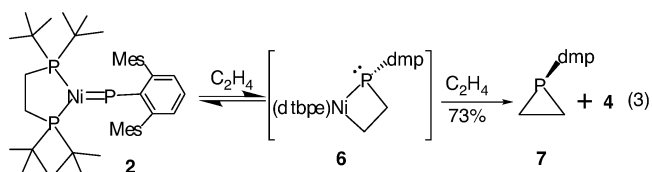
metallacycle resonate as complex multiplets at δ 1.37 and 1.21. There are multiple *tert*-butyl resonances for the dtbpe ligand supporting an asymmetric complex, but a complete assignment of the ¹H spectrum of **6** was hampered by overlap with resonances of **2** and **4**. Reaction of **2** with less than 2 equiv of ethylene leads to initial formation of **6**, but upon equilibration only a mixture of **2**, **4**, and **7** is observed (eq 3). Despite variation of ethylene concentration and temperature, steady-state concentrations of **6** were always low relative to the concentration of **2** and final products. Phosphinidene group transfer has been a synthetically valuable tool in organophosphorus chemistry, yet isolated metal phosphinidene complexes have not previously been shown to provide phosphiranes in reactions with olefins.[14]

Reaction of **2** with *trans*-ethylene-d_2 gives **7-d_2** in 70% isolated yield (eq 4, single enantiomer of **7-d_2** shown for clarity). In the ¹H
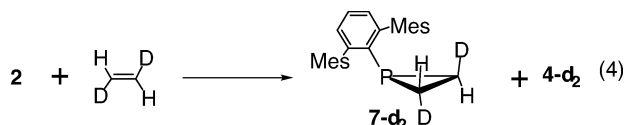
NMR spectrum of **7-d_2**, only anti disposed phosphirane (³J_{HH} =

8.2 Hz) is observed. One simple conclusion, based on the exclusively anti heterocycles in the reaction of both **1** and **2** with ethylene, is that these reactions proceed by the same mechanism involving [2+2] cycloaddition and reductive elimination. Such a mechanism would differ from the [1+2] additions of olefins to transient, electrophilic phosphinidene species.[14]

Heating toluene solutions of the diphenyl carbene complex **3** under an atmosphere of ethylene (110 °C, 5 d) provides 1,1-diphenylcyclopropane (**8**) in 85% isolated yield (eq 5).[8] When the reaction is monitored by NMR (C_6D_6), no intermediate complexes are detected, formation of **4** is quantitative, and no decomposition products are observed. Recently, preparation of **8** using a rhodium carbene complex ((dtbpe)Rh(Cl)=CPh$_2$) has been reported.[15] For rhodium, **8** was isolated in high yield with minor amounts of both 1,1- and 3,3-diphenylpropene. No constitutional isomers were observed in the reaction of **3** with ethylene as determined by NMR (^{1}H, ^{13}C) and GC/MS. Stoichiometric transformation of olefins to cyclopropanes by carbene complexes is relatively common among early transition metals and iron,[7c] and several isolated carbene complexes of Ru[16] and Os[17] are effective cyclopropanation catalysts.[18] When toluene solutions of N_2CPh_2 with 10 mol % of **3** are heated under ethylene, **8** can be isolated in 41% yield (TON = 4.1).[8] Nickel(0) compounds are known to catalyze cyclopropanation of olefins with diazoalkanes.[19]
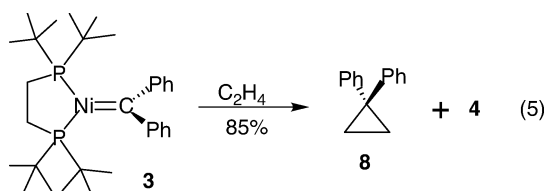
Because the methylene protons of **8** are equivalent, no stereochemical information regarding the cyclopropanation of ethylene can be gleaned from the reaction of **3** with ethylene-d_2. However, it is noteworthy that we have recently prepared simple metallacyclobutane complexes of the type (dtbpe)Ni(CH$_2$CR$_2$CH$_2$) by independent methods, and upon heating they cleanly undergo reductive elimination to give the corresponding cyclopropanes.[20] This suggests that [2+2] cycloaddition is also a mechanistically viable route for the cyclopropanation reaction shown in eq 5. A [2+2] cycloaddition of olefin to a transient carbene has been proposed by Grubbs and co-workers to account for cyclopropanes observed in the decomposition of nickel metallacycles.[21]

In summary, isolated imido (**1**), phosphinidene (**2**), and carbene (**3**) complexes of nickel undergo group transfer to ethylene forming the respective three-membered-ring compounds. For the imido and phosphinidene complexes, these appear to be the first examples of isolated species undergoing this type of group transfer. Both **1** and **2** react with *trans*-ethylene-d_2 to give aziridine **5-d_2** and phosphirane **7-d_2** in which the trans stereochemistry of the olefin is preserved. This suggests that if these reactions proceed via [2+2] cycloaddition intermediates, then the reductive elimination event proceeds with retention of stereochemistry. The nickel carbene complex **3** not only performs clean stoichiometric cyclopropanation, but it is also mildly catalytically competent. This chemistry complements our initial

studies of group-transfer reactions of compounds **1**,[22] **2**,[13] and **3**[5] to carbon monoxide. We are currently exploring the scope and mechanism of these reactions as well as their potential for catalytic chemistry.

Supporting Information Available: Experimental and spectroscopic details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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