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Preliminary communication

REACTION OF PALLADIUM DIENE AND 2-PHENYLAZOPHENYL COMPLEXES WITH SOME SULPHUR-CONTAINING NUCLEOPHILES

M.C. CORNOCK, R.C. DAVIS, D. LEAVER and T.A. STEPHENSON*
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)

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Summary

The syntheses of $[PdX(S—S)]_2$ [$X = Cl, Br$; $(S—S)^- = {}^-S_2CNR_2, {}^-S_2COR$] via $[C_8H_{12}PdCl_2]$ or $[PhN_2C_6H_4Pd(OCOCH_3)]_2$ are reported and some reactions of these compounds are described.

The activation of olefins towards nucleophilic attack by coordination to palladium(II) is now well established and of commercial importance. Extensive studies on reactions of $[dienePdCl_2]$ complexes with various nucleophiles containing oxygen or nitrogen donor atoms (e.g. ^-OR, ^-OCOR, NH_2R etc.) show that, usually, attack on one of the coordinated double bonds occurs to give substituted alkenyl complexes [1].

We now report that the reaction between $[C_8H_{12}PdCl_2]$ (C_8H_{12} = 1,5-cyclooctadiene) and S-containing nucleophiles such as *N,N'*-dialkyl- and *O*-alkyl-dithiocarbamate anions $(S—S^-)$ (1 : 1 molar ratios) leads, in contrast, to complete diene displacement with formation of compounds of empirical formula $[PdCl(S—S)]_n$**. Molecular weight measurements in chloroform reveal that $n = 2$ and thus, these compounds are best formulated with the square planar, chloride bridged structure (I). With excess $(S—S)^-$, $[Pd(S—S)_2]$ is formed. The probable mechanism of formation is given in eq. 1.

As outlined in Scheme 1 for $(S—S)^- = {}^-S_2CNR_2$, these dimers prove to be excellent precursors for a variety of reactions. For example, the chloride bridges are readily cleaved by a wide range of Lewis bases (L) to give the monomeric $[PdCl(S_2CNR_2)L]$ (II) ($L = PPh_3$, $AsPh_3$, $SbPh_3$, C_5H_5N, CO etc.). For L = tertiary phosphine, these complexes can also be synthesised by reaction of $[PdCl_2(PR_3)]_2$ with either $Me_2SnCl(S_2CNR_2)$ [3] or Na(S—S) ($(S—S)^- = {}^-S_2CNR_2$ [3,4], ^-S_2COR [4], $^-S_2PR_2$ [4]) but, with weaker Lewis

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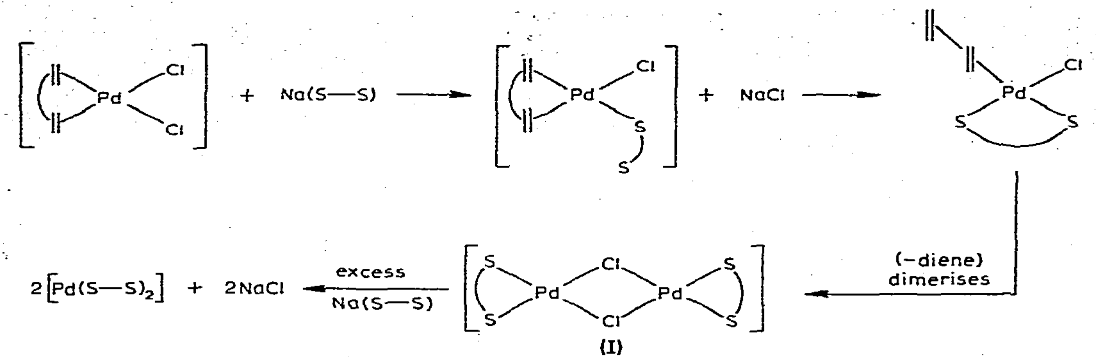
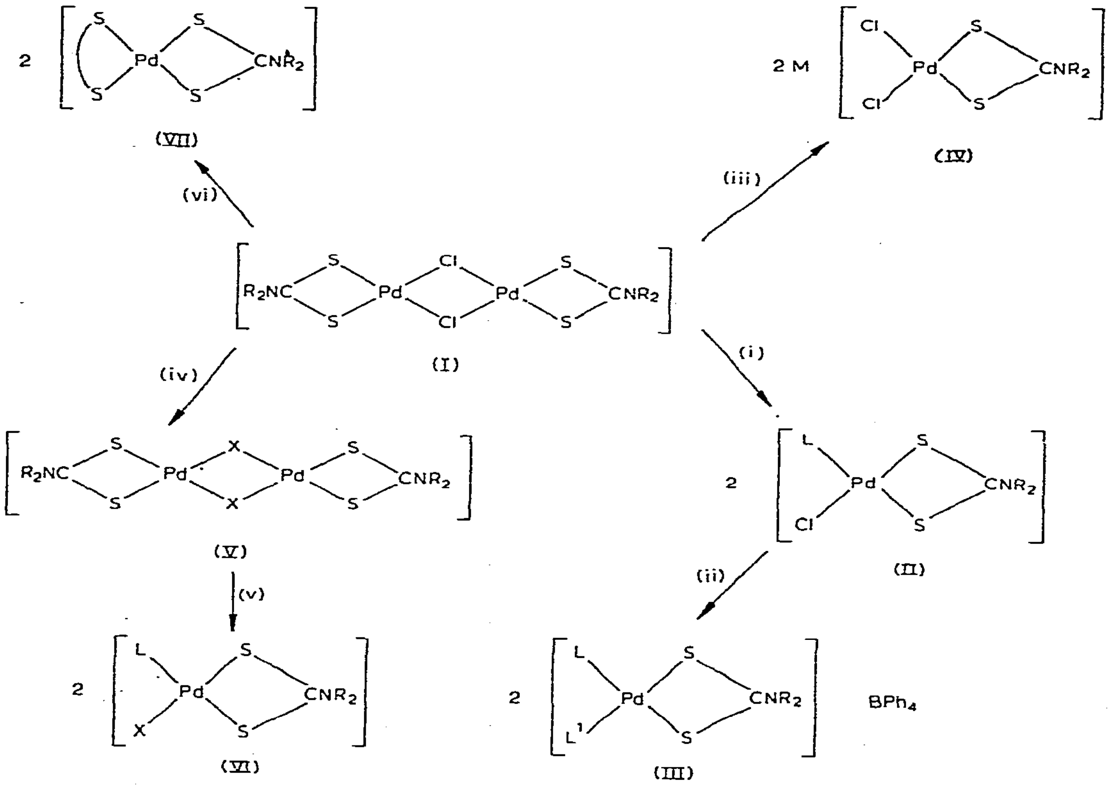
[*] To whom correspondence should be addressed.

[**] With the exception of CF_3S^- [2], this appears to be the first reported reaction between anionic sulphur-containing nucleophiles and $[dienePdCl_2]$ compounds.



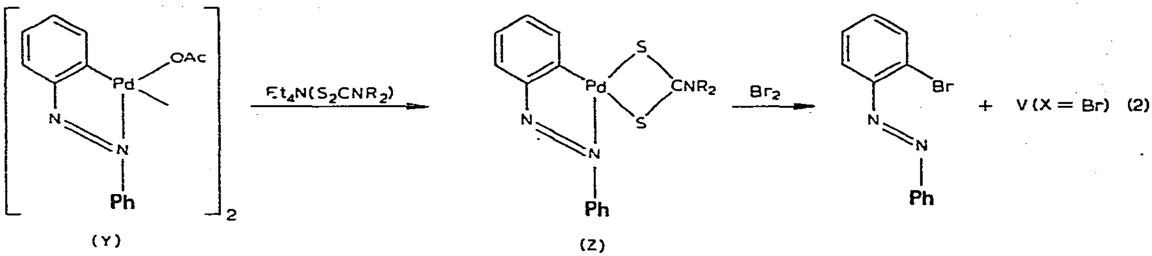
(1)

bases in the coordination sphere, only $[Pd(S{-}S)_2]$ are formed by this route. Reaction of II with $AgBF_4$ in tetrahydrofuran, followed by addition of another Lewis base (L′) and $NaBPh_4$ readily gives the mixed ligand complexes $[Pd(S_2CNR_2)LL']BPh_4$ (III) (e.g. L = PPh_3, L′ = $AsPh_3$, C_5H_5N etc). Similarly, reaction of I with Ph_3PhCH_2PCl/HCl gives the anionic $Ph_3PhCH_2P[PdCl_2(S_2CNR_2)]$ (IV). The related $[Pd(S_2COR)_3]^-$ has been described elsewhere [5].



SCHEME 1. (i) L = PPh_3, $AsPh_3$, $SbPh_3$, C_5H_5N, CO etc.; (ii) L = PPh_3; L′ = $AsPh_3$, C_5H_5N etc.; (iii) M = $Ph_3PhCH_2P^+$; (iv) X^- = Br^-, I^-, ^-SPh; (v) L = PPh_3, X = ^-SPh; L = PPh_3, X = Br^-; (vi) $(S{-}S)^-$ = $^-S_2PMe_2$, $^-S_2COEt$.

The chloride bridges in I can be readily exchanged for Br^-, I^-, PhS^- (X^-) by treatment with the corresponding lithium or sodium salt, giving $[PdX(S_2CNR_2)]_2$ (V). The compound V with X = Br can also be prepared from the (2-phenylazophenyl)dithiocarbamato complex (Z) by treatment with bromine, the 2-phenylazophenyl ligand being removed as 2-bromoazobenzene. The complexes Z are readily obtained by reaction of the known acetate complex Y [6] with $Et_4N(S_2CNR_2)$ (1:2 molar ratio) (eq. 2).



The related thiol bridged complex $[Pd(S\text{-}t\text{-}Bu)(S_2CNEt_2)]_2$ has been synthesised by reaction of $[Pd(S\text{-}t\text{-}Bu)(S_2CS\text{-}t\text{-}Bu)]_2$ [7] with Et_2NH [8]. Reaction of these compounds with $PMePh_2$ is reported to give $[Pd(S\text{-}t\text{-}Bu)(S{-}S)PMePh_2]_n$, originally formulated from ^1H NMR studies as five coordinate dimers [8] *. However, we have found that reaction of $[Pd(SPh)(S_2CNEt_2)]_2$ with PPh_3 gives the red, crystalline monomeric $[Pd(SPh)(S_2CNEt_2)PPh_3]$ (VI).

Finally, preliminary studies indicate that reaction of $[PdCl(S_2CNR_2)]_2$ with other dithioacid anions gives the mixed $[Pd(S_2CNR_2)(S{-}S)]$ (VII) complexes ($S{-}S^- = {}^-S_2PR_2, {}^-S_2COR$)** and reactions of these compounds with Lewis bases are now in progress.

Acknowledgement

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References

1 For detailed references, see P.M. Henry, Advan. Organometal. Chem., 13 (1975) 363; M. Green in M.T.P. International Review of Science Inorganic Chemistry, Vol. 6, Series 1, 1972, p. 183.
2 R.B. King and A. Efraty, Inorg. Chem., 10 (1971) 1376.
3 N. Sonoda and T. Tanaka, Inorg. Chim. Acta, 12 (1975) 261.
4 M.C. Cornock and T.A. Stephenson, Inorg. Nuclear Chem. Letters, submitted for publication.
5 M.C. Cornock, D.F. Steele and T.A. Stephenson, Inorg. Nuclear Chem. Letters, 10 (1974) 785.
6 J.M. Thompson and R.F. Heck, J. Org. Chem., 40 (1975) 2667.
7 J.A.M. Andrews, J.P. Fackler Jr. and D. Coucouvanis, Inorg. Chem., 11 (1972) 494.
8 J.A.M. Andrews, Ph.D. thesis, Case Western Reserve University, 1971.

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*Very recently, Professor Fackler (private communication) has suggested that these compounds might be monomeric but unfortunately, they could isolate no solids to confirm this statement unequivocally.

**All the compounds reported in this note have been characterised satisfactorily by elemental analyses, molecular weight determinations and ^1H NMR spectroscopy.