Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

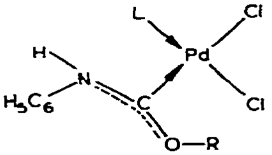
The formation of palladium(II)–carbon σ bonds from carbene derivatives

B. CROCIANI and T. BOSCHI

Centro Chimica Tecnologia Composti Metallorganici Elementi di Transizione, C.N.R., Facoltà di Chimica Industriale, The University, Bologna (Italy)

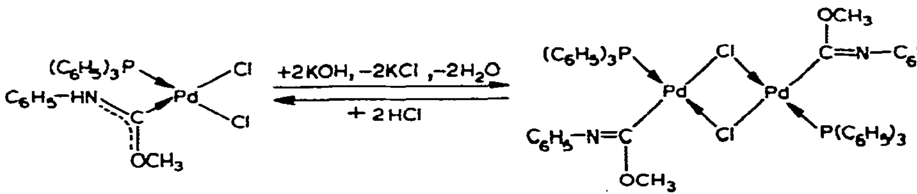
(Received June 2nd, 1970)

We have previously shown that isocyanides coordinated to palladium(II) undergo nucleophilic attack by alcohols and primary amines, as does the CO group in carbonyl derivatives of manganese, rhenium, iridium and iron[2]. The reaction of alcohols with the carbonyl compounds lead directly to metal–carbon σ-bonded derivatives of the type M–C(O)–OR, but with palladium(III)–isocyanide complexes the products are "carbene" derivatives of type (I), where L = phenylisocyanide or triphenylphosphine.



(I)

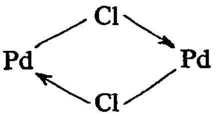
We have now found that the compounds of type (I) can be converted into new derivatives containing palladium–carbon σ bonds. Thus complex (I) having L = triphenylphosphine and R = CH_3, reacts with the stoicheiometric amount of alcoholic KOH at room temperature according to eq. 1. The reaction is very fast and almost quantitative; potassium chloride is precipitated. From the red solution the brick coloured compound (II) is recovered in 92% yield. It is non-conducting in 1,2-dichloroethane solution and partially dissociated in the same solvent, as shown by molecular weight measurements: at $c = 2.25$g/l the experimental molecular weight is 850, while at $c = 5.35$g/l it is 963 (Theor. mol.wt., 1076). The elemental analysis corresponds to the composition



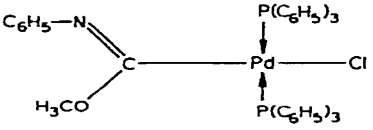
(II)

(1)

$C_{26}H_{23}ClNOPPd$: (Found: C, 57.8; H, 4.2; Cl, 6.7; N, 2.6%. Calcd.: C, 58.01; H, 4.31; Cl, 6.59; N, 2.60%).

The presence of the bridging unit  is indicated by the far IR spectrum, which shows two intense bands at 274 and 256 cm^{-1} respectively (*cf.* ref. 3).

As a further evidence of the bridging structure the compound (II) reacts smoothly with the equivalent amount of triphenylphosphine (Pd/P = 1/1), to give a quantitative yield of complex (III).



(III)

Complex (III) has been characterised by elemental analysis (Found: C, 65.7; H, 4.7; Cl, 4.5; N, 1.8%; mol.wt. 790 (1,2-dichloroethane at 37°). $C_{44}H_{38}ClNOP_2Pd$ Calcd.: C, 66.01; H, 4.78; Cl, 4.43; N, 1.75%, mol.wt., 800) and by IR and PMR spectra. Its far IR spectrum shows only one ν(Pd–Cl) band at 276 cm^{-1}. On the basis of *trans* influence arguments, the position of this band favours the proposed structure, having the terminal chloride *trans* to the palladium–carbon σ bond[4]. If the chloride were *trans* to the phosphine, ν(Pd–Cl) would be at somewhat higher frequency[1,5].

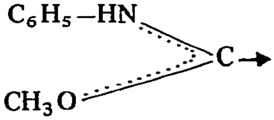
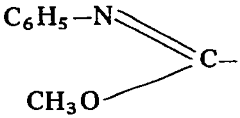
On passing from the carbene group  of complex (I) to the σ-bonded group  of complexes (II) and (III) some important changes appear in the IR and PMR spectra of the organic moieties, as shown in Table 1. Thus, ν(N–H) stretching frequencies and the N–H PMR signal at τ 8.42 of compound (I) disappear in the compounds (II) and (III). The ν(C⩵N—C_6H_5) stretching

TABLE 1

SPECTRAL DATA

Compound	Infrared spectrum (cm^{-1})[a]			PMR spectrum (τ)[b]
	ν(N–H)	ν(C=N–C_6H_5)	ν(C–O–CH_3)	
I	3148m, 3103mw	1547s	1261 ms	2.2–3 [20]; 5.6 [3]; 8.42
II		1597s, 1578s	1115s,br	not recorded
III		1577s	1115s	2.1–3.1 [35]; 7.07 [3]

[a] Hexachlorobutadiene and nujol mulls; w, weak; m, medium; s, strong; br, broad.
[b] $CDCl_3$ solutions.

frequencies of (II) and (III) are increased by 30–50 $\mathrm{cm^{-1}}$ above that of (I), while the corresponding $\nu(\mathrm{C\overset{\cdots}{—}O—CH_3})$ decrease by 146 $\mathrm{cm^{-1}}$. These observations can be associated with an increased bond order between the C and N atoms and to a decreased bond order between the C and O atoms of the organic group of the complexes (II) and (III). This is consistent also with the shift from τ 5.6 to 7.07 of the PMR signal of the $—\mathrm{O—CH_3}$ groups in the compounds (I) and (III).

The values of $\nu(\mathrm{C\overset{\cdots}{—}N—C_6H_5})$ and $\nu(\mathrm{C\overset{\cdots}{—}O—CH_3})$ in (II) and (III) fall in the ranges typical of organic compounds containing C=N bonds and $\mathrm{C—O—CH_3}$ groups[6].

Reaction 1 can be easily reversed. In fact, if the complex (II) is refluxed for 30 min with methanol containing 0.1 *M* HCl, complex (I) is obtained in a 90% high yield.

ACKNOWLEDGEMENTS

We thank Prof. U. Belluco for stimulating discussion and Dr. L. Busetto for recording the PMR spectra.

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