Studies on Some *N*-Metallated Hydrazone Complexes of Molybdenum and Tungsten

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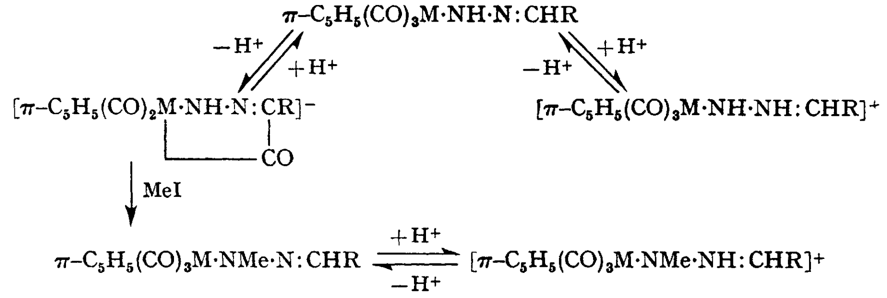
RECENTLY several compounds have been described containing transition metal–nitrogen systems[1] or transition metal–unsaturated nitrogen systems which may be regarded as substituted nitrogen derivatives,[2] *e.g.*, M–N_2Ph. However, little is known of the reactions of unsaturated nitrogen systems attached to transition metals and these are of interest in relation to nitrogen fixation by transition-metal catalysts.

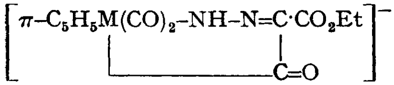
Treatment of the sodium of the anions $[\pi\text{-}C_5H_5\text{-}Mo(\text{or } W)(CO)_3]^-$ with diazoacetic ester affords yellow crystalline complexes, unstable to oxygen and bright light. They have been studied by analysis, molecular-weight determination, mass i.r., and ^{1}H n.m.r. spectra. This evidence is most convincingly interpreted in terms of the hydrazone complexes

$\pi\text{-}C_5H_5Mo\text{-}(\text{or } W)(CO)_3\text{–}NH{\cdot}N{:}CH{\cdot}CO_2Et$, (I).



They undergo rapid exchange in deuterium oxide–tetrahydrofuran mixtures giving the dideuterated species π-C_5H_5Mo(or W)$(CO)_3$–ND·N:CD·CO_2Et.

The hydrazone complexes (I) protonate reversibly in aqueous acids, forming cations which may be isolated as their red tetrafluoroborate or hexafluorophosphate salts. Spectral studies on the cations and their deuterated analogues suggest that a proton adds to the nitrogen in the β-position with respect to the metal. We suggest the structures [π-C_5H_5Mo(or W)$(CO)_3$–NH·NH:CH·CO_2Et]$^+$ for these cations. The neutral hydrazones (I) also react reversibly with bases such as aqueous alkali, forming anionic species, which have been isolated as tetra-n-butylammonium salts. On the basis of analysis, ^{1}H n.m.r., and i.r. spectra, the structure for the anions,


$$\left[\pi\text{-}C_5H_5M(CO)_2\text{-}NH\text{-}N{=}C{\cdot}CO_2Et \text{ (M–C=O–C ring)}\right]^-$$

is tentatively suggested. Treatment of tetrahydrofuran solutions of the anions with methyl iodide gives the neutral *N*-methyl compounds π-C_5H_5Mo(or W)$(CO)_3$–NMe·N:CH·CO_2Et (II). These compounds also protonate forming the cations [π-C_5H_5Mo (or W)$(CO)_3$–NMe·NH:CH·CO_2Et]$^+$. Studies of the electronic spectra of aqueous solutions of the hydrazones (I) and (II) at varying pH show the acid–base character of the compounds; (I) and the cations formed from (I) are dibasic acids with pK = 1·8 and 8—9 (for Mo), and 2·0 and 8—9 (for W). The cation formed from the *N*-methyl derivative (II) is, as would be expected, a monobasic acid, pK = 5·6. Thus the versatile equilibria found for the complexes (I) and (II) are (where R = CO_2Et):

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