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PRELIMINARY COMMUNICATION

A NOVEL NITROGEN-CONTAINING LIGAND

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The ability of various unsaturated organonitrogen systems to act as both σ- and π-bonding ligands to transition metals is well established[1-6]. Among the most interesting unsaturated ligands, $R_2NC{\equiv}N$[2,3], $R_2C{=}C{=}NR$[4,5] and $RCH{=}CHC{\equiv}N$[1] are believed to coordinate between three or four atoms. No allylic organonitrogen ligands appear to have been reported, however. We here describe what we believe to be the first example of such a ligand, in the complex π-$C_5H_5Mo(CO)_2(Ph_2CNCPh_2)$.

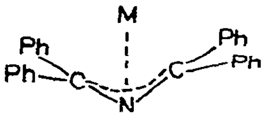
$Ph_2C{=}NLi$[7] and π-$C_5H_5Mo(CO)_3Cl$ in a 2:1 molar ratio react in ether solution at room temperature to produce golden brown crystals, which gave correct analyses for π-$C_5H_5Mo(CO)_2(Ph_2CNCPh_2)$. Carbon monoxide group determination by iodine cleavage confirmed the presence of two carbonyl groups. The product is stable for several months in air at room temperature Its solution in polar organic solvents are intensely purple even when dilute, although the solid never appears this colour.

In the mass spectrum the parent ion corresponds to the mononuclear species $[C_5H_5Mo(CO)_2(Ph_2CNCPh_2)]^+$, and mass measurements of the parent ion, P^+, and $(P\text{-}2CO)^+$ agree within 2 ppm with those calculated. The largest organic fragment detected, at *m/e* 346, had a breakdown pattern appropriate for $[Ph_2CNCPh_2]^+$. The IR spectrum is consistent with a dicarbonyl complex (ν(C–O) 1938 s and 1835 s cm^{-1} in $CHCl_3$ and as a nujol mull) but no absorption could be assigned to ν(C=N). The ^1H NMR spectrum in $CDCl_3$ solution consists of a sharp singlet (5.24τ) arising from the π-C_5H_5 ring protons, and a multiplet (2.7τ) typical of equivalent phenyl groups. The intensity ratio of 1:4 indicates the presence of four phenyl groups per cyclopentadienyl group.

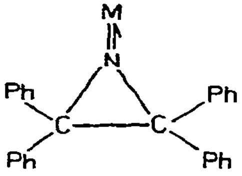
In the preparation of the complex, complete reaction occurs only after the addition of 2 moles $Ph_2C{-}NLi$ to 1 mole π-$C_5H_5Mo(CO)_3Cl$. Thus condensation of two ketimine units appears to occur as in the formation of $Ph_2C{=}NCHPh_2$ from $Ph_2C{=}NH$ and Et_3M[8].

Since the complex contains only two carbonyl groups, the ligand Ph_2CNCPh_2 probably acts as a three electron donor. The equivalence of the phenyl groups, as shown by the ^1H NMR spectrum, and the absence of a C=N stretching frequency suggests two possible modes for the bonding of the ligand to the metal. The ligand may be pseudo-allylic (I) in which case the metal will be coordinated to the nitrogen and its two adjacent carbon atoms, or alternatively the ligand may be a substituted aziridine, with the metal forming σ- and π-bonds only to the nitrogen atom (II). Complexes containing the aziridine group

π-bonded in this way to a transition metal have not been previously reported, although the group is well known attached to main group elements[9]. Structure I is favoured in view of the absence of an infrared absorption band in the region 850–900 cm^{-1}, which has been used as diagnostic of the aziridine ring system[10], but X-ray crystallographic data will be required finally to deduce the bonding mode of the ligand. Both forms of the ligand would be expected to interact strongly with the metal. The strength of the metal carbonyl bonds (as indicated by ν(C–O))and the failure of the complex to undergo reaction with triphenylphosphine (over several days in refluxing chloroform or toluene) are accordingly readily understood.



(I)



(II)

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