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Preliminary communication

Reactions of palladium(II)-isocyanide complexes with phenyl derivatives of heavy metals

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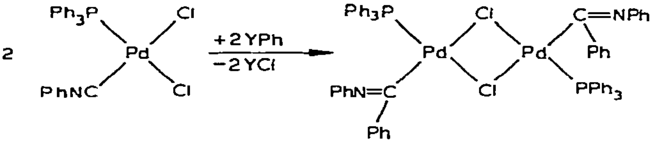
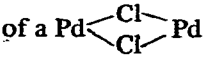
In the course of our studies on the reactions of isocyanides coordinated to palladium(II), we have found that the complex *cis*-[$Pd(PPh_3)(PhNC)Cl_2$] reacts smoothly with a variety of phenyl derivatives of heavy metals according to the following scheme:

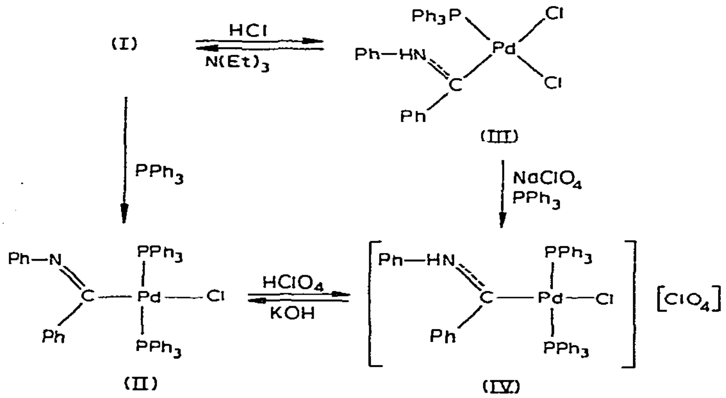


(I) (1)

where Y = HgPh, $PbPh_3$, $PbPh_2Cl$, $SnPh_3$, $BiPh_2$.

From the reaction mixture the binuclear compound (I) is recovered in 75–80% yields. It is non-conducting in nitromethane, and molecular weight measurements show that it is slightly dissociated in 1,1-dichloroethane at 37° (at *c* 2.57 g/l the experimental molecular weight is 960, while at *c* 6.08 g/l it is 1070; calcd. mol. wt., 1168). Analysis (Table 1) and IR data (Table 2) support the above formulation. The $\nu(N{\equiv}C)$ band at 2212 cm^{-1} arising from the coordinated isocyanide in the starting complex disappears and two strong absorptions at 1584 and 1609 cm^{-1} appear in the products. These bands are assigned to the N=C stretches of the *N*-phenylimino group σ-bonded to the central metal. The Pd–Cl stretching frequencies fall in the range 276–250 cm^{-1}, typical of a  $Pd\langle{}^{Cl}_{Cl}\rangle Pd$ bridging unit[1]. $HgPh_2$ is known to react also with carbon monoxide coordinated to Pt^{II} to give a benzoyl group σ-bonded to the central metal[2].

Compound (I) undergoes bridge-splitting and reversible protonation reactions as follows:



The complexes (II), (III), and (IV) have been characterized by elemental analysis (Table 1) an IR spectra (Table 2). Molecular weight measurements of (II) in 1,2-dichloroethane at 37° give a value of 854 (calcd. mol. wt., 846). Complex (IV) behaves as a uni-univalent electrolyte in nitromethane solution.

TABLE 1

ANALYTICAL AND PHYSICAL DATA

Complex	Colour	Analysis: Found (calcd.)				M.p.[a] (°C)
		C	H	N	Cl	
$\{Pd(PPh_3)[C(=N{\cdot}Ph)Ph]Cl\}_2$	deep-yellow	63.2	4.3	2.4	6.3	225 dec.
		(63.61)	(4.31)	(2.39)	(6.23)	
$\{Pd(PPh_3)_2[C(=N{\cdot}Ph)Ph]Cl\}$	yellow	69.5	4.7	1.7	4.2	215 dec.
		(69.51)	(4.76)	(1.65)	(4.19)	
$\{Pd(PPh_3)[C(NH{\cdot}Ph)Ph]Cl_2\}$	pale-yellow	60.1	4.2	2.3	11.4	263 dec.
		(60.01)	(4.16	(2.26)	(11.43)	
$\{Pd(PPh_3)_2[C(NH{\cdot}Ph)Ph]Cl\}(ClO_4)$	pale-yellow	61.9	4.4	1.5	7.5	240 dec.
		(62.14)	(4.36)	(1.48)	(7.49)	

[a] All melting points are uncorrected.

TABLE 2

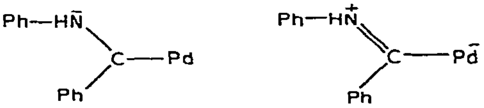
CHARACTERISTIC IR ABSORPTIONS

Complex	ν(NH)[a]	ν(CN)[b]	ν(PdCl)[b]
(I)	—	1609s, 1584s	276ms, 266ms, 250(sh)
(II)	—	1568s(br)	275ms
(III)	3165m, 3120m	1554s	306s, 280(sh), 267s
(IV)	3200m, 3140mw	1550s	313s

[a] Hexachlorobutadiene mulls. [b] Nujol mulls.

A *trans* configuration is tentatively assigned to complex (II) because the far IR spectrum of (II) shows only one ν(Pd-Cl) band at 275 cm^{-1}, suggesting that the terminal chloride is *trans* to the palladium-carbon σ bond.[3] This band shifts to 313 cm^{-1} in the protonated product (IV), an effect which can be attributed to a decreased *trans* influence of the ligand *trans* to chloride and/or to an increased effective charge on the central metal. A *cis* structure for compound (III) is suggested by the number of ν(Pd–Cl) bands in its spectrum (see Table 2).

The reversible protonation of complexes (I) and (II) can be related to analogous reactions of the groups $>$C=NR σ-bonded to transition metals[3,4]. On the basis of IR data, the electronic configuration of the organic moiety in the compounds (III) and (IV) is better represented by the two limiting structures:



The ν(CN) range (1550–1554 cm^{-1}) indicates a bond order higher than one between the carbon and nitrogen atoms, and, correspondingly, the low values of ν(NH) may arise from the presence of a partial positive charge on the nitrogen atom[5].

REFERENCES

1 (a) D.M. Adams and P.J. Chandler, *Chem. Commun.*, (1966) 69; (b) D.M. Adams, P.J. Chandler and R.G. Churchill, *J. Chem. Soc. A*, (1967) 1272; (c) R.J. Goodfellow, P.L. Goggin and L.M. Venanzi, *J. Chem. Soc. A*, (1967) 1897; (d) B. Crociani, P. Uguagliati, T. Boschi and U. Belluco, *J. Chem. Soc. A*, (1968) 2869; (e) D.M. Adams and P.J. Chandler, *J. Chem. Soc. A*, (1969) 588.
2 R.J. Cross and R. Wardle, *J. Chem. Soc. A*, (1970) 840.
3 B. Crociani and T. Boschi, *J. Organometal. Chem.*, 24 (1970) C1 and references therein.
4 P.M. Treichel, J.J. Benedict, R.W. Hess and J.P. Stenson, *Chem. Commun.*, (1970) 1627.
5 B. Crociani, T. Boschi and U. Belluco, *Inorg. Chem.*, 9 (1970) 2021.