

***ortho*-Metallation of Benzylideneaniline: Structure of $C_6H_5N:CH \cdot C_6H_4Mn(CO)_4$**

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Summary Transition metal derivatives of benzylideneaniline have been obtained; the structure of $C_6H_5N:CH \cdot C_6H_4Mn(CO)_4$ shows that the ligand is bonded *via* the nitrogen lone pair, and a metal-carbon σ bond formed in an *ortho*-metallation reaction.

ALTHOUGH many reactions between azobenzene and transition metal complexes have been studied,¹ accounts of similar compounds retaining a benzylideneaniline moiety are limited to a series of palladium complexes,² a cyclopentadienyl-nickel derivative,³ and a rhodium(I)-rhodium(III) complex.⁴

We have found that benzylideneaniline (bzaH) reacts with many transition metal compounds to afford complexes containing the $C_6H_5N:CH-C_6H_4$ group. For example, reaction between $MeMn(CO)_5$ and the ligand afforded a 37% yield of $(bza)Mn(CO)_4$ (I). These reactions generally proceed less readily than analogous reactions with azobenzene.

The 1H n.m.r. spectra of the new complexes exhibit the multiplet structure characteristic of an *ortho*-metallated phenyl ring, together with a resonance at τ 1.5–2.0, assigned to the $CH:N$ proton (*cf.* benzylideneaniline, τ 1.73). These observations suggest that there is little interaction of the $CH:N$ π system with the metal atom, supporting a formulation for these complexes involving a $C_6H_5N:CH-C_6H_4$ ligand chelated to the metal *via* the nitrogen lone pair and a metal-carbon σ -bond. This has now been confirmed in the case of complex (I) by a single crystal X-ray study.

Crystals of (I) are monoclinic, space group $P2_1/c$, with $a = 9.548(4)$, $b = 9.154(3)$, $c = 18.201(6)$ Å, $\beta = 102^\circ 4'(1')$. $D_m = 1.47$ g cm $^{-3}$, ($Z = 4$), $D_c = 1.48$ g cm $^{-3}$. The structural determination was based upon 1530 independent nonzero reflections with θ ($Mo-K_\alpha$) $\leq 25^\circ$ collected by the $\theta-2\theta$ scan technique. The structure was solved by heavy-atom methods. Full-matrix least-squares refinement (Mn anisotropic; C, N, O isotropic; H atoms included as fixed contributions) has converged to conventional discrepancy factors $R_1 = 0.071$ and $R_2 = 0.041$.

The molecular structure of $C_6H_5N:CH-C_6H_4Mn(CO)_4$ is shown in the Figure. The manganese atom is co-ordinated in a distorted octahedral configuration to the four carbonyl groups and to the chelated ligand. The binding of the ligand *via* a metal-nitrogen bond and a metal-carbon σ -bond to the *ortho* position of the benzylidene phenyl ring is as suggested above, and is analogous to that found in acetatobis-[2-(phenylazo)phenyl]rhodium.⁵

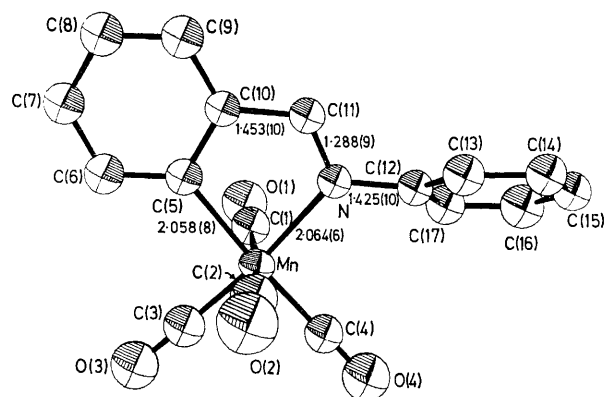


FIGURE. A view of the molecular structure of $C_6H_5N:CH-C_6H_4-Mn(CO)_4$. Atoms are represented by 50% probability surfaces with the exception of C(15), whose thermal parameter has been reduced for clarity. Mean Mn-C(carbonyl) = 1.782(10), mean C-C(phenyl) = 1.397(12) Å.

Unlike the latter complex, however, the Mn-C and Mn-N bond distances in the chelate ring are identical. In contrast to the near-coplanarity of the two ligand phenyl rings observed in the rhodium azobenzene complex, the dihedral angle between the planes of the two rings here is 61.5° . This observation is in agreement with crystallographic and n.m.r. results⁶ which show that the aniline ring in benzylideneaniline is twisted out of the C-N=C plane by 55° . A similar conclusion was drawn from an n.m.r. study of protonated benzylideneaniline.⁷ This nonplanarity contrasts with the planarity of azobenzene and stilbene, isoelectronic with benzylideneaniline.

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¹ *Cf.*, M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 3204; *Chem. Comm.*, 1970, 1325; W. T. Flannigan, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. (C)*, 1969, 2077.

² S. P. Molnar and M. Orchin, *J. Organometallic Chem.*, 1969, 16, 196.

³ Y. A. Ustynyuk, V. A. Chertkov, and I. V. Barinov, *J. Organometallic Chem.*, 1971, 29, C53.

⁴ M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *Chem. Comm.*, 1971, 661.

⁵ A. R. M. Craik, G. R. Knox, P. L. Pauson, R. J. Hoare, and O. S. Mills, *Chem. Comm.*, 1971, 168.

⁶ H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1970, 53, 1747; A. van Putten and J. W. Pavlik, *Tetrahedron*, 1971, 27, 3007.

⁷ J. W. Pavlik and A. van Putten, *Tetrahedron*, 1971, 27, 3301.