Six-Membered *ortho*-Metallated Ring Systems

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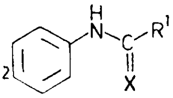
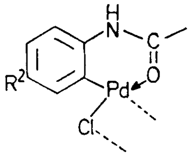
Summary Novel 6-membered *ortho*-metallated ring systems result from the palladation of *N*-aryl-amidines and amides; some reactions of the resultant complexes, which retain the 6-membered metallo-ring, are reported.

CYCLOMETALLATION reactions of aromatic compounds having nitrogen, oxygen, sulphur, or phosphorus in their side chains show a strong tendency to form 5-membered rings.[1,2] Where a choice of position of attack exists, the formation of a 5-membered ring is apparently the dominant factor and in the series $Ph[CH_2]_nNMe_2$[3] metallation occurs only for that compound ($n = 1$) which is able to form a 5-membered ring. 4-Membered rings are known for phosphines,[4] but no 6-membered rings have been reported previously. We find that the palladation products of *N*-aryl-amidines and -amides have such 6-membered *ortho*-metallated rings.

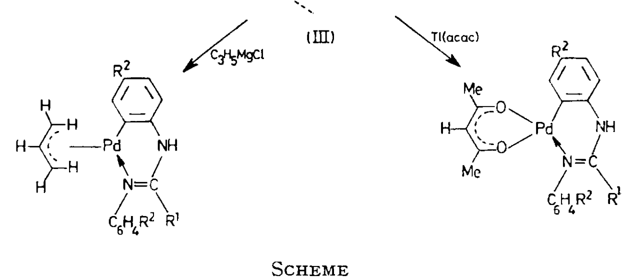


(I) R1=Me, R2=H or Me,
X=O, NPh, or N(*p*-tolyl)



(II) R1 = Me, R2 = H or Me

The amidines [I; $R^1 = Me$; $R^2 = H$ or Me; X = NPh or N(*p*-tolyl)] react with K_2PdCl_4 or $PdCl_2$ in 5:2 aqueous methanol at the reflux temperature to form the grey-green sparingly soluble $[Pd(Am\text{-}H)Cl]_n$† (III). Similarly *N*-arylamide complexes (II; $R^1 = Me$, $R^2 = H$ or Me) are formed, which on methanol extraction yield green-yellow complexes $[Pd(Ad\text{-}H)Cl]_m$† of a lower degree of aggregation than (II). Treatment of (III) with pyridine (Py) yielded yellow $[Pd(Am\text{-}H)Cl]_2$ and white [Pd(Am-H)ClPy]. Some further reactions are given in the Scheme, and involve the replacement of chloro-bridged units by the groups: acetylacetonato-, π-allyl, amidino-, and π-cyclopentadienyl. Mass spectral data demonstrate the mononuclear nature of these complexes and ^1H n.m.r. data at 60 MHz provide evidence for the occurrence of *ortho*-metallated aromatic rings, [5] *e.g.* the η^5-C_5H_5 derivative (IV) in $CDCl_3$ solution, τ 8·20 (3H), 7·75 (3H), 7·60 (3H), 4·67 (5H), 3·10 (2H), 2·90 (4H), and 2·69 (1H). ^1H N.m.r. measurements at 90 MHz show the same type of attachment of the amidine to the metal in (III) [$(CD_3)_2SO$ solution, τ: 8·09 (3H), 7·84 (3H), 7·69 (3H), 3·27 (2H), 2·98 (4H, m), 2·35 (1H), and −0·10 (1H)].



SCHEME

The presence of two potential donor atoms in the side chains of these amidines and amides gives the possibility of

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† Am-H and Ad-H refer to *ortho*-metallated amidines and amides respectively.

either 4- or 6-membered metallo-rings. Four-membered PdC_2N rings are sterically unfavourable,[2] but a 6-membered ring has additional stability arising from reduced steric strain and extensive π-electron delocalisation involving the six ring atoms. The lowering of the amide asymmetrical ν(NCO) stretching frequency [*e.g.* from 1662 cm^{-1} for (*p*-tolyl)NHCOMe to 1610 cm^{-1} for the complex] is consistent with bonding through the oxygen but not the nitrogen of the amide group,[6] and further supports the presence of 6-membered rings.

Two effects have been proposed as the cause of *ortho*-metallation reactions: the presence of bulky substituents which force groups close to the metal, and entropy effects.[2] Although the aryl-amidines and -amides used are relatively bulky, the presence of a delocalised π-system in the aryl side chain appears to be an additional factor necessary for the formation of a 6-membered metallo-ring. Interestingly, attempts to prepare *ortho*-metallated derivatives with oxygen or NMe groups in place of the NH group in (I) were unsuccessful, suggesting that the occurrence of tautomerism may also be an important factor in the formation of 6-membered metallo-rings.

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