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Preliminary communication

ORTHOPALLADATION OF CHELATING AROMATIC COMPOUNDS

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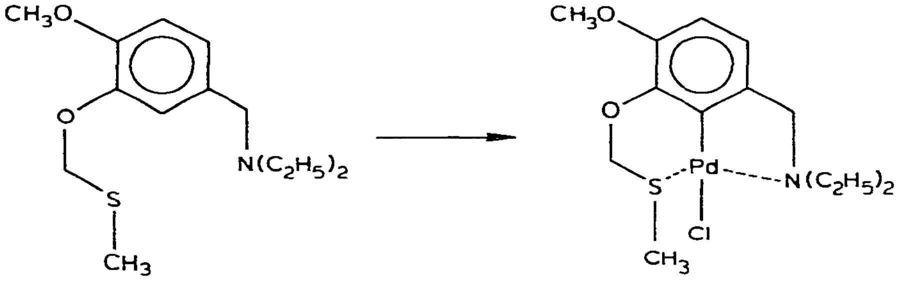
Summary

Aromatic substrates possessing either nitrogen or sulfur ligands *meta* to one another have been found to undergo regiospecific orthometallation with lithium tetrachloropalladate. In some cases, this metallation has been found to be catalyzed by silica gel. This is the first report of the palladation of a phenethyl amine or a benzyl alkyl sulfide.

We have recently shown that tertiary benzylic amines containing a *meta* MTM group, e.g., I, undergo very rapid and regiospecific orthopalladation to give chelated complexes like II [1]. It had previously been found that tertiary phenethyl amines do not undergo orthopalladation with lithium tetrachloropalladate (LTP) [2]. We have confirmed this finding, and have also learned that a single MTM group does not direct orthopalladation; i.e., when phenol MTM (III) was treated with LTP, no orthopalladation was observed [1,3]. The signif-



(I) (II)

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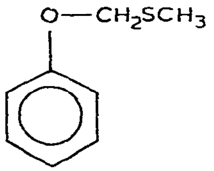
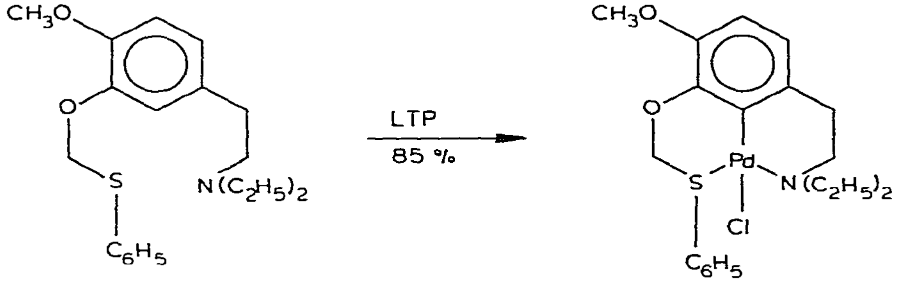


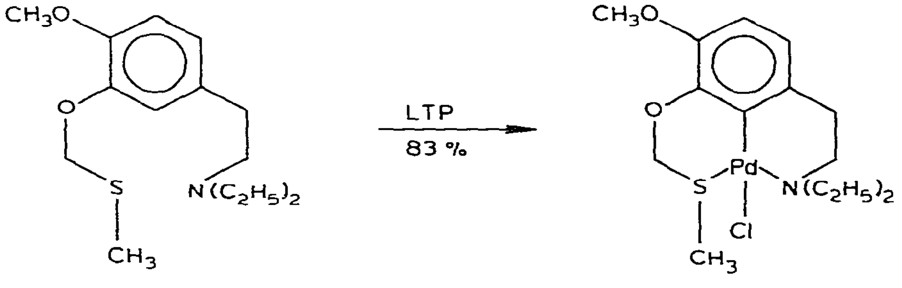
(III)

icant rate enhancement observed for the metallation of I led us to explore the possibility of metallating phenethyl amines and benzylic sulfides containing chelating ligands in the *meta* position.

When PTM phenethyl amine IV* [4] was treated with LTP in anhydrous methanol at 0°C in the presence of diisopropylethylamine there was an immediate precipitation of a yellow solid. Upon isolation, NMR analysis indicated that metallation had occurred to give V. Treatment of the MTM phenethylamine VI [5] with LTP as before gave the metallated product VII. Both



(IV) (V)



(VI) (VII)

reactions appeared to be essentially quantitative although purification reduced the yield by 10—15%. The isolated yield** of pure V was 85%; the yield of pure VII was 83%.

When the sulfide VIII*** was added to a methanolic LTP solution an im-

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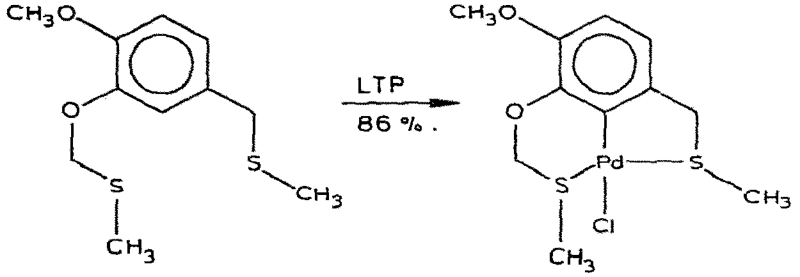
*Compounds IV, V, VII, VIII, IX, X, XI, XIII, XIV, XVI, XVII and XVIII were characterized by complete (IR,NMR,MS) spectral analysis along with correct (±0.3) combustion analysis.

**All yields refer to isolated, spectrally and chromatographically homogeneous materials.

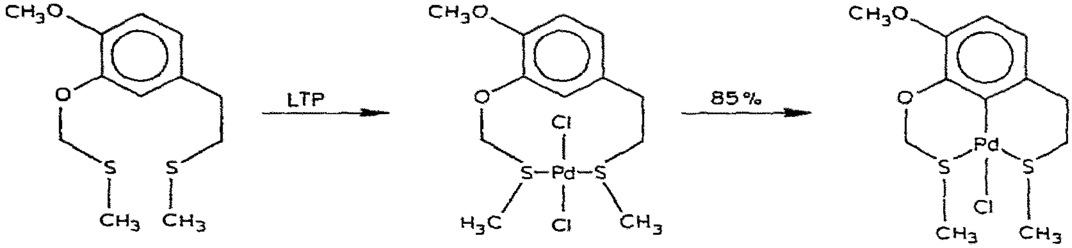
***Compounds VIII, XVI and XVII were prepared using conventional methodology from the MTM ether [6] of isovanillin.

mediate yellow precipitate of the metallated complex IX was obtained in 85% yield.



(VIII) (IX)

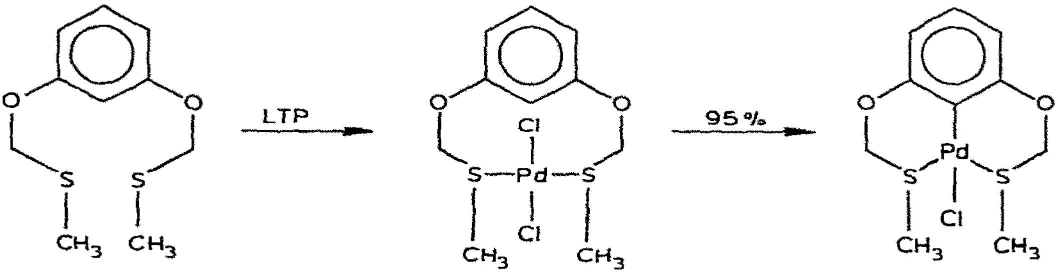
However, upon treatment of phenethyl sulfide X [4] with LTP only a small amount of complex XI was formed along with a substantial amount of the bis-coordinated species XII. When TLC separation of XI and XII was attempted, it became apparent that XII was converted to XI in the presence of silica gel.



(X) (XII) (XI)

The action of silica gel was confirmed by treating X with LTP, then allowing the resulting mixture of XI and XII to stand in chloroform solution for 3 days at 25°C. After this time complete palladation had occurred to give XI in 85% yield.

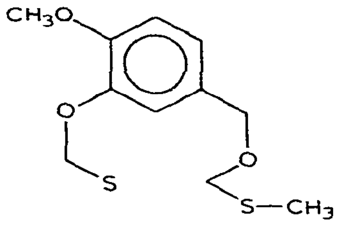
Silica gel played an equally dramatic part in the palladation of XIII [5] to give XIV in 95% yield. Two metallation reactions of XII were run simultane-



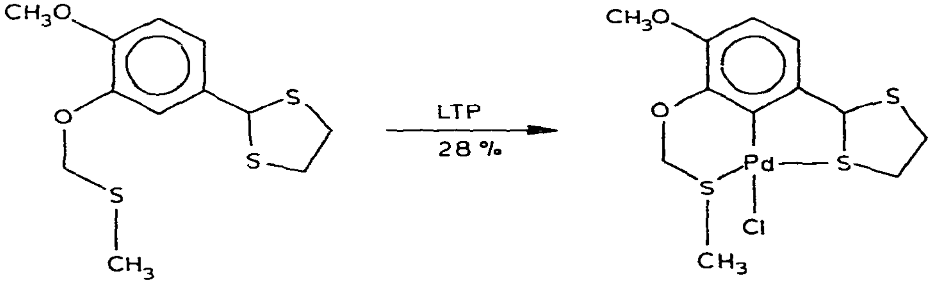
(XIII) (XV) (XIV)

ously; one contained silica gel, the other did not. After 24 h at room temperature, the mixture containing silica gel contained mostly XIV, whereas the reaction mixture without silica gel contained primarily complex XV.

Attempted metallation of XVI and XVII did not give orthopalladated com-



(XVI)



(XVII)

(XVIII)

plexes cleanly. Treatment of compound XVI with LTP gave rise to several products, but no orthometallated material could be isolated. Complex XVIII was isolated by TLC on silica gel, but only in 28% yield. The low yield of XVIII may result from competitive interaction of the three sulfur atoms with the palladium atom.

These are the first reported examples of orthopalladation of aromatic sulfides or phenethylamines [6]. These results indicate for the first time that the electrophilic substitution by palladium(II) may be a Lewis acid catalyzed phenomenon.

Further, these results seem to indicate that metallation of a substrate containing a *meta* coligand is useful only for the formation of six-five and six-six fused ring palladocycles.

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