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NICKEL(0)-MEDIATED HYDROCYANATION AND CARBONYLATION REACTIONS OF ALKYNES WITH TRIMETHYLSILYL(ISO)CYANIDE[1]

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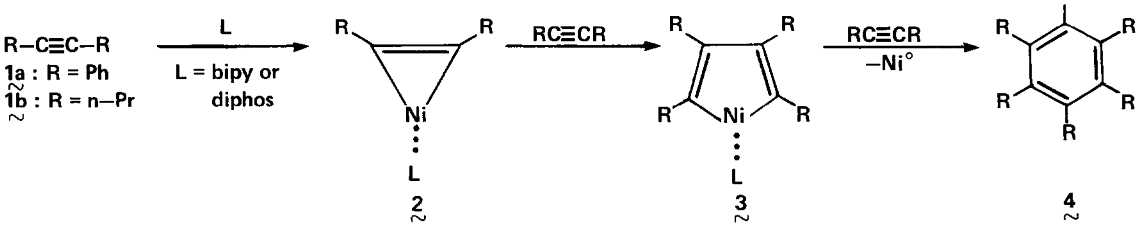
Abstract: Under nickel(0) mediation, trimethylsilyl(iso)cyanide serves as both a useful *syn*-hydrocyanating agent and a carbonylating agent for alkynes.

Metallacyclopentadienes have often been proposed as essential intermediates in the cyclotrimerization of alkynes into benzene derivatives.[2] Specifically in the case of nickel(0) catalysts, substantial evidence has been adduced for the stepwise formation of nickelacyclopropene,[3] nickelacyclopentadiene[4-8] and, in a special case, even nickelacycloheptatriene[7,8] intermediates in the oligomerization of alkynes (Scheme I). We now wish to report that the stepwise interaction of an alkyne with nickel(0) complexes can both be observed and controlled by employing strong chelating ligands, such as 2,2'-bipyridyl and bis(1,2-diphenylphosphino) ethane.[3,9,10] Furthermore, by utilizing reagents, such as trimethylsilyl(iso)cyanide and electrophilic alkynes, transient organonickel intermediates can be trapped in a manner advantageous for the novel synthesis of carbocycles and substituted olefins.

Scheme I



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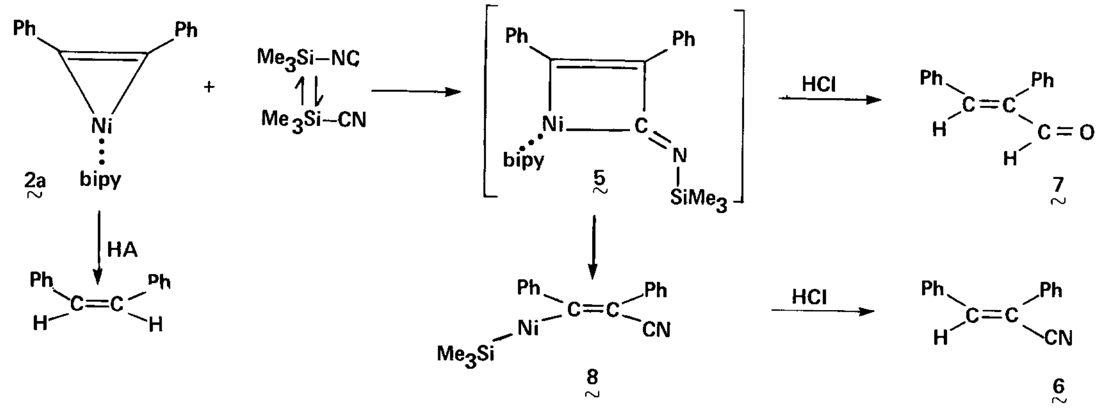
Thus, the interaction of diphenylacetylene (1a, R = Ph) with bis(1,5-cyclooctadiene)nickel(0) either in THF with 2,2'-bipyridyl or in toluene with bis(1,2-diphenylphosphino)ethane, gave 1:1:1 complexes of 1, Ni(0) and the ligand (2, R = Ph, L = bipy or diphos).[11] Protolysis of either complex with 85% H_3PO_4 or 12N-HCl gave >90% of cis-stilbene. Moreover, intermediate 2a could be chemically diverted by treatment with trimethylsilyl(iso)cyanide to yield products indicative of the formation of the nickelacyclobutenimine intermediate 5. Thus, the interaction of 2a with two equivalents of $Me_3Si(CN)$ in THF solution for 24 h at 25°C and work-up with 6N-HCl gave a 70% yield of nitrile 6[12] and 15% of aldehyde 7[13] (Scheme II). Ring opening of intermediate 5 before hydrolysis would produce 8,[14] whose protodenickelation would yield nitrile 6.

The formation of intermediate 5 is facilitated by the ready interconversion of $Me_3Si\text{-}CN$ and $Me_3Si\text{-}NC$.[15] Since isocyanides are isoelectronic with carbon monoxide, they can form an extensive array of complexes with transition metals. Indeed, $Me_3Si(CN)$ has been found to complex selectively with iron(0) compounds in its isocyanide form.[16]

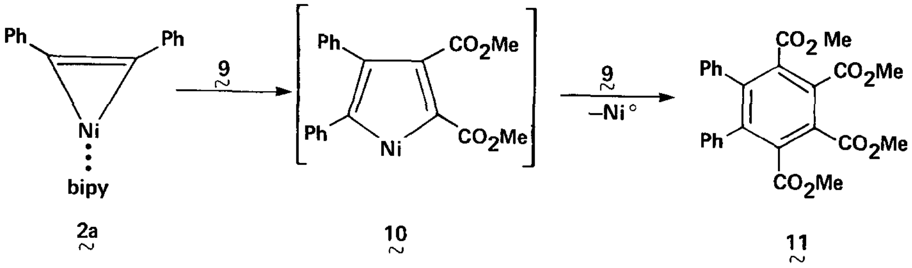
Scheme II



Alternatively, complex 2a could be heated in refluxing THF with two equivalents of $MeO_2CC{\equiv}CCO_2Me$ (9) and the transitory nickelole 10 trapped as 1,2,3,4-tetrakis(methoxycarbonyl)-5,6-diphenylbenzene 11.[17] The nickel(0) released by the formation of 10 cyclotrimerized some of 9 (Scheme III).

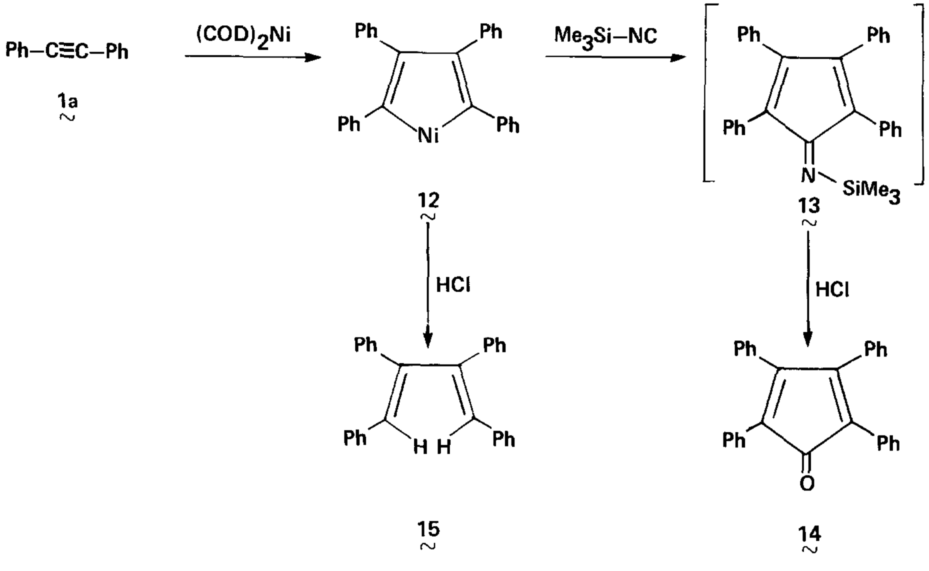
Finally, in the absence of strong donor ligands, nickel(0) complexes react with two or three alkyne units to yield butadienes or cyclotrimeric benzene derivatives.[4,5] When such interactions were conducted with trapping agents, nickelole intermediates could be diverted to yield useful products. Thus, the heating of bis(1,5-cyclooctadiene)nickel(0) with two equivalents each of 1a and $Me_3Si(CN)$ in refluxing THF and subsequent hydrolysis with 6N-HCl gave more than a 50% yield of tetracyclone (14) and small amounts of diene 15

Scheme III



and the cyclotrimer of **1a**. Formation of these products points to the formation of nickelole **12** and its efficient trapping as cyclopentadienimine **13** (Scheme IV).

Scheme IV



Reactions analogous to those depicted in Schemes I-IV have been also observed for dialkylacetylenes, such as 4-octyne. It is worthy of note that the reaction pathway depicted in Scheme I may be entered at alternative points: $(C_8H_{12})_2Ni$ reacts either with diphenylcyclopropenone by decarbonylation or with tetraphenyl-α-pyrone by decarboxylation to generate reactive intermediates **2a** and **12**, respectively.

In summary, the present work demonstrates that trimethylsilylisocyanide can insert readily into nickel-carbon bonds, in a reaction analogous to that of carbon monoxide. The facile rearrangement (**5** → **8**) and hydrolysis of the resulting N-trimethylsilylketimines (**5** and **13**) permit such Me_3SiNC-insertion reactions to serve as convenient alternatives to hydrocyanation and carbonylation reactions, respectively, for the synthesis of olefinic and carbonyl compounds. Unlike HCN and CO reactions, insertion reactions with liquid Me_3SiNC do not require manipulating gases under pressure.

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(11) Satisfactory elemental analyses were obtained for **2a**, **6**, **7** and **11**; mp comparison and appropriate spectral data were used to identify known compounds.

(12) Spectral data for **6**: ^1H NMR ($CDCl_3$) δ 7.17 (*s*, 5H), 7.30 (*s*, 6H); IR (neat) 2210, 1600, 1490, 1445 and 770 cm^{-1}.

(13) Spectral data for **7**, mp 92-94°C: ^1H NMR ($CDCl_3$) δ 7.20 (*s*, 7H), 7.32 (*m*, 4H), 9.62 (s, 1H); IR (Nujol) 1665, 1628 and 1600 cm^{-1}.

(14) In the absence of 2,2'-bipyridyl, **2a** reacts with Me_3SiNC at 25°C to yield 12% of E- and Z-1,2-diphenyl-2-cyanoethenyl(trimethyl)silane in ∿1:1 ratio, in addition to the usual products. These indicate the occurrence of some reductive elimination of Ni° from **8**.

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(17) Spectral data for **11**, mp 221-222°C: ^1H NMR ($CDCl_3$) δ 3.42 (*s*, 12H), 7.03 (*s*, 10H); IR (Nujol) 3090 (*w*), 1725 (*s*), 1460 (*s*), 1380 (m).

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