A considerable body of highly useful chemistry based on nickel has been developed, largely by the German chemist, G. Wilke. Many of these reactions involve what are called \(\text{\(\pi\)-propenyl (\(\pi\)-allyl)}\) complexes and their formation has a close analogy in the formation of ferrocene from cyclopentadienylmagnesium compounds and ferric chloride (Section 31-1). Treatment of \(\text{NiBr}_2\) with two moles of 2-propenylmagnesium bromide gives a stable (albeit oxygen sensitive) substance of composition \(\text{Ni}(\text{C}_3\text{H}_5)_2\):

\[
2\text{CH}_2=\text{CHCH}_2\text{MgBr} + \text{NiBr}_2 \rightarrow \begin{array}{c}
\text{trans (75\%)} \\
\text{cis (25\%)}
\end{array}
\]

Unlike \(\text{C}_3\text{H}_5\text{MgBr}\), the metal compound has a very complex proton NMR spectrum. Analysis of the spectrum indicates it arises from a mixture (75:25) of two \(\text{Ni}(\text{C}_3\text{H}_5)_2\) isomers with each isomer having its \(\text{C}_3\text{H}_5\) groups in a rigid planar arrangement as follows:

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\]

These facts can be accommodated by the trans- and cis-di-\(\text{\(\pi\)-propenyl}\)-nickel structures. Di-\(\text{\(\pi\)-propenyl}\)-nickel has many interesting reactions, among which are the following examples:

\[
\begin{array}{c}
4\text{CO} \\
\text{H}_2
\end{array} \rightarrow \text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2=\text{CH}_2 + \text{Ni(CO)}_4
\]

The \(\text{\(\pi\)-propenyl}\)-type structures are more stable for nickel than for other metals such as iron. With 1,3-butadiene, \(\text{Fe(CO)}_5\) forms a double \(\text{\(\pi\)}\) complex, whereas \(\text{Ni(CO)}_4\) produces a bis-\(\text{\(\pi\)}\)-propenyl-type structure, \(\text{(21)}\):
With more 1,3-butadiene, (21) is converted first to (22), which after rearrangement reacts with 1,3-butadiene to give back (21) with liberation of \(\text{trans,trans,trans-1,5,9-cyclododecatriene}\):

![Chemical structure](image)

The overall sequence thus provides a catalytic route for the cyclic trimerization of 1,3-butadiene.

Ethene and alkynes react with (21) in the presence of excess carbon monoxide to give ten-membered ring compounds, whereas the reaction of (21) with excess carbon monoxide results in formation of a mixture of six- and eight-membered rings:

![Chemical structures](image)

**Contributors**
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