Methyl Maleate– or Methyl Fumarate–Nickel Bromide

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WE have found that π-allylnickel bromide reacts with methyl maleate or methyl fumarate under mild conditions in benzene solution to give compounds with chemical analyses in good agreement with the formula:

$$[(MeO_2C{\cdot}CH{:}CH{\cdot}CO_2Me)NiBr]$$

The same complexes can be prepared by reaction of methyl maleate with allyl bromide and nickel carbonyl.[1] The new complexes are very sensitive to oxygen; they are insoluble in benzene and n-hexane and soluble in water, dimethylformamide, and methanol. In the last solvent [methyl maleate]NiBr decomposes, at room temperature, after some time, into a mixture of methyl succinate and methyl maleate and fumarate with separation of metallic nickel. Under the same conditions [methyl fumarate]NiBr decomposes only into methyl fumarate with separation of metallic nickel.

The products are paramagnetic. The i.r. spectrum (Nujol, perfluorokerosene) of [methyl maleate]-NiBr (green dark) shows absorptions at: 1669 (vs), 1480 (vs), 1440 (vs), 1400 (vs), 1212 (vs), 1188 (s), 1030 (w), 965 (w), 820 (w) cm.$^{-1}$.

[Methyl fumarate]NiBr (red–brown) shows absorptions at: 1700 (s), 1615 (vs), 1470 (w), 1430 (vs), 1300 (s), 1278 (s), 1200 (w), 1165 (s), 1030 (s), 768 (w), 686 (w).

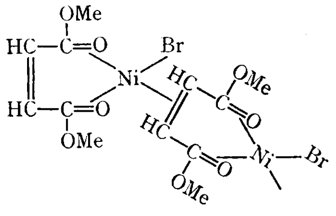
The complexes give rise to a mixture of methyl succinate (about 50%) and methyl fumarate and maleate by reaction in benzene with anhydrous hydrochloric acid. Thermal decomposition of the complexes, *in vacuo*, at 100°, yields metallic nickel, nickel bromide, and methyl fumarate or maleate.

[Methyl maleate]NiBr reacts with triphenylphosphine and the addition product can be isolated; the chemical analysis is in agreement with the formula [methyl maleate]NiBrPPh$_3$. The compound has an i.r. spectrum like that of [methyl maleate]NiBr. On the other hand, [methyl fumarate]NiBr is decomposed by triphenylphosphine; methyl fumarate and $(Ph_3P)_2NiBr_2$[2] can be isolated.

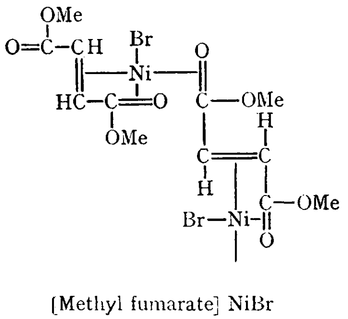
The downward shift of the $\nu_{C=C}$ band to 1480—1470 cm^{-1} suggests a π-bond of the carbon–carbon double bond to the nickel atom;[3] this fact is also supported by the chemical behaviour with hydrochloric acid and methanol. A bond like this was found in $C_5H_5NiC_5H_5C_2(CO_2Me)_2$.[4] The strong bands at 1669 (maleate) and 1615 (fumarate) cm.$^{-1}$ may arise from the ν_{CO} of a complexed ester carbonyl group. The shift of 60 (maleate), 100 (fumarate) cm.$^{-1}$ below normal ν_{CO} for the free ligands, suggests a delocalized π-bond of the carbon–oxygen double bond to the nickel atom. The downward shift is not so drastic as the one found for ketonic and aldehydic ligands.[5]

The hexadiene present after the reaction of methyl maleate or fumarate with π-allylnickel bromide suggests that methyl ester removes the allyl group from the complex, accepting a negative charge. Although several determinations of the magnetic moment of the complex have given a value corresponding to Ni^{2+}, this point is under investigation in order to obtain reliable results. So far we cannot exclude that the negative charge is transferred to Ni yielding an Ni^{+} complex.

The manner by which the organic ligand is bound to nickel has not been elucidated; a polymeric structure in which methyl maleate and fumarate are maintaining their own conformation can be suggested, as in the following:



[Methyl maleate] NiBr



[Methyl fumarate] NiBr

Triphenylphosphine can be co-ordinated, maintaining the polymeric structure of [methyl maleate]-NiBr; for steric reasons [methyl fumarate]NiBr cannot give the same reaction.

Methyl maleate– or methyl fumarate–nickel bromide polymerizes acetylene and buta-1,3-diene to *trans*-polybutadiene in methanol–water solution.

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