Intramolecular Rearrangement of *NN'*-Diaryldi-imidosulphur Complexes of Zerovalent Platinum to a Compound of Bivalent Platinum Involving N=S Bond Cleavage and Concomitant Hydrogen Migration and N-C(aryl) Bond Formation; *X*-Ray Crystal Structure of One of the Products

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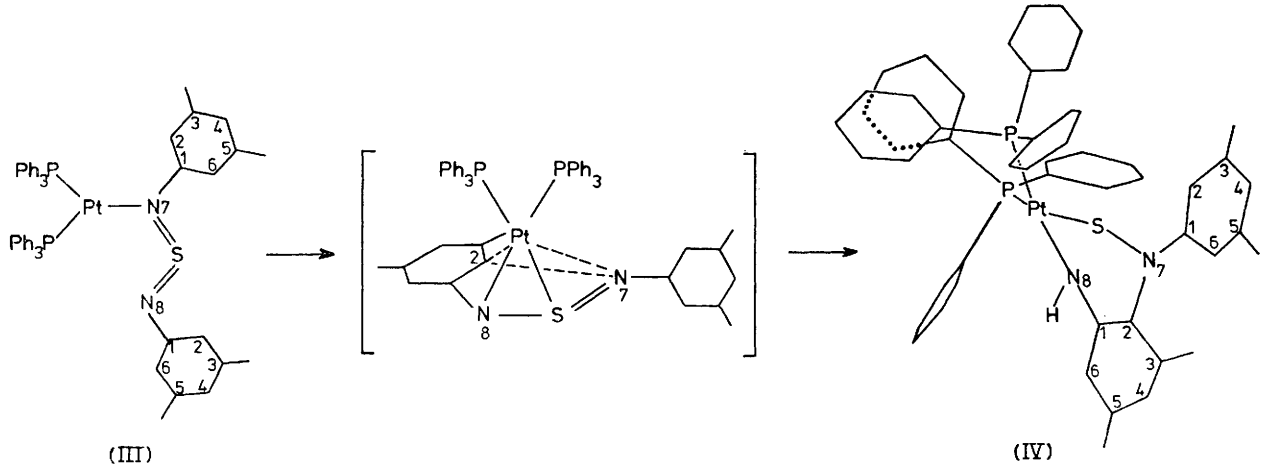
Summary Reaction of $\mathrm{Pt(PPh_3)_2(C_2H_4)}$ with *NN'*-diaryldi-imidosulphur ligands affords the new compounds $[\mathrm{Pt(PPh_3)_2}$(*NN'*-diaryldi-imidosulphur)] (aryl=*p*-tolyl, *p*-chlorophenyl, or *m,m'*-xylyl), which rearrange, as shown by spectroscopy (n.m.r., i.r., u.v.) and a single-crystal structure determination, to a bivalent platinum complex by way of N=S bond breaking, N–C(aryl) bond formation, and hydrogen migration.

The co-ordination properties of *NN'*-dialkyl- and -diaryl-di-imidosulphur groups[1] and the recent interesting chemical behaviour of the novel *SNN'*-substituted di-imidosulphur compounds of $\mathrm{Li^I}$, $\mathrm{Mg^{II}}$, $\mathrm{Cu^I}$, $\mathrm{Ag^I}$, $\mathrm{Rh^I}$, and $\mathrm{Pd^{II}}$ [2] prompted us to investigate the interaction of di-imidosulphur ligands with zerovalent metal complexes of the Ni-triad, as co-ordination *via* the cumulene double bonds and subsequent activation might be feasible.

We report here the novel monomeric complexes $[\mathrm{Pt(PPh_3)_2(ArN{=}S{=}NAr)}]$ [Ar=*p*-tolyl (I), *p*-chlorophenyl (II), and *m,m'*-xylyl (III)], which were prepared from $[\mathrm{Pt(PPh_3)_2(C_2H_4)}]$ and the appropriate *NN'*-diaryldi-imidosulphur compounds in ether. The most likely structure involves three-co-ordinated Pt(0) to which the di-imidosulphur ligand is probably bonded *via* one of the N-atoms, while the ligand itself is in the *trans,trans*-configuration (Figure). This proposal is based on the following observations: i, the π–π^* transitions of the ligand at *ca.* 425 nm do not change upon co-ordination, while ν_s(NSN) increases slightly, *e.g.* from *ca.* 950 to 970 $\mathrm{cm^{-1}}$ for (III), which indicates that there is no strong interaction of the metal with the N=S=N π-bonds. An alternative structure in which Pt is bonded to one of the N=S double bonds is therefore very unlikely, as a lowering of the ν_s(NSN) frequency and a large change in the u.v. spectra should be observed in that case. ii, the ^{1}H n.m.r. spectrum at -30 °C shows that the aryl groups are non-equivalent [*e.g.* for (III) δ (Me) 1·97 and 1·76]. This is also reflected in the ^{31}P n.m.r. spectrum which shows at -30 °C two absorptions at δ $-21{\cdot}1$ [$^1J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ 3304 Hz] and $-17{\cdot}7$ p.p.m. [$^1J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ 4305 Hz], while $^2J(^{31}\mathrm{P}–\mathrm{Pt}–^{31}\mathrm{P})$ = 5 Hz.

At higher temperatures (-10 °C) an intramolecular reversible process occurs, whereby the aryl groups of the di-imidosulphur ligand and the phosphine groups become magnetically equivalent. This process probably involves a movement of the Pt-atom from one N-atom to the other and *vice versa*,[3] while in addition a rotation about the Pt–N bond may occur. It was not possible to study ^{31}P n.m.r. spectra in the fast exchange situation, as then an irreversible process (see below) sets in.

At 30 °C an irreversible process commences which gives rise to the formation of a bivalent platinum compound for which ν_s(NSN) and the π–π^* transitions of the NSN ligands are completely missing and a ν(NH) bond is present at 3368 $\mathrm{cm^{-1}}$. Complex (IV), formed from (III) (Ar = *m,m'*-xylyl) shows ^{31}P n.m.r. signals at δ $-17{\cdot}7$ [$^1J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ 3274 Hz] and $-23{\cdot}6$ p.p.m. [$^1J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ 2477 Hz]; $^2J(^{31}\mathrm{P}–\mathrm{Pt}–^{31}\mathrm{P})$ = 18 Hz. A single-crystal *X*-ray structure determination shows that compound (IV) has the structural formula $[\overline{\mathrm{PtS\{N(1\text{-}N}}\mathrm{H\text{-}3,5\text{-}Me_2C_6H_2)\text{-}(3,5\text{-}Me_2C_6H_3)\}(PPh_3)_2}]$ (Figure). *Crystal data*: triclinic, a = 13·10, b = 13·51, c = 14·72 Å, α = 78·68, β = 72·28,



(III) (IV)

Figure. Mechanism for conversion of (III) into (IV) and *X*-ray crystal structure of (IV).

$\gamma = 71{\cdot}53°$, $U = 2370$ Å^3, $Z = 2$, space group P$\bar{1}$. 5547 independent reflections, measured on a NONIUS CAD 4 diffractometer, were considered to be observed [$I > 5\sigma(I)$]. The current R-factor is 0·07 and refinement will be continued.‡

The formation of (IV) from (III) can be rationalized on the basis of initial isomerization of the di-imidosulphur ligand from the *trans,trans* to the *trans,cis* configuration[1,3] leading to an intermediate in which the $(PPh_3)_2Pt$ unit can act as a template for the intramolecular rearrangement. C–H bond activation by Pt assists nucleophilic attack of N(7) on C(2), which in this intermediate are in close proximity (Figure B) (*cf.* molecular geometry of *p*-MeC_6H_4 N=S=N C_6H_4Me-*p* which is in the *cis,trans* configuration in the solid[4]). Concomitant intramolecular electron transfer from Pt(0) to the ligand and S=N bond breaking then produces the compound (IV).

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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