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DESULPHURIZATION OF THIOANILIDES VIA PALLADIUM COMPLEXES

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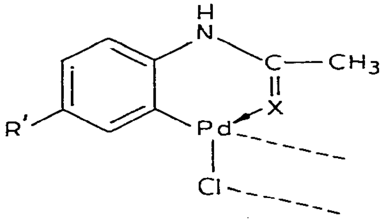
Summary

Thioanilides (ArNHCSR) react with disodium tetrachloropalladate at room temperature to give bidentate complexes of structural type $[(ArN{=}C(R)S)PdCl]_2$. These complexes are quantitatively converted to amides by wet dimethylsulphoxide at room temperature. The desulphurization of thioanilides can be effected catalytically as well.

Introduction

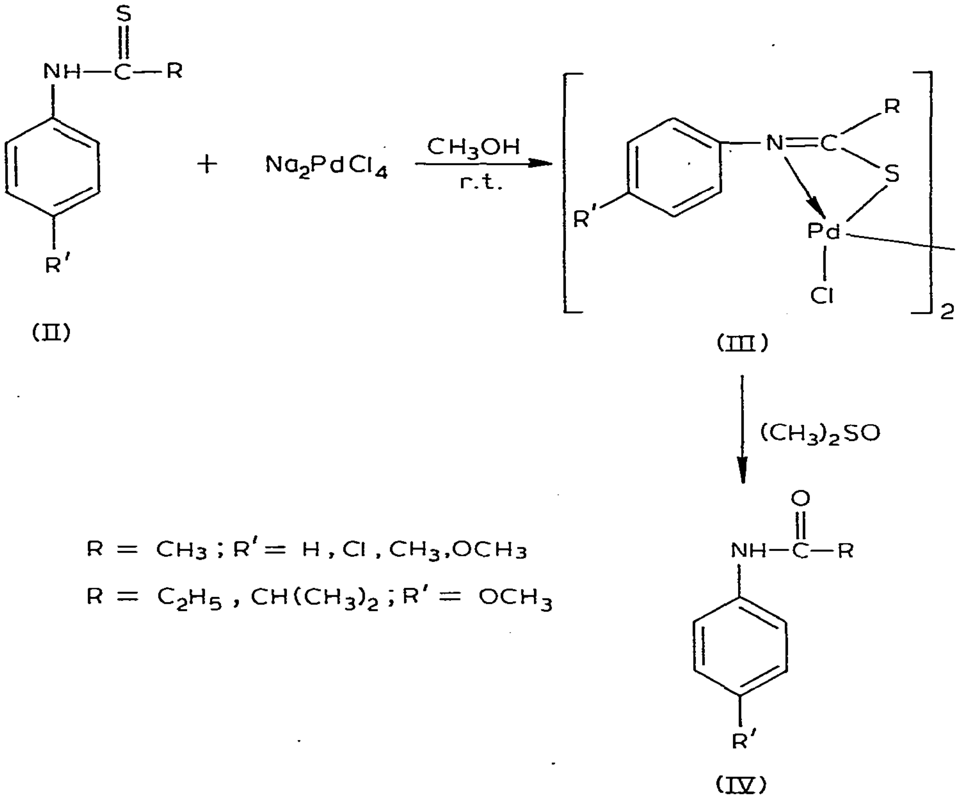
Intramolecular *ortho*-metalation reactions is one of the most active research areas in transition metal organometallic chemistry [1]. The majority of *ortho*-metalated complexes contain the metal in a five-membered ring, although four-membered ring metallocycles are also known. Several years ago, Cameron and Kilner [2] reported that *N*-arylamidines and amides react with palladium(II) compounds to form novel six-membered ring *ortho*-palladated complexes [I, X = O, NPh, N(*p*-tolyl)]. In connection with our research on sulphur-donor ligand *ortho*-metalated complexes [3] and thioamide complexes [4], we investigated the reactions of thioacetanilides with sodium tetrachloropalladate with the expectation that sulphur analogs of I (X = S) would be produced. We now wish to report that such reactions result in the formation of nitrogen donor ligand complexes, and that these complexes undergo desulphurization very readily.



(I)

Results and discussion

Treatment of a thioacetanilide [II, R = CH_3; R′ = H, Cl, CH_3, OCH_3] with an equimolar amount of disodium tetrachloropalladate in methanol at room temperature gave III in 46—72% yield (Table 1). The thioanilides II, R = C_2H_5, $CH(CH_3)_2$; R′ = OCH_3, reacted with the palladium compound in an identical fashion. The structure of these complexes was assigned on the basis of analytical and spectral data (Table 1).



Conversion of II to III resulted in the disappearance of the NH stretching absorption at 3300—3400 cm^{-1} in the infrared (CH_2Cl_2), and appearance of a new intense band at 1534—1542 cm^{-1} assigned to the carbon—nitrogen stretching vibration. The proton magnetic resonance spectra [$(CD_3)_2SO$] of the thioacetanilides [II, R = CH_3] showed a singlet signal at δ 2.50—2.60 ppm due to the methyl protons. The signal for these protons occurred at δ 3.07—3.14 ppm in the PMR spectra of III. Similar downfield shifts were noted for III, R = C_2H_5, $CH(CH_3)_2$; R′ = OCH_3 [i.e. for the proton(s) on the carbon adjacent to that bearing the sulphur and nitrogen atoms]. A normal aromatic pattern (i.e. no *ortho*-metalation) was observed in the PMR spectra of all of the complexes. The carbon magnetic resonance spectrum of III [R = CH_3, R′ = OCH_3] gave signals at δ 36.6 and δ 56.5 ppm due to the methyl and methoxy carbons, respectively (each appeared as a quartet in the partially decoupled spectrum).

It was while the PMR spectra were recorded that we noticed the conversion

TABLE 1

YIELDS, ANALYTICAL, AND SPECTRAL DATA FOR III

R = , R′ =	Yield [a] (%)	Anal.: Found (calcd.) (%)				IR, ν_{CN} [b] (cm^{-1})	NMR, δ [c] (ppm)
		C	H	N	Pd		
CH_3, H	60	32.77(32.90)	3.03(2.76)	4.24(4.80)		1540	3.15 (s, 3 H, CH_3), 7.27 (m, 5 H, aromatic)
CH_3, Cl	55	29.48(29.43)	2.56(2.16)	3.75(4.29)	32.30(32.59)	1534	3.04 (s, 3 H, CH_3), 7.53 (s, 4 H, aromatic)
CH_3, CH_3	46	34.97(35.31)	3.51(3.29)	4.73(4.58)		1540	2.33 (s, 3 H, CH_3 attached to aromatic carbon), 3.12 (s, 3 H, CH3), 7.23 (d, 2 H, J = 8 Hz, protons on carbons *ortho* to the methyl containing carbon), 7.47 (d, 2 H, other aromatic protons)
CH_3, OCH_3	72	33.34(33.56)	3.27(3.13)	3.90(4.35)	33.40(33.03)	1542	3.14 (s, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 7.04 (d, 2 H, J = 8 Hz, protons on carbons *ortho* to the methoxy bearing carbon), 7.46 (d, 2 H, other aromatic protons)
C_2H_5, OCH_3 [d]	48	34.53(35.73)	3.08(3.60)	3.48(4.17)		1535	1.60(t, 3 H, CH_3), 3.40 (q, 2 H, CH_2), 3.82 (s, 3 H, OCH_3), 6.85 (d, 2 H, J = 9 Hz, protons on carbons *ortho* to the methoxy bearing carbon), 7.60 (d, 2 H, other aromatic protons)
$CH(CH_3)_2$, OCH_3	46	38.11(37.73)	3.66(4.03)	3.69(4.00)		1540	1.37 (d, 6 H, J = 6 Hz, $CH(\underline{CH_3})_2$), 3.20 (m, 1 H, $\underline{CH}(CH_3)_2$), 3.80 (s, 3 H, OCH_3), 6.76 (d, 2 H, J = 9 Hz, protons on carbons *ortho* to the methoxy bearing carbon), 7.43 (d, 2 H, other aromatic protons)

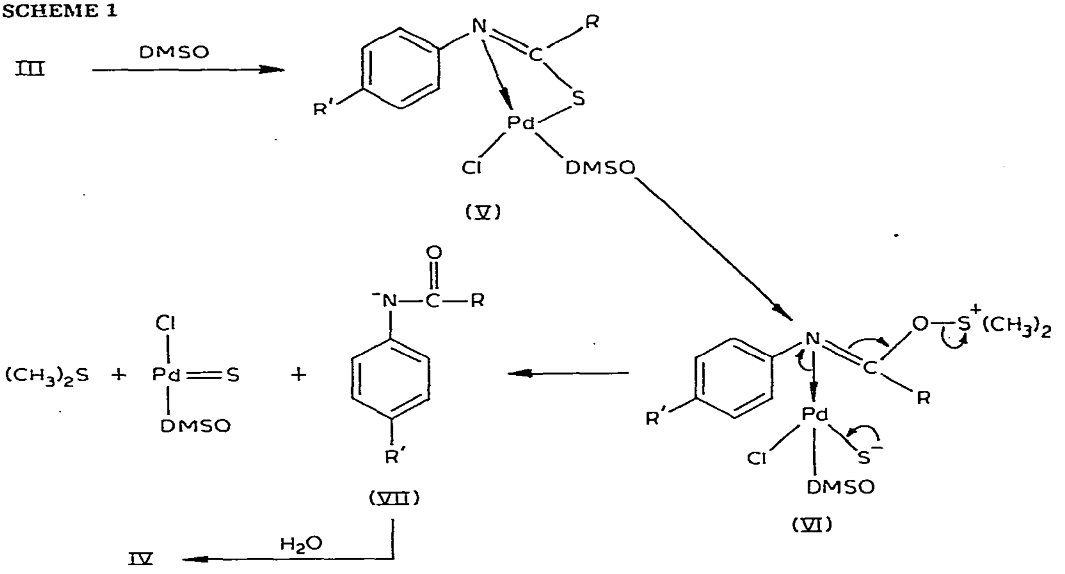
[a] Yield is based on reactant thioamide. [b] In CH_2Cl_2. [c] $(CD_3)_2SO$ with tetramethylsilane as internal standard. [d] The analytical data for this complex are not satisfactory. However, the spectral properties are in accord with structure III, and desulphurization ($(CH_3)_2SO$) gives the amide in 98% yield.

of the bidentate complex III to the amide IV. Only signals due to III were observed if a freshly prepared sample [in$(CD_3)_2SO$] was used for the PMR determination. However, quantitative conversion of the complex to the amide (IV) occurred if the dimethyl sulphoxide-d_6 solution was left overnight at room temperature. Of course, the same conversion occurs with commercial dimethyl sulphoxide. The amides (IV) were identified by comparison of melting points and spectral data (IR, NMR, MS) with authentic samples.

The conversion of thioamides to amides (IV) can be achieved catalytically using a 10/1 ratio of thioanilide/Na_2PdCl_4 in dimethyl sulphoxide (e.g. II, IV, $R = CH_3$, $R' = OCH_3$). However, the reaction requires longer reaction times (2—4 days).

A possible mechanism for the desulphurization reaction is shown in Scheme 1.

SCHEME 1



Initial cleavage of the Pd—Cl bridge of III by dimethyl sulphoxide would give V. Such bridge cleavage reactions by a variety of Lewis bases are known for related systems [5,6]. Attack by a second molecule of dimethyl sulphoxide at the carbon atom of the carbon—nitrogen double bond of V would afford VI. Decomplexation of the latter would produce the amide anion VII, which on protonation gives IV.

Experimental

General

Elemental analyses were performed by Drs. F. and E. Pascher, Bonn, G.F.R; Butterworths Microanalytical Consultancy, Ltd., Teddington, England; and M-H-W Laboratories, Phoenix, Arizona. Infrared spectra were recorded on a Unicam SP1100 spectrometer, equipped with a calibration standard. Proton magnetic resonance spectra were determined using a Varian T-60 or HA-100 spectrometer, while a FT-80 spectrometer, operating in the fully or partially decoupled mode, was used for carbon magnetic resonance spectra.

General procedure for reaction of thioanilides (II) with Na_2PdCl_4

To a stirred methanol solution (50 ml) of Na_2PdCl_4 [0.50 g, 1.70 mmol, obtained commercially (Alfa/Ventron), or better, freshly prepared from palladium dichloride and sodium chloride] was added, in small portions, an equimolar amount of the thioanilide. The reaction mixture was stirred for 30 min at room temperature and then filtered. The precipitate (III) was washed successively with methanol, ethanol, water, diethyl ether, and then dried in vacuo. The filtrate was found to contain thioanilide and additional III.

General procedure for desulphurization of III

Complex III was dissolved in dimethyl sulphoxide (ca. 10% solution) and the solution was left overnight at room temperature. The mixture was poured into water and the resulting amide (IV) was filtered, and then dried. Quantitative yields of IV were obtained.

Acknowledgements

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