## Methyl Maleate- or Methyl Fumarate-Nickel Bromide

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WE have found that  $\pi$ -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.<sup>1</sup> The new complexes are very sensitive to oxygen; they are insoluble in benzene and nhexane 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.<sup>-1</sup>.

[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]NiBrPh<sub>3</sub>. 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  $v_{c=c}$  band to 1480— 1470 cm<sup>-1</sup> suggests a  $\pi$ -bond of the carbon-carbon double bond to the nickel atom;<sup>3</sup> this fact is also supported by the chemical behaviour with hydrochloric acid and methanol. A bond like this was found in C<sub>5</sub>H<sub>5</sub>NiC<sub>5</sub>H<sub>5</sub>C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>.<sup>4</sup> The strong bands at 1669 (maleate) and 1615 (fumarate) cm.<sup>-1</sup> may arise from the  $\nu_{\rm CO}$  of a complexed ester carbonyl group. The shift of 60 (maleate), 100 (fumarate) cm.<sup>-1</sup> below normal  $\nu_{\rm CO}$  for the free ligands, suggests a delocalized  $\pi$ -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.<sup>5</sup>

The hexadiene present after the reaction of methyl maleate or fumarate with  $\pi$ -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<sup>2+</sup>, 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<sup>+</sup> 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

## CHEMICAL COMMUNICATIONS

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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<sup>1</sup> M. Dubini and F. Montino, J. Organometallic Chem., 1966, 6, 188.

- <sup>2</sup> L. M. Venanzi, J. Chem. Soc., 1958, 719; J. Inorg. Nuclear Chem., 1958, 8, 137. <sup>3</sup> E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, Helv. Chim. Acta, 1963, 46, 288.
- M. Dubeck, J. Amer. Chem. Soc., 1960, 82, 6193; L. F. Dahl and C. H. Wei, Inorg. Chem., 1964, 2, 713.
  H. P. Fritz and G. N. Schrauzer, Chem. Ber., 1961, 94, 650; D. P. Tate, A. A. Buss, J. M. Augl, N. L. Ross, J. C. Grasselli, U. M. Ritchey, and F. Knoll, Inorg. Chem., 1965, 4, 1323; R. B. King and A. Fronzaglia, Chem. Comm., 1966, 275.