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Preliminary communication

REACTIVITY OF *o*-*N*,*N*-DIMETHYLAMINOTOLUENE WITH PALLADIUM(II) COMPOUNDS, CYCLOMETALLATION AND DEMETHYLATION OF THE NITROGEN ATOM

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Summary

o-*N*,*N*-Dimethylaminotoluene (dmat) reacts with Li_2PdCl_4 in methanol to give *trans*-$Pd(mat)_2Cl_2$ (mat = *o*-*N*-methylaminotoluene) by demethylation of the nitrogen. With $Pd(PhCN)_2Cl_2$ in dichloromethane an unstable dimeric adduct of the tertiary amine is obtained. With palladium acetate cyclopalladation occurs by metallation of the *ortho*-methyl group, while reaction with palladium trifluoroacetate affords *trans*-$Pd(dmat)_2(O_2CCF_3)_2$.

Though cyclopalladated compounds are well known for nitrogen-containing ligands with an aromatic carbon, there are still very few compounds of that type in which the palladium carbon σ bond is formed with an aliphatic moiety [1]. The *ortho*-methyl group of the *o*-*N*,*N*-dimethylaminotoluene ligand (dmat) is easily metallated by lithium which can then be substituted by transition metals [2]. During the study of the reactivity of dmat and related amines with palladium, we have isolated a cyclopalladated compound by direct activation of the *ortho*-methyl group of that ligand. The recent report by Shaw et al. [3] of several new examples of cyclopalladation of *N*,*N*-dimethyl-hydrazones or -oximes bearing only alkyl groups prompt us to publish our preliminary results.

Treatment of Li_2PdCl_4 with dmat in methanol in a 1/2 molar ratio at room temperature gives after one day a mixture of metallic palladium, $(PdCl_4)(o\text{-}MePhNMe_2H)_2$ and *trans*-$Pd(mat)_2Cl_2$ (I) in approximately 50% yield (mat = *o*-*N*-methylaminotoluene). The latter two compounds have been fully characterised by infrared and ^1H NMR spectroscopy**. Identification of I was confirmed by synthesis of an authentic sample by treating Li_2PdCl_4 with the secondary amine. There have been several studies of demethylation of tertiary or secondary

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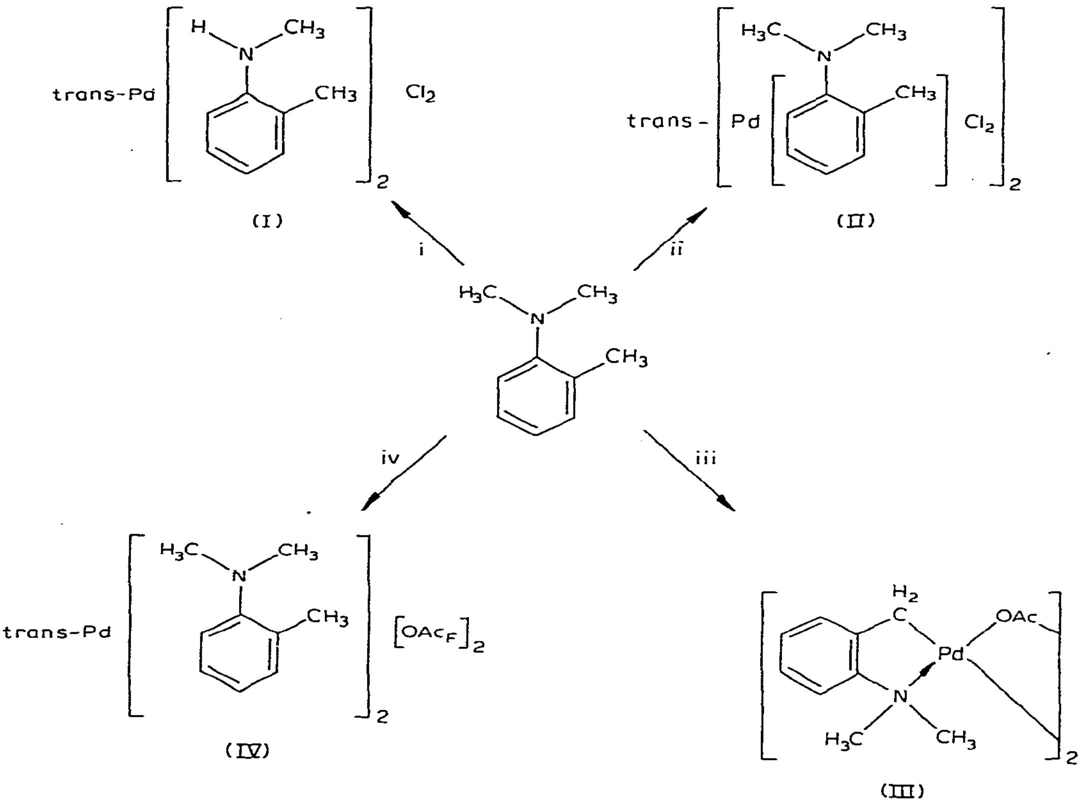
**All the new compounds give satisfactory C, H and N analyses.

amines in the presence of transition metals, but this is the first report of such a reaction in the case of palladium [4]. The mechanism of the reaction is still unclear and we have not been able to determine unambiguously the origin of the proton*. In accordance with other authors, we believe that it comes from the methyl group which is released during the reaction.

Reaction of $Pd(PhCN)_2Cl_2$ with an excess of dmat in the dichloromethane affords II in quantitative yield. Its stereochemistry is supported by the presence in the far infrared of a strong band at 341 cm^{-1} together with strong absorptions at 312 and 298 cm^{-1} which are assigned to stretching vibrations of terminal and bridging chlorine atoms respectively. This complex is not very soluble in organic solvents, and is quite unstable in solution, giving $PdCl_2$ and free dmat. It was thus not possible to characterise it by NMR spectroscopy. To our knowledge such dimeric compounds with nitrogen donor ligands have not yet been reported



(i) Li_2PdCl_4
(ii) $Pd(PhCN)_2Cl_2$
(iii) $[Pd(OAc)_2]_3$, OAc = O_2CCH_3
(iv) $[Pd(OAc_F)_2]_2$, OAc_F = O_2CCF_3

SCHEME 1

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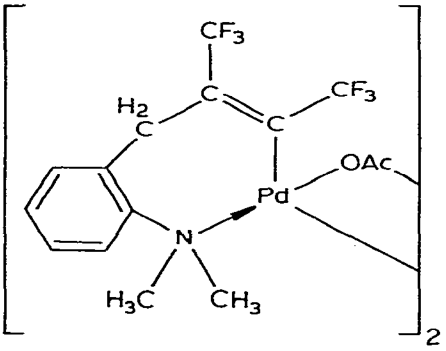
*Reaction in CD_3OD gives a compound containing the unmodified mat ligand, only a part of the N—H having exchanged with the deuterium of methanol-d_4.

for palladium, the only known examples being those of phosphine and arsine ligands [5].

Palladium acetate is known to be a good starting material for synthesis of cyclopalladated species [6]. Thus treatment of palladium acetate with one equivalent of dmat in acetic acid at 50°C affords the desired product (III) in high yield (up to 80%). In the ^{13}C NMR and ^{1}H NMR spectra the metallated methyl gives raise to two signals (22.7 and 23.5 ppm for the ^{13}C spectrum; 3.34 and 3.30 ppm (singlets) for the ^{1}H NMR). This shows that III is a mixture of *cis* and *trans* isomers, as is the chloride analogue which is obtained by treatment with lithium chloride. For the chloride the Pd—Cl stretching frequencies are at 315 and 258 cm^{-1}, close to those of related species [7]. Hexafluorobut-2-yne reacts with III to give the product V, which is similar to previously reported compounds [8].



(V)

The reaction of dmat with palladium trifluoroacetate in diethyl ether gives IV (Scheme 1). Compound IV is stable in solution and the ^{1}H NMR spectrum indicates the signal from the *ortho*-methyl group is shifted from 2.32 (for the free amine) to 3.77 ppm. In NMR terms, this indicates a very strong methyl—palladium non-bonding interaction [9].

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