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

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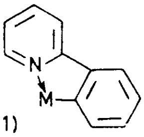
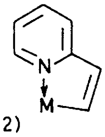
Summary In a new type of metallation reaction 2-substituted pyridines and quinolines are metallated at the 6- and 2-position, respectively by dicyclopentadienylmethyltitanium prepared *in situ*.

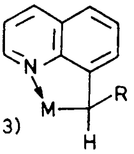
Metallation of heterocyclic amines by several transition metals has been reported. The cyclometallated products formed normally consist of five-membered chelate rings [*e.g.* compounds (**1**)—(**3**)[1-5]]. However, similar metallations have not been described for Ti. The activating properties of compounds Cp$_2$TiR towards unsaturated substrates[6] prompted us to investigate cyclometallation reactions of these compounds with heterocyclic amines analogous to those giving (**1**)—(**3**).



(1)

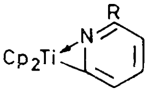


(2)



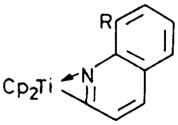
(3)

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$_2$TiMe prepared *in situ* (Cp = η^5-C_5H_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 titanocycle in which the ligands act as bidentate three-electron donors [*e.g.* compounds (**4**) and (**5**)].



(4)

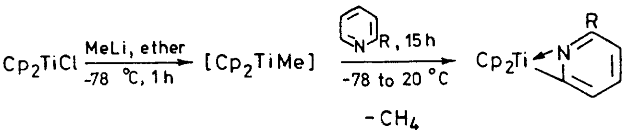
R = Me, Ph, or vinyl



(5)

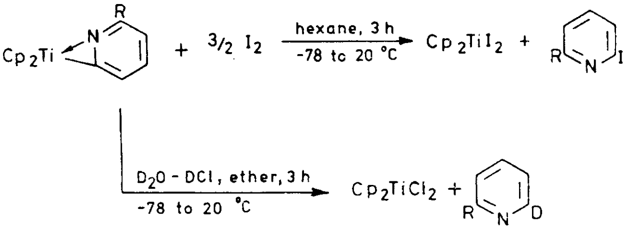
R = H or Me

In a typical reaction Cp$_2$TiCl (made by reduction of Cp$_2$TiCl$_2$ with 1 equiv. of Pr^{i}MgCl[7]) was treated with 1 equiv. of MeLi at −78 °C. After 1 h the Cp$_2$TiMe 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$_2$TiMe. 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]

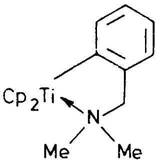


Scheme 1

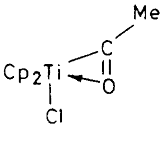
The purple crystalline compounds (isolated in *ca.* 25% yield by crystallization from n-pentane) are stable at room temperature and probably have structures (**4**) and (**5**). This was established by elemental analysis, i.r. spectroscopy (characteristic absorptions of η^5-C_5H_5 groups; specific C–H 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$_2$TiR). 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 D$_2$O–DCl. In all cases the expected 6-iodo- or 6-deuterio-pyridines and 2-iodo- or 2-deuterio-quinolines, respectively were obtained quantitatively (Scheme 2), as established by i.r., mass, and ^{1}H-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$_2$TiR in which Ti and R form a metallocycle as in (**6**)[9] and far greater than that of compounds Cp$_2$TiR 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, titanocycle has recently been described by Fachinetti and Floriani in their work on Cp$_2$Ti–acyl com-



Scheme 2



(6)



(7)

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† The identity of Cp$_2$TiMe as the reactive species was not completely established. It is possible that addition compounds of Cp$_2$TiMe and Mg or Li compounds are the true active species.

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

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