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.

Cyclometallation 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)]. However, similar metallations have not been described for Ti. The activating properties of compounds Cp₂TiR towards unsaturated substrates 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 Cp₂TiMe prepared in situ (Cp = η⁵-C₅H₅). 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 Cp₂TiCl (made by reduction of Cp₂TiCl₃ with 1 equiv. of PrMgCl) was treated with 1 equiv. of MeLi at -78 °C. After 1 h the Cp₂TiMe formed was treated with a slight excess of the heterocyclic amine. A dark green mixture formed, presumably owing to coordination of the Lewis base to the intermediate Cp₂TiMe. On warming to room temperature the colour changed to brown-purple while methane (g.Lc.) 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.

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 η⁵-C₅H₅ 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 η⁶-chelated Cp₂TiR). 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 I₂ and D₂O-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-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 Cp₂TiR in which Ti and R form a metallacycle as in (6) and far greater than that of compounds Cp₂TiR with R = alkyl or aryl where Ti is co-ordinatively unsaturated. The new compounds do not react with N₂ 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 Cp₂Ti-acyl com-

Scheme 2


† The identity of Cp₂TiMe as the reactive species was not completely established. It is possible that addition compounds of Cp₂TiMe and Mg or Li compounds are the true active species.
pounds containing TiIV.11 X-Ray studies showed that this compound had the structure (7).

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