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Novel Type of Metallation Reaction: Cyclometallation of Heterocyclic Amines by Dicyclopentadienylmethyltitanium

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Summary In a new type of metallation reaction 2-substituted pyridines and quinolines are metallated at the 6- and 2-position, respectively by dicyclopentadienylmethyltitanium prepared *in situ*.

METALLATION of heterocyclic amines by several transition metals has been reported. The cyclometallated products formed normally consist of five-membered chelate rings [e.g. compounds (1)—(3)¹⁻⁵]. However, similar metallations have not been described for Ti. The activating properties of compounds Cp_2TiR towards unsaturated substrates⁶ prompted us to investigate cyclometallation reactions of these compounds with heterocyclic amines analogous to those giving (1)—(3).

We now report an unusual cyclometallation of 2-substituted pyridines and quinolines (e.g., 2-methyl-, 2-phenyl-, or 2-vinyl-pyridine, quinoline, or 8-methylquinoline) by Cp_2TiMe prepared *in situ* ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$).[†] The metallation takes place at the 6-position of the pyridines and at the 2-position of the quinolines, yielding products probably containing a three-membered titanacycle in which the ligands act as bidentate three-electron donors [e.g. compounds (4) and (5)].

In a typical reaction Cp_2TiCl (made by reduction of Cp_2TiCl_2 with 1 equiv. of Pr^iMgCl) was treated with 1 equiv. of MeLi at -78°C . After 1 h the Cp_2TiMe formed was treated with a slight excess of the heterocyclic amine. A dark green mixture formed, presumably owing to co-ordination of the Lewis base to the intermediate Cp_2TiMe . On warming to room temperature the colour changed to brown-purple while methane (g.l.c.) was evolved (see Scheme 1; pyridines are used as an example; the same Scheme holds for the quinolines). Methane formation is a normal consequence of metallation which is also observed for other cyclometallations.⁸

[†] The identity of Cp_2TiMe as the reactive species was not completely established. It is possible that addition compounds of Cp_2TiMe and Mg or Li compounds are the true active species.

SCHEME 1

The purple crystalline compounds (isolated in *ca.* 25% yield by crystallization from n-pentane) are stable at room temperature and probably have structures (4) and (5). This was established by elemental analysis, i.r. spectroscopy (characteristic absorptions of $\eta^5\text{-C}_5\text{H}_5$ groups; specific C-H out of plane deformation modes for the ligands), molecular weight (all compounds are monomeric), and magnetic moments (close to the spin-only value of 1.73 B.M. expected for a Ti^{III} compound Cp_2TiR). The existence of a Ti-C σ bond at the 6-position in the pyridines and at the 2-position in the quinolines was demonstrated by reactions of the compounds with I_2 and $\text{D}_2\text{O-DCl}$. In all cases the expected 6-iodo- or 6-deutero-pyridines and 2-iodo- or 2-deutero-quinolines, respectively were obtained quantitatively (Scheme 2), as established by i.r., mass, and ^1H -

SCHEME 2

n.m.r. spectroscopy. The presence of a co-ordinative Ti-N bond is indicated by the stability of the compounds which is comparable to that of other compounds Cp_2TiR in which Ti and R form a metallocycle as in (6)⁹ and far greater than that of compounds Cp_2TiR with R = alkyl or aryl where Ti is co-ordinatively unsaturated.¹⁰ The new compounds do not react with N_2 even at very low temperatures indicating that in this case Ti is co-ordinatively saturated by internal co-ordination. A related three-membered, internally co-ordinated, titanacycle has recently been described by Fachinetti and Floriani in their work on $\text{Cp}_2\text{Ti-acyl}$ com-

pounds containing Ti^{IV} .¹¹ X-Ray studies showed that this compound had the structure (7).

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