ments. Finally, we wish to thank Mr. J. R. Parrish, Jr., for his interest and for helpful criticisms of this work. We acknowledge with thanks the financial support provided by the National Institutes of Health in the form of a predoctoral fellowship to D. L. C. and by U. S. Public Health Service Grant No. AM07300 to E. R. B.

Communications to the Editor

The Course of Allylic Coupling Reactions Involving Allylnickel Complexes

Sir:

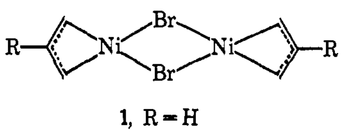
The reaction of π-allylnickel(I) halide complexes with a wide variety of organic halides to form *cross-coupling* products selectively has recently been reported.[1] We describe herein the sharply contrasting and relatively complex behavior of *allylic halides* toward π-allylnickel complexes and its relevance to the intermolecular[2] and intramolecular[3-5] coupling of allylic halides by nickel carbonyl.

Although solutions of pure[1] π-allylnickel(I) bromide (**1**) (blood red in color) in tetrahydrofuran or glyme solvents are *stable*[6] at least for several days at 25°, the addition of allyl bromide (2 moles/mole of **1**) at 25° results in quantitative formation of biallyl within a few minutes.[7] That this latter reaction is not a simple cross-coupling process is indicated by the fact that treatment of the allyl complex **1** with *methallyl* bromide (2 moles/mole of **1**) in tetraglyme leads in high yield (>95%) to a *mixture* of all three possible coupling products, biallyl (35%), allylmethallyl (25%), and bimethallyl (40%); similarly, reaction of the methallyl complex **2** with allyl bromide produces (>95%) a *mixture* of biallyl (22%), allylmethallyl (53%), and bimethallyl (25%).[8] Nonspecific coupling also results when allylic iodides, chlorides, or tosylates are substituted for bromides in these reactions or with dimethylformamide as solvent. A major reason for this nonspecificity is the occurrence of a rapid exchange reaction according to eq 1 (A = allyl) under normal coupling conditions. Experimentally the exchange can be demonstrated by slow addition (by motor-driven syringe) of the complex **1** (1 mmole) in dimethylformamide to methallyl bromide (30 mmoles) in the same solvent at 22°; this affords a mixture of the expected hydrocarbon coupling products (0.32 mmole of C_6, 0.8 mmole of C_7, and 0.8 mmole of C_8) and, *in addition, allyl bromide* (0.68 mmole), with excess methallyl bromide remaining unchanged. A strictly analogous experiment in which complex **2** was added to allyl bromide afforded a mixture of the expected hydrocarbon coupling products (1.36 mmoles of C_6, 0.6 mmole of C_7, and 0.04 mmole of C_8) and *methallyl bromide* (1.2 mmoles), as well as unchanged allyl bromide. The rapid exchange described by eq 1 can even be demonstrated in toluene as solvent under conditions where the coupling reaction is very slow.[7] Ten minutes after mixing 1 mole of **2** with 2 moles of allyl bromide in toluene at 25°, methallyl bromide was formed in substantial amount (allyl: methallyl bromide = 2.3 by vpc analysis).

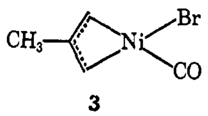
$$[\pi\text{-A}^1\text{NiBr}]_2 + \text{A}^2\text{Br} \rightleftharpoons [\pi\text{-A}^2\text{NiBr}]_2 + \text{A}^1\text{Br} \qquad (1)$$

It has also been possible to show that the reaction between allylic halides and nickel carbonyl to form π-allylnickel(I) complexes is *easily reversible* and that this is a factor of considerable importance in the allylic coupling reaction with nickel carbonyl. Introduction of carbon monoxide to a mixture of π-methallylnickel(I) bromide and methallyl bromide in tetrahydrofuran results in a substantial acceleration of allylic coupling to bimethallyl. Indeed, carbon monoxide causes the conversion of π-methallylnickel(I) bromide in tetrahydrofuran solution to bimethallyl even in the *absence* of methallyl bromide, according to eq 2. Toluene solutions of π-methallylnickel(I) bromide rapidly absorb one molecule of carbon monoxide per nickel atom to form complex **3**,[9] which reacts with additional carbon monoxide more slowly to give (among other products) methallyl bromide and nickel carbonyl. In addition, when reaction 2 is carried out under coupling conditions at 0° in tetraglyme in the presence of carbon monoxide

$$[\pi\text{-MeANiBr}]_2 + 4\text{CO} \longrightarrow (\text{MeA})_2 + \text{Ni(CO)}_4 + \text{NiBr}_2 \qquad (2)$$



1, R = H
2, R = CH_3



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[1] E. J. Corey and M. F. Semmelhack, *J. Am. Chem. Soc.*, **89**, 2755 (1967). See also E. J. Corey and G. H. Posner, *ibid.*, **89**, 3911 (1967), for another cross-coupling method.

[2] See (a) Belgian Patent 448,844 (I. G. Farbenind) (1943); *Chem. Abstr.*, **41**, 6576 (1947); (b) I. D. Webb and G. T. Borcherdt, *J. Am. Chem. Soc.*, 73, 2654 (1951).

[3] E. J. Corey and E. Hamanaka, *ibid.*, **86**, 1641 (1964); **89**, 2758 (1967).

[4] E. J. Corey and E. K. W. Wat, *ibid.*, **89**, 2757 (1967).

[5] E. J. Corey and M. F. Semmelhack, *Tetrahedron Letters*, 6237 (1966).

[6] All transformations with organonickel compounds were conducted under an argon atmosphere with rigorous exclusion of oxygen.

[7] The rate of formation of π-allylnickel(I) complexes such as 1 from allylic halides and nickel carbonyl is not nearly as sensitive to solvent change as is the coupling reaction. For example, at 50° in benzene formation of complex 1, though slower than in tetrahydrofuran or glyme solvents, is complete in a few hours; however, the extent of coupling reaction of 1 with allyl bromide is only slight under these conditions. For this reason the preparation of complexes such as 1 is best carried out with hydrocarbon solvents.

[8] Product analyses were performed by vapor phase chromatography (vpc) using columns containing LAC 446 or 728 on Chromosorb P at 75–100° with an F&M Model 609 or 810 unit with flame-ionization detector. Toluene was used as a standard; reproducibility of these results was ±3%.

[9] Complex **3** has been obtained only in solution, since attempted isolation results in loss of carbon monoxide with formation of π-methallylnickel(I) bromide (**2**). Solutions of **3** in benzene exhibit infrared absorption due to carbonyl at 4.80 and 4.88 μ and nmr singlet peaks at 1.48 (downfield from internal tetramethylsilane) (3 H), 2.35 (2 H), and 3.65 ppm (2 H); they do not show the nmr peaks characteristic of **2** at 1.37, 1.60, and 2.37 ppm (ratio, 2:3:2).

(1 atm), the intermediate formation of methallyl bromide can be demonstrated by vpc analysis concurrent with reaction (*e.g.*, after 40 min at 0° with 0.14 *M* **2**, the observed ratio of bimethallyl to methallyl bromide was 1.5; eventually, the latter disappeared and only coupling product remained). A simple explanation is thus available for the fact that in the reaction of allylic halides with excess nickel carbonyl in ether-type solvents, the allylic halide is rapidly converted to red nickel(I) complex which gives coupling product relatively slowly; clearly, the presence of carbon monoxide causes both the regeneration of allylic halide and the formation of coupling product from the intermediate(s).

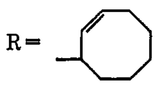
The accompanying communication[10] presents evidence for the occurrence of equilibria 3 and 4 between π-allylnickel(0) and π-allylnickel(I) complexes. The intermediacy of zero-valent complexes in the coupling of allylic halides by nickel carbonyl must therefore be considered, since it is known that bis(π-allyl)nickel and certain other members of this class are converted to hydrocarbon coupling products by treatment with carbon monoxide. Evidence against the nickel(0) pathway for the coupling of allylic halides by nickel carbonyl for the case of 2-cyclooctenyl bromide has been obtained from the observation that this reaction (*e.g.*, in dimethylformamide at 20–50°) affords >99% of bis(2-cyclooctenyl) (**4**) and no detectable bis(2-cyclooctenyl) ketone (**5**), whereas the reaction of bis(π-cyclooctenyl)nickel(0)[10,11] with carbon monoxide alone or with added nickel carbonyl and/or nickel bromide under the same conditions gives a 1 : 1 mixture of hydrocarbons **4** and ketones **5**. In common with the reaction of 2-cyclooctenyl bromide with nickel carbonyl, π-2-cyclooctenylnickel(I) bromide in dimethylformamide affords only hydrocarbon coupling product **4** in >99% yield (1) by reaction with 2-cyclooctenyl bromide, (2) by reaction with 2-cyclooctenyl bromide in the presence of carbon monoxide (1 atm) catalyst, or (3) by reaction with carbon monoxide alone. The formation of the ketones **5** from bis(π-cyclooctenyl)nickel and their absence in the other coupling reactions provide strong evidence that the reaction of nickel carbonyl with 2-cyclooctenyl bromide to form **4** proceeds *via* nickel(I) complexes. To the extent that the behavior of the 2-cyclooctenyl system may be general, it would seem that the most important pathway for the coupling of allylic halides by nickel carbonyl involves nickel(I) rather than nickel(0) intermediates in the coupling step.

$$[\pi\text{-ANiBr}]_2 \rightleftharpoons [\pi\text{-A}]_2\text{Ni} + \text{NiBr}_2 \qquad (3)$$

$$[\pi\text{-A}^1]_2\text{Ni} + [\pi\text{-A}^2\text{NiBr}]_2 \rightleftharpoons [\pi\text{-A}^2]_2\text{Ni} + [\pi\text{-A}^1\text{NiBr}]_2 \qquad (4)$$

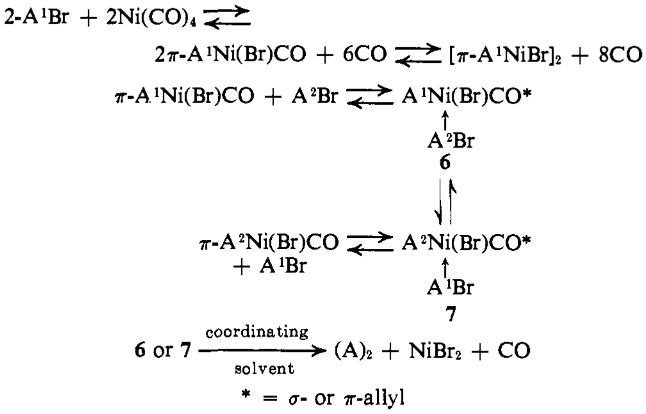
R–R RCOR

4, *meso* + *dl* **5**, *meso* + *dl*



Scheme I, together with eq 1–4, accommodates all the information currently available on the various exchange and coupling processes which are involved in the reaction of allylic halides with nickel carbonyl.[12–14]

Scheme I



$$2\text{-A}^1\text{Br} + 2\text{Ni(CO)}_4 \rightleftharpoons 2\pi\text{-A}^1\text{Ni(Br)CO} + 6\text{CO} \rightleftharpoons [\pi\text{-A}^1\text{NiBr}]_2 + 8\text{CO}$$

$$\pi\text{-A}^1\text{Ni(Br)CO} + \text{A}^2\text{Br} \rightleftharpoons \underset{\mathbf{6}}{\underset{\text{A}^2\text{Br}}{\overset{\uparrow}{\text{A}^1\text{Ni(Br)CO*}}}}$$

$$\downarrow\uparrow$$

$$\pi\text{-A}^2\text{Ni(Br)CO} + \text{A}^1\text{Br} \rightleftharpoons \underset{\mathbf{7}}{\underset{\text{A}^1\text{Br}}{\overset{\uparrow}{\text{A}^2\text{Ni(Br)CO*}}}}$$

$$\mathbf{6} \text{ or } \mathbf{7} \xrightarrow[\text{solvent}]{\text{coordinating}} (\text{A})_2 + \text{NiBr}_2 + \text{CO}$$

$$* = \sigma\text{- or } \pi\text{-allyl}$$

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[10] E. J. Corey, L. Hegedus, and M. F. Semmelhack, *J. Am. Chem. Soc.*, **90**, 2417 (1968).

[11] It has been reported by G. Wilke, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966), that the reaction of bis(π-cyclooctenyl)nickel with carbon monoxide (conditions unspecified) produces mainly the ketones **5** and only minor amounts of hydrocarbon. This observation suggested the use of the cyclooctenyl system as a test case.

[12] The coupling of allylic halides which can exist as *cis* and *trans* forms is stereochemically nonspecific (see ref 3 and 4 and also M. F. Semmelhack, Ph.D. Thesis, Harvard University, 1967). *cis–trans* interconversion of allyl groups can be explained by 1,3 rearrangement of the allylic halide and also by 1,3 rearrangement of σ-allylnickel intermediates using the reversible reactions shown.

[13] Additional ligands or steps which are not shown in this scheme may be involved.

[14] This work was supported by the National Science Foundation and the National Institutes of Health.

E. J. Corey, M. F. Semmelhack, L. S. Hegedus
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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Interconversion of Lower Valence States of π-Allylnickel Complexes. A New Synthesis of π-Allylnickel Derivatives

Sir:

This note describes the detection of a facile redox equilibrium involving π-allylnickel complexes according to eq 1 in both allyl and methallyl series. In addition, a useful and general synthesis of complexes of type **2** by reduction of the corresponding π-allylnickel bromide derivatives **1** is reported.

$$\underset{\mathbf{1}}{[\pi\text{-RNiBr}]_2} \rightleftharpoons \underset{\mathbf{2}}{[\pi\text{-R}]_2\text{Ni}} + \text{NiBr}_2 \qquad (1)$$

$$\text{R} = \text{CH}_2\cdots\text{CH}\cdots\text{CH}_2 \text{ or } \text{CH}_2\cdots\text{C(CH}_3)\cdots\text{CH}_2$$

In contrast to the dark red allyl- and methallylnickel(I) (**1**) which are nonvolatile, the yellow bis(π-allyl)- and bis(π-methallyl)nickel(0) (**2**) sublime readily at 0° and pressures below 1 mm.[1,2] The fact that the latter complexes are the only volatile participants in process 1 suggests that even a *small* degree of disproportionation of **1** to **2** and nickel bromide might be detected at pressures sufficiently low to remove **2** from the system. The following data provide experimental evidence of such behavior. In the case of complex **1**, R = allyl, for example, evacuation of stirred solutions in dimethylformamide, N-methylpyrrolidone, or hexamethylphosphoric amide at 25° to 0.005 mm or less results in the collection of *ca.* 60% of the theoretical amount of the

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[1] See (a) G. Wilke, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966); (b) G. Wilke, *ibid.*, **2**, 105 (1963).

[2] It is convenient to use the arbitrary description of complexes 1 and 2 as nickel(I) and nickel(0) derivatives, respectively; see E. J. Corey, M. F. Semmelhack, and L. S. Hegedus, *J. Am. Chem. Soc.*, **90**, 2416 (1968).