

σ - π Interaction in Aza-allyl Complexes. ^1H Nuclear Magnetic Resonance Studies of $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2[(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{CNC}(p\text{-CH}_3\text{C}_6\text{H}_4)_2]$ ($\text{M} = \text{Mo}, \text{W}$)

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Summary ^1H n.m.r. studies of $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2[(p\text{-MeC}_6\text{H}_4)_2\text{CNC}(p\text{-MeC}_6\text{H}_4)_2]$ ($\text{M} = \text{Mo}, \text{W}$) in the temperature range -20 to 70° showed the bonding of the aza-allyl group to the metals to be of the σ - π type: epimerisation occurs at the higher temperatures through processes of rotation and interchange of σ - π bonding.

FOLLOWING the synthesis of the first aza-allyl complex, the mode of attachment of the aza-allyl group, (R_2CNCR_2), to the metal has been the subject of speculation.¹ In addition to the modes found for the normal allyl group, the aza-allyl group has the additional possibility of having a linear or bent skeleton depending on the extent to which the nitrogen lone pair is involved in the bonding to the metal. Since the phenyl substituents in the original complexes [$\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{Ph}_2\text{CNCPh}_2)$] ($\text{M} = \text{Mo}, \text{W}$) are unsuitable for detailed study of the mode of attachment of the aza-allyl group (known only with aryl substituents), we have synthesised

the related *p*-tolyl derivatives $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2[(p\text{-MeC}_6\text{H}_4)_2\text{CNC}(p\text{-MeC}_6\text{H}_4)_2]$ ($\text{M} = \text{Mo}, \text{W}$) (I) to use the methyl protons as ^1H n.m.r. probes to obtain structural information and resolve the bonding type.

Bonding of allyl groups to transition metals has received increased interest in recent years due primarily to the 'dynamic' nature of the bonding in many complexes.^{2,3} Several theories exist to explain the observed equilibration of allyl methylene protons. Van Leeuwen and Praat³ consider the mechanism for $\text{C}_4\text{H}_7\text{Pd}(\text{PPh}_3)(\text{OAc})$ to involve σ - π intermediates, whereas, *e.g.* for $(\text{C}_3\text{H}_5)_2\text{Pd}$ and $(\text{C}_3\text{H}_5)_4\text{Zr}$, Beconsall and O'Brien⁴ consider restricted rotation of the methylene groups whilst the allyl group remains π -bonded to the metal. We report the occurrence of related epimerisation in the aza-allyl complexes at 70° , and the adoption of σ - π type bonding at lower temperatures. The present studies do not however distinguish between a linear or bent skeleton.

$\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$) reacts with $(p\text{-tolyl})_2\text{C}=\text{NLi}$ in diethyl ether (1:2 molar ratio) at room temperature, to produce complexes (I) which were identified by analytical, molecular weight, m.s., and i.r. data.[†] Satisfactory analytical and molecular weight data were obtained. ^1H n.m.r. data for the molybdenum and tungsten complexes are similar, and those for the tungsten complex are given in the Figure. At -20° , four methyl proton signals

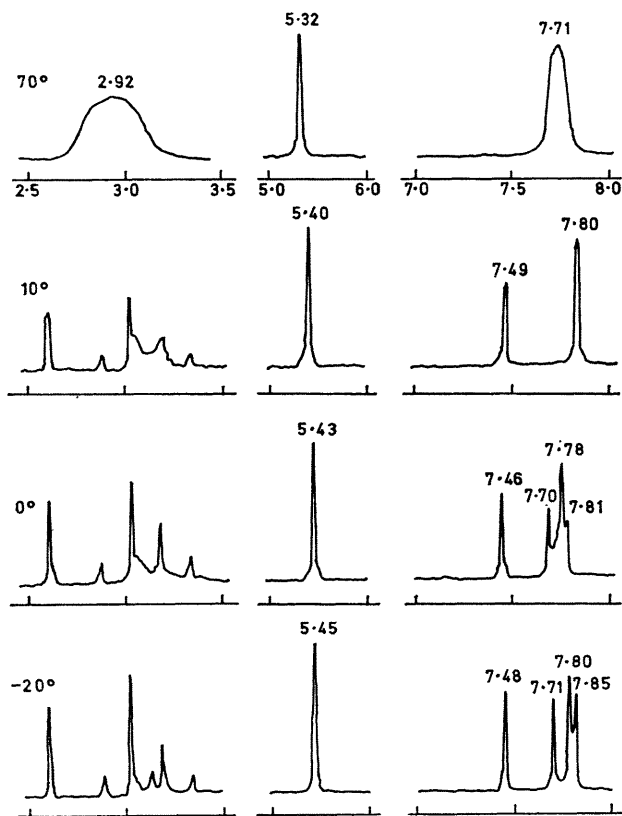
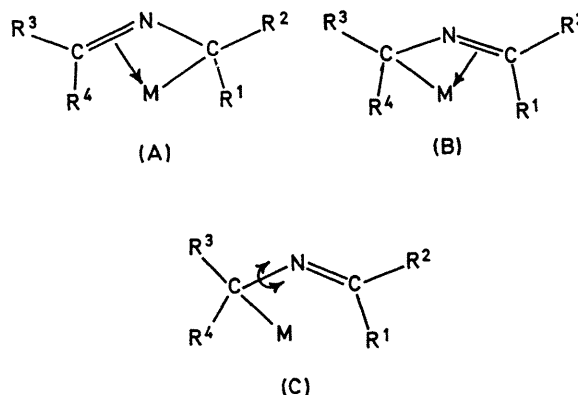


FIGURE. ^1H n.m.r. spectra for $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[(p\text{-MeC}_6\text{H}_4)_2\text{CNC}(p\text{-MeC}_6\text{H}_4)_2]$ in CS_2 .

[†] m/e (P^+): ⁹⁸Mo, 621; ¹⁸⁴W, 707. ν_{CO} (hexane solution): Mo, 1949vs, 1858vs cm^{-1} ; W, 1945vs, 1853vs cm^{-1} .

[‡] The presence of *cis-trans* isomers,⁵ isomers derived from the orientation of a π -aza-allyl group with respect to the carbonyl groups, and structural isomers having linear or bent aza-allyl skeletons, have been eliminated by the integral ratio of the integrated intensities of the signals at temperatures between -20 and 70° .



of equal intensity are observed, but on warming, two of the signals (τ 7.71 and 7.85) broaden and decrease in intensity, before coalescing to a signal which is superimposed on the signal originally at τ 7.80. Consequently at 10° , two signals are observed with an intensity ratio 1:3. At 70° , these signals coalesce to a broader time-averaged signal.

At low temperatures, the ^1H n.m.r. spectral data are consistent with an aza-allyl group having non-equivalent

skeletal carbon atoms [A, skeleton bent or linear (*cis*-complex only)].[‡] The presence of a π -aza-allyl group, and mixtures of isomers is not confirmed by the data. Coalescing of signals at 10° is interpreted as detachment of the carbon-nitrogen π -system from the metal and rotation of the $-\text{N}=\text{C}(\text{tolyl})_2$ group about the single C-N bond (C), thus

making two groups equivalent (R^3 and R^4 for bent skeleton, R^1 and R^2 for linear skeleton). At 70°, interchange of σ - π bonding (A and B) and rotation about the C-N bonds is thought to occur to produce four equivalent groups.

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