(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).

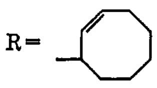
The accompanying communication[10] presents evidence for the occurrence of equilibria 3 and 4 between π-allylnickel(0) and π-allylnickel(I) complexes. The intermediacy of zero-valent complexes in the coupling of allylic halides by nickel carbonyl must therefore be considered, since it is known that bis(π-allyl)nickel 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.

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

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

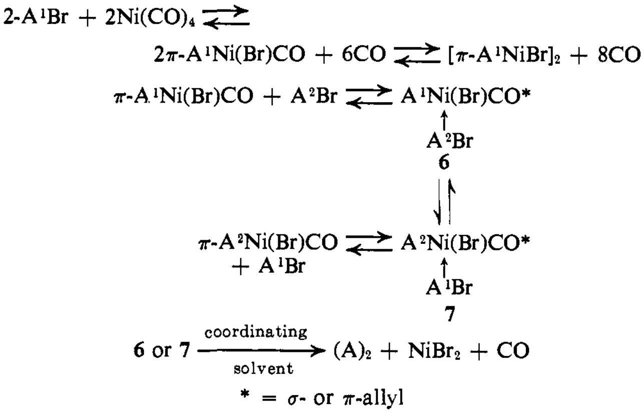
R-R RCOR

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



$$2\text{-A}^1\text{Br} + 2\text{Ni(CO)}_4 \rightleftharpoons$$

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

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

$$\mathbf{6} \rightleftharpoons \mathbf{7}$$

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

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

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

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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.

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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).

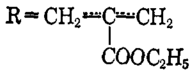
[2] It is convenient to use the arbitrary description of complexes **1** and **2** as nickel(I) and nickel(0) derivatives, respectively; see E. J. Corey, M. F. Semmelhack, and L. S. Hegedus, *J. Am. Chem. Soc.*, **90**, 2416 (1968).

yellow "zero-valent" complex **2**, R = allyl, in a trap cooled by liquid nitrogen.[3] Even higher yields (>80%) of this product can be obtained by the addition in portions of triethylenetetramine to the solutions of **1** and nickel bromide during the disproportionation reaction. Confirmation of the bis(π-allyl) structure **2** for the volatile substance was obtained from the mass spectrum[4] and from the comparison of its nmr[5,6] spectrum with that of **2** derived from the reaction of allylmagnesium halide with nickel(II) halide.[1] The yellow "zero-valent" complex **2**, R = methallyl, was similarly obtained from **1**, R = methallyl, and identified by its mass[7] and nmr[6,8] spectra and also by its chemical properties, including (1) conversion to methallyl iodide with excess I_2, (2) reaction with nickel bromide to form **1**, R = methallyl, and (3) reaction with allyl bromide in dimethylformamide to give a mixture of biallyl, allylmethallyl, and bimethallyl by allylic coupling.[2]

The extension of this technique for the conversion of π-allylnickel(I) complexes of type **1** to bis(π-allyl)-nickel(0) complexes is clearly limited by the requirement that the latter possess substantial volatility and therefore low molecular weight. The medium used is also critical. For example, only small amounts of **2**, R = allyl or methallyl, can be distilled from solutions of **1** in tetraglyme, presumably because the equilibrium is less favorable to disproportionation in that medium.[9] The transformation **1** → **2** can be achieved much more generally by the use of a suitable reducing agent, *e.g.*, zinc–copper couple. The allyl and methallyl complexes **2** can be obtained in >90% yield by reaction with an excess of zinc–copper couple[10] (granules) at 25° in hexamethylphosphoric amide or dimethylformamide at 0.01 mm by collection of the volatile product in a liquid nitrogen cooled trap. The nonvolatile bis(π-allyl)nickel complexes **3–5** have been obtained (in yields of 60–80%) simply by reduction of the corresponding π-allylnickel(I) complexes using zinc–copper couple under 1 atm of argon and isolation by extraction with pentane after addition of a small amount of water.[11]

The complexes **3–5** were characterized by their chemical properties, including protonation to R–H with *p*-toluenesulfonic acid and allylic coupling *via* R–I to R–R using 1 equiv of I_2, and by their reaction with CO which produced R–R from **3** and mixtures of R–R and RCOR from **4** and **5**.

π-R_2Ni

3, 

$R = CH_2 \cdots \underset{COOC_2H_5}{\underset{|}{C}} \cdots CH_2$

4, $R = (CH_3)_2C \cdots CH \cdots CH_2$

5, R = 

The formation of nickel(0) complexes by reduction of π-allylnickel(I) halide complexes with zinc is apparently the result of the direct interaction of zinc with the nickel(I) complexes rather than the displacement of equilibrium 1 by reduction of nickel bromide by zinc. We have been able to demonstrate that nickel bromide is not reduced by zinc–copper couple in dimethylformamide under the conditions which allow the conversion of nickel(I) to nickel(0) complexes.

The synthetic route to bis(π-allyl)nickel derivatives by the reduction of π-allylnickel(I) halide complexes is more convenient than the method[1] based on the reaction of an allylic Grignard reagent with a nickel halide and also allows the synthesis of complexes such as **3** which contain functional groups that would interfere with the Grignard synthesis. The intermediate π-allylnickel(I) complexes are easily obtained in high yield from the reaction of nickel carbonyl with an allylic halide.[12–14]

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(3) Some solvent codistils with **2**, the amount being smallest with hexamethylphosphoric amide, the least volatile of these solvents. Solvent-free **2** can be obtained by a redistillation of the product obtained using hexamethylphosphoric amide.

(4) See G. Wilke and B. Bogdanović, *Angew. Chem.*, **73**, 756 (1961).

(5) J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc.*, 423 (1967).

(6) H. Bönnemann, B. Bogdanović, and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **6**, 804 (1967), report that solutions of bis(π-allyl)-nickel contain two geometrical isomers in the ratio 3:1. In the present work a 2.5:1 ratio of these forms was found by nmr analysis in benzene as solvent.

(7) The mass spectra of the complexes **2**, R = allyl, and **2**, R = methallyl, show molecular ion peaks corresponding to ^{58}Ni and ^{60}Ni isotopes in a ratio 2.5:1 as well as fragments corresponding to RNi^+, $RNiH^+$, and $(RR - H)^+$.

(8) Two isomeric forms of **2**, R = methallyl, in the ratio 2.1:1 (in C_6H_6) were indicated by the nmr spectrum (*cf.* previously reported[6] ratio of 2.3:1).

(9) The most critical solvent interaction in controlling the position of equilibrium 1 is likely the coordination and solvation of nickel(II) bromide.

(10) E. Le Goff, *J. Org. Chem.*, **29**, 2048 (1964).

(11) Because of the extreme sensitivity of the bis(π-allyl)nickel complexes to oxygen, air must be rigorously excluded during these experimental operations.

(12) E. J. Corey and M. F. Semmelhack, *J. Am. Chem. Soc.*, **89**, 2755 (1967).

(13) In connection with the role of bis(π-allyl)nickel compounds in allylic coupling reactions it has been observed that, although facile coupling occurs with allylic halides,[2] the reaction with *nonallylic* halides[12] such as iodobenzene or cyclohexyl iodide is much slower with the zero-valent complexes **2** than with the nickel(I) complexes **1**.

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Stereoelectronic Factor in the Chloranil Dehydrogenation of Cannabinoids. Total Synthesis of *dl*-Cannabichromene[1,2]

Sir:

We wish to present evidence suggesting that the dehydrogenation of hydroaromatic compounds by chloranil can be added to the list of reactions in which stereoelectronic factors have been found to influence the course, stereochemistry, and rate. Among these are enolization, protonation and bromination of enols,[4] bimolecular eliminations,[5] oxidation of allylic alcohols by manganese dioxide,[6] dichlorodicyanoquinone,[7] and

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(1) Hashish. XII. For part XI see R. Mechoulam, P. Braun, and Y. Gaoni, *J. Am. Chem. Soc.*, **89**, 4552 (1967).

(2) The term *cannabinoids* has been proposed[3] for the group of C_{21} compounds typical of and present in *Cannabis sativa* L., as well as for their analogs and transformation products.

(3) R. Mechoulam and Y. Gaoni, *Fortschr. Chem. Organ. Naturstoffe*, **25**, 175 (1967).

(4) For example, E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **78**, 6269 (1956), and earlier papers; R. Villotti, H. J. Ringold, and C. Djerassi, *ibid.*, **82**, 5693 (1960); S. K. Malhotra and H. J. Ringold, *ibid.*, **86**, 1997 (1964); *cf.* G. Stork and S. D. Darling, *ibid.*, **86**, 1761 (1964).

(5) For a recent summary see E. L. Eliel, N. L. Allinger, S. T. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 291.

(6) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961); G. Stork, *Alkaloids*, **6**, 223 (1960).