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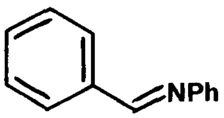
CYCLOPALLADATION AS A ROUTE TO CATIONIC CONDENSED RING SYSTEMS CONTAINING ISOTHIAZOLE OR 1,2-DITHIOLE NUCLEI

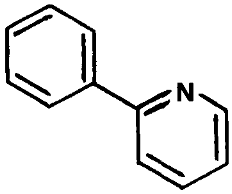
By Robert C. Davis, Trevor J. Grinter, Derek Leaver* and Robert M. O'Neil
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ.

Abstract. Isothiazolium and 1,2-dithiolylium salts containing fused rings have been synthesised from cyclometalated palladium complexes.

The process of cyclometalation in transition metal complexes has recently been reviewed[1] and its potential as a route to metal-free heterocycles has been realised in the synthesis of indazolones,[2,3] dihydroisoindolones,[3] quinolones,[4] dihydrobenzo[c]thiophenones,[5] and cyclopenta[c]cinnolines.[6] Hitherto, however, the formation of such heterocycles has involved a replacement of the transition metal atom by one or more carbon atoms derived from carbon monoxide[2,3,4,5] isocyanides,[7] hexafluorobut-2-yne,[4] or cyclopentadiene.[6] We now report two variants of a general procedure for the replacement of palladium, in cyclopalladated complexes, by sulphur, thus providing a route to a series of novel isothiazolium and 1,2-dithiolylium salts containing condensed ring systems. The organic starting materials used in this work are shown in formulae (A)-(G) which may be represented collectively by the general formula (1)[8] where the atom (X) is nitrogen or sulphur.



(A)



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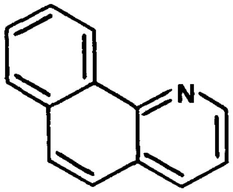

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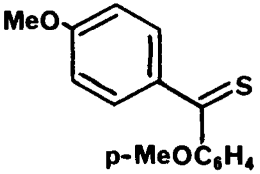

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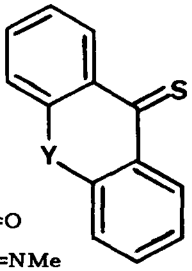
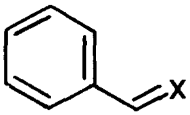


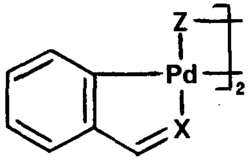
(E) : Y=O
(F) : Y=NMe

(G)

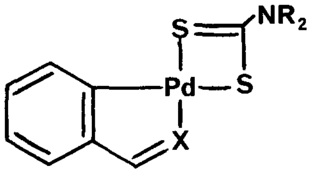
Reaction of substrates (A)[9]-(C) with palladium acetate or of (D)[10]-(G) with sodium or lithium tetrachloropalladate gave the dimeric complexes (2; Z=OAc or Cl)[11] but these, for various reasons, did not react cleanly with reagents considered likely to introduce sulphur. For efficient replacement of palladium, it was necessary first to convert the dimeric complexes (2) into monomeric dithiocarbamato-complexes (3; R=Me or iPr)[12] by reaction with a tetraethylammonium N,N-dialkyldithiocarbamate in chloroform [for (2; Z=OAc)] or with the corresponding sodium salt in N,N-dimethylformamide [for (2; Z=Cl)]. The complexes (3A-E; R=Me) reacted with thiocyanogen, in chloroform, to give the thiocyanato-compounds (4A-E),[13] which remained in solution, together with the highly insoluble dimeric palladium complex, $[Pd(Me_2NCS_2)SCN]_2$. Treatment of the thiocyanates (4) with perchloric acid gave the isothiazolium perchlorates (5A-C) and the 1,2-dithiolylium perchlorates (5D and 5E) (Table).



(1)



(2)



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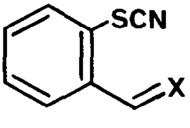

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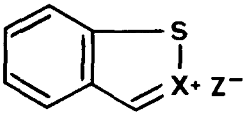
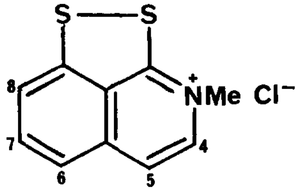
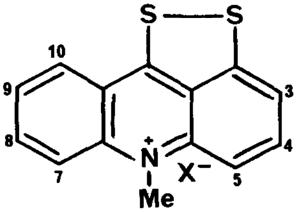


(5)



(6)



(7)

The complexes (3F) and (3G) reacted with thiocyanogen to give products, not yet completely identified, in which the heterocyclic ligand remained bound to palladium. In these cases, however, the salts (6) and (7) (Table) were obtained by slowly adding solutions of the dithiocarbamato-complexes (3F and 3G; R=iPr), in chloroform, to a two-fold excess of morpholine-N-sulphenyl chloride[14] in the same solvent. Removal of the chloroform by

Table: Data for the Salts (5)

Compound[a]	Yield[b] (%)	M. p. (°C)	δ ^{1}H (ppm)[c]
(5A; Z=ClO_4)	34	212° (dec)	7.7-8.2 (7H, m) 8.34 (1H, d) 8.58 (1H, d) 9.74 (1H, s)
(5B; Z=ClO_4)	25	168-169°	7.8-8.2 (4H, m) 8.40-8.62 (2H, m) 8.80 (1H, dd) 9.26 (1H, d)
(5C; Z=ClO_4)	58	140° (dec)	8.1-8.7 (7H, m) 9.54 (1H, dd)
(5D; Z=ClO_4)	90	220° (dec)	4.01 (3H, s) 4.16 (3H, s) 7.30 (2H, d) 7.54 (1H, dd) 7.84 (1H, d) 7.88 (2H, d) 8.34 (1H, d)
(5E; Z=ClO_4)	48	235° (dec)	7.65-8.5 (m)
(6)	91	decomp. 230-235°	4.16 (3H, s) 7.86 (1H, d, H-5) 7.92 (1H, d, H-8) 8.18 (1H, t, H-7) 8.30 (1H, d, H-6) 8.35 (1H, d, H-4)
(7; X=ClO_4)	81	266-268° (dec)	4.36 (3H, s) 7.82 (1H, t, H-9) 8.07 (1H, d, H-3) 8.17 (1H, d, H-5) 8.31 (1H, td, H-8) 8.34 (1H, t, H-4) 8.44 (1H, d, H-7) 8.47 (1H, d, H-10)

[a] Satisfactory elemental analyses were obtained in all cases. [b] Overall yields from the dithiocarbamato-complexes (3). [c] Spectra of (5A-E) measured in CF_3CO_2H at 100 MHz; spectra of (6) and (7) in Me_2SO-d_6 at 360 MHz.

evaporation left solid residues containing the chloride salt (6) or (7), di(N-morpholinyl) sulphide, and the dimeric palladium complex, $[Pd(iPr_2NCS_2)Cl]_2$. Treatment of these mixtures with pyridine, in dichloromethane, converted the dimeric complex into the soluble monomeric derivative, $Pd(iPr_2NCS_2)(C_5H_5N)Cl$, leaving the salts as the only insoluble products.

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References and Notes

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8. Products derived from these substrates are specified by using both a numeral and a letter. For example, (2A) indicates the complex of type (2) derived from substrate (A).
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11. The substrates (B) and (C) were known to give chloride-bridged complexes (see ref. 1) but the corresponding acetate-bridged complexes are new. Substrates (E)-(G) had not previously been cyclopalladated. Yields of dimeric complexes (2) were 75-95% and satisfactory elemental analyses were obtained for those that are new.
12. Satisfactory elemental analyses were obtained for all dithiocarbamato-complexes (3) and ^{1}H n. m. r. and mass spectrometric data were consistent with the assigned structures. Yields of these complexes were 50-80%.
13. Satisfactory elemental analyses were obtained for the thiocyanato-compounds (4B) and (4C). The other thiocyanates, being less stable, were characterised by i. r. and mass spectrometry (M^+ and strong M^+-CN fragment) before being converted into the salts (5). Accurate mass measurements (M^+) were obtained for (4A) and (4E).
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