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

PALLADIUM(II) AND PLATINUM(II) CARBENE COMPLEXES CONTAINING METAL–TIN BONDS

FLAVIO BONATI AND GIOVANNI MINGHETTI
Istituto di Chimica Generale dell'Università, via Venezian 21, 20133 Milano (Italy)
TRISTANO BOSCHI AND BRUNO CROCIANI
Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Facoltà di Chimica Industriale, viale Risorgimento 4 - Bologna (Italy)

(Received June 16th, 1970)

SUMMARY

Reaction of *cis*-Pt(CNR)L'Cl_2 and of PdLL'Cl_2 [L = isocyanide or Ph_3P; L' = bis(*N*-arylamino)carbene or (*N*-arylamino)(alkoxy)carbene] with tin(II) chloride gave the corresponding LL'M$(SnCl_3)_2$ complexes, which were characterized by IR and NMR spectra.

INTRODUCTION

In our studies of isocyanide complexes[1], we have characterized some new platinum[2] and palladium[3] compounds, investigated their reactions with alcohols and amines, and isolated carbene[4] complexes.

In view of the importance for homogeneous catalysis of compounds containing transition-metals bonded to tin[5], we have now prepared carbene complexes containing such a linkage by means of the insertion reaction[6]. The products are the first examples of carbene complexes with M–M' bonds.

RESULTS AND DISCUSSION

The starting compounds are new; they were obtained according to the reactions:

$$PdL(CNR)Cl_2 + R'NH_2 \rightarrow PdL(R'\text{-}NH\text{-}C\text{-}NHR)Cl_2 \quad (L = CNR \text{ or } Ph_3P)$$

$$cis\text{-}Pt(CNR)_2Cl_2 + R'NH_2 \rightarrow cis\text{-}Pt(CNR)(RNH\text{-}C\text{-}NHR')Cl_2$$

$$cis\text{-}Pt(CNR)_2Cl_2 + R'OH \rightarrow cis\text{-}Pt(CNR)(RNH\text{-}C\text{-}OR')Cl_2$$

The relevant analytical and spectral data are presented in Tables 1–3. With stannous chloride insertion into the M–Cl bond took place according to the equation[6]:

$$MLL'Cl_2 + 2\,SnCl_2 \rightarrow MLL'(SnCl_3)_2$$

TABLE 1

ANALYTICAL AND OTHER DATA

Compound[a] and colour	M.p. (°C)	Analysis found (calcd.((%)			
		C	H	Cl	N
$Pd(CNPh)(PhNH{-}C{-}NHC_7H_7)(SnCl_3)_2$[d,e] (I), yellow	212 decomp.	29.3 (28.99)	2.3 (2.2)	24.3 (24.45)	4.9 (4.83)
$Pd(Ph_3P)(PhNH{-}C{-}NHC_7H_7)(SnCl_3)_2$ (II), yellow	203 decomp.	37.2 (37.35)	2.8 (2.84)	21.0 (20.67)	2.7 (2.72)
$Pd(Ph_3P)(O_2NC_6H_4{-}NH{-}C_7H_7)Cl_2$ (III), pale yellow	237 decomp.	55.2 (55.31)	3.9 (4.06)	10.5 (10.20)	6.0 (6.05)
$Pd(Ph_3P)(O_2NC_6H_4{-}NH{-}C_7H_7)(SnCl_3)_2$ (IV), yellow	235 decomp.	36.1 (35.78)	2.8 (2.63)	19.6 (19.80)	3.9 (3.91)
$Pt(CNC_6H_{11})(C_7H_7NH{-}C{-}NHC_6H_{11})Cl_2$ (V), dirty white[f]	124	43.00 (42.63)	5.23 (5.24)		7.07 (7.11)
$Pt(CNC_6H_{11})(C_7H_7NH{-}C{-}NHC_6H_{11})(SnCl_3)_2$ (VI) orange	ca. 152	26.76 (25.98)	3.37 (3.19)	21.47 (21.92)	4.51 (4.33)
$Pt(CNC_7H_7)[(C_7H_7NH)_2C]Cl_2$[b,c] (VII), white	217	45.84 (45.46)	3.68 (3.79)	11.42 (11.69)	6.84 (6.93)
$Pt(CNC_7H_7)[(C_7H_7NH)_2C]Cl_2$[b,c] (VIII), pale yellow	134 decomp.	29.35 (27.99)	2.07 (2.37)	21.0 (21.57)	4.47 (4.26)
$Pt(CNC_6H_{11})(CH_3O{-}C{-}NHC_6H_{11})(SnCl_3)_2$ (X), white	145–147	20.53 (20.11)	2.91 (2.90)		2.91 (3.01)
$Pt(CNC_6H_{11})(C_2H_5O{-}C{-}NHC_6H_{11})Cl_2$[c] (XI), white	131	35.68 (36.23)	5.17 (5.28)		5.33 (5.28)

[a] C_7H_7 is *p*-tolyl, $O_2NC_6H_4$ is *p*-nitrophenyl, C_6H_{11} is cyclohexyl. [b] Pt found 31.5, calcd. 32.1%. [c] Not conducting in nitrobenzene. [d] Not conducting in $(CH_2Cl)_2$. [e] Mol.wt. in $(CH_2Cl)_2$ found 910, calcd. 870. [f] Mol.wt. in $CHCl_3$ (1.4% w/w): found 1210, calcd. 591.

This reaction was carried out in chloroform solution to which tin(II) chloride was added either as a solid (M = Pt) or as an ethereal solution (M = Pd). The rate of insertion of the second mole of tin(II) chloride into an M–Cl bond seems to be faster than that of the first: even when the isocyanide complex/tin(II) chloride ratio was one, only the $LL'M(SnCl_3)_2$ complex was isolated.

The reaction products are pale yellow to orange crystalline solids, stable to air, and moderately or sparingly soluble in organic solvents, yielding non-conducting solutions. Their stability is similar to that of other platinum(II) or palladium(II) complexes[7] containing both tin–metal bond and an unsaturated carbon atom bonded to the transition metal.

The tin–palladium and tin–platinum bonds were cleaved smoothly by iodine:

$$LL'Pd(SnCl_3)_2 + I_2 \rightarrow LL'PdL_2 + 2\ ISnCl_3$$

and the corresponding palladium(II) complex[3] was isolated in nearly quantitative yield. The tin–platinum bonds were cleaved by chlorine to give tin-free yellow isocyanide complexes which are under investigation[8].

Although a final conclusion cannot be reached from the available data, a

TABLE 2

INFRARED DATA

Compound[a]	ν(N–H) δ(N–H)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	ν(CN)[b]	ν(M–Cl) δ(M–Cl)	ν(M–Sn)
(XII)	3205 ms, 3180 (sh), 3120 w 1597 m, 1587 ms	1549 s	2206 s	319 m, 287 m, 270 m	
(I)	3322 ms, 3306 (sh), 3300 s 1588 ms, 1584 (sh)	1531 s	2202 s	322 vs, 311 s 134 s, 125 (sh)	213 m
(XIII)	3158 s, 3106 m 1588 m	1538 s		295 m, 285 (sh), 273 m	
(II)	3258 s, 3239 s 1591 mw	1530 s		335 (sh), 331 vs, 312 s 142 s, 131 m, 121 (sh)	142 s, 131 m, 121 (sh)
(III)	3140 ms, 3080 (sh) 1616 m	1530[c]		303 ms, 286 m, 274 m	
(IV)	3240 m (br) 1608 m	1530[c]		333 s (br), 310 (sh) 140 m (br), 125 (sh)	
(V)	3228 m (br) 1588 (sh)	1555 s	2208 s 2216 s	320 s	
(VI)	3350 m, 3329 m 1586 (sh)	1557 s	2221 s	335 s, 322 m 127 ms, 133 m	202 w or 194 w
(VII)	3230 m (br) 1587 s	1552 s	2198 s 2203 s	328 s, 320 (sh)	
(VIII)	3352, 3310 m 1584 s	1534 s	2198 s 2203 s	331 vs (br) 127 ms	209 mw, 202 (sh)
(IX)	3200 m [1564 s (br)]	[1564 s (br)]	2215 s 2218 s	325 ms	
(X)	3290 m [1554 s (br)]	[1554 s (br)]	2230 s 2224 s	335 vs	

[a] Compound (IX) is Pt(CNC_6H_{11})(CH_3O–C–NHC_6H_{11})($SnCl_3$)$_2$, compound (XII) is Pd(CNPh)(PhNH–C–NHC_7H_7)Cl_2, and compound (XIII) Pd(Ph_3P)(PhNH–C–NHC_7H_7)Cl_2. [b] CN of the coordinated isocyanide: upper line nujol mull, lower line $CHCl_3$ solution. [c] Partially overlapping with strong $\nu(NO_2)$ at 1505 cm^{-1}.

TABLE 3

NMR DATA[a]

Compound	Aromatic ring	Cyclohexyl[b]	p-CH_3– (singlet)	Others
(V)	2.2–3.2	ca. 6.3; ca. 8.6	7.74	
(VI)[c]	2.73 singlet	ca. 6; ca. 8 and 8.45	7.61	
(VII)[e]	2.4–3.1		7.68; 7.44[d]	8.44[f]
(VIII)[c]	2.4–2.8		7.66; 7.59[d]	
(X)		ca. 6; ca. 8 and 8.40		5.73[h]
(XI)[c,e]		ca. 6; 7.8–8.8		ca. 5.0[g]

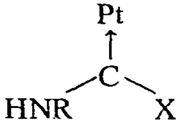
[a] Perkin–Elmer R-10 instrument, at 33°, $CDCl_3$ solution. [b] Generally broad bands. [c] No additional signal down to τ −10. [d] More intense of the two signals due to p-CH_3. [e] Sparingly soluble. [f] Probably –NH–; displaced by adding CF_3COOH. [g] Broad band due to –OCH_2– protons. [h] Methoxy group.

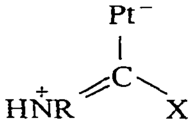
trans-structure is likely for the trichlorostannyl complexes. A formally similar insertion[2] reaction yields *trans*-$(RNC)_2M(SnCl_3)_2$ from *cis*-$(RNC)_2MCl_2$ showing that the bulky $-SnCl_3$ groups favours the *trans*-structure.

The ^{1}H NMR spectra (Table 3) are in agreement with the proposed formulae. The presence of a $(p\text{-}CH_3C_6H_4NH)_2C$ and of a $p\text{-}CH_3C_6H_4NC$ ligand in the same molecule, *e.g.* in compounds (VII) and (VIII), gave rise to separate signals for the two kinds of p-methyl groups, which were not distinguishable when p-tolyl isocyanide and $p\text{-}CH_3C_6NH{-}C{-}OCH_3$ were the ligands. The signal corresponding to a –NH– group was detected only in the case of compound (VII): in the other cases, proton exchange and/or broadness of the peak makes it difficult to prove through NMR spectroscopy the presence of the NH group easily detected by IR spectroscopy.

The IR spectra (Table 2) support the formulae given: ν(N–H) was found above 3100, ν(CN) of the isocyanide at ca. 2200, δ(N–H) and ν(C=N) of the carbene in the range 1530–1630, and ν(Sn–Cl) and δ(Sn–Cl) at ca. 310–340 and 120–150 cm^{-1} respectively. The coordinated isocyanide stretching frequencies, ν(CN) were found in a rather narrow range. When R was cyclohexyl, ν(CN) was at 2251 and 2222 for *cis*-$(RNC)_2PtCl_2$, 2218 for *cis*-$(RNC)(RNH{-}C{-}OCH_3)PtCl_2$, 2206 for *cis*-$(PhNC)(PhNH{-}C{-}NHC_6H_4CH_3)PdCl_2$, and at 2226, 2230 and 2202 cm^{-1} for the corresponding trichlorostannyl derivatives. The rather small change in ν(CN) in the series suggest that the small amount of π back-donation from the metal to the isocyanide ligand is of much the same importance in all the complexes, irrespective of change of the other ligands. On the other hand, the $M{-}SnCl_3$ bond is likely to have some $d_\pi{-}p_\pi$ character because of the tendency to remove the excess of electron density caused by the coordination of SnX_3; this behaviour was found for $X_3SnCo(CO)_4$ compounds[9].

A remarkable shift towards higher frequency, together with an opposite but smaller shift of ν(C=N), was observed for ν(N–H) (nujol mull) on going from the chloride to the trichlorostannyl complexes. This suggests that the contribution of the canonical form (A) is more significant in the $SnCl_3^-$ than in Cl^- derivatives: chlorine is the more electronegative group and favours structure (B), but the variable contribution to the shift of N–H of a possible hydrogen bond in the solid state cannot be evaluated; this type of bond might be responsible for the molecular weight found for compound (V) in chloroform solution.


(A)


(B)

Very intense ν(Sn–Cl) bands are present in the 335–311 cm^{-1} region, and are broad because of overlapping of vibrations; the range of observed vibrations is that typical for a coordinated $SnCl_3$ group[10]. The δ(Sn–Cl) bands occur in the 121–145 cm^{-1} range. Although coordination does not affect the δ(Sn–Cl) vibrations as much as ν(Sn–Cl), tin–chlorine bending motions are shifted toward higher frequency by coordination in comparison with those of the free $SnCl_3^-$ ion, which occur at 128 and 103 cm^{-1}[11]. A band which is tentatively assigned to the M–Sn stretching vibration was observed at ca. 200 cm^{-1} (*cf.* refs. 7 and 12).

EXPERIMENTAL

Concentration was always carried out under vacuum.

(Phenyl isocyanide)[(phenylamino)(p-tolylamino)carbene]bis(trichlorotin)-palladium(II) (I).

A solution of (phenyl isocyanide)[(phenylamino)(*p*-tolylamino)carbene]-dichloropalladium(II) (1 mmole) in chloroform (20 ml) was mixed with an ethereal solution of tin(II) chloride dihydrate (12 mmole). After 1 h of stirring the pale yellow solution was evaporated to dryness and the residue was extracted with CH_2Cl_2. Addition of a 1/1 mixture of diethyl ether and petroleum ether to the concentrated CH_2Cl_2 solution gave (I), in ca. 60% yield.

Compounds (II) and (IV) were prepared analogously.

Compound (III) was prepared as previously described[3]. A solution of compound (I) (0.5 mmole) in chloroform reacted at once with a solution of iodine in CCl_4 (10 ml, 0.1 *M*), and addition of diethyl ether gave $(PhNC)(PhNH{-}C{-}NHC_7H_7)PdI_2$, which was identified by comparison of m.p. and the IR spectrum with those of authentic sample[3].

(p-Tolyl isocyanide)[bis(p-tolylamino)carbene]dichloroplatinum(II) (VII)

To a chloroform solution of *cis*-bis(*p*-tolyl isocyanide)dichloroplatinum(II) (0.5 g) *p*-toluidine was added (0.107 g). After 24 h the solution was concentrated to a small volume and the white precipitate was filtered off. The analytical sample was obtained by crystallization from chloroform.

(Cyclohexyl isocyanide)[(p-tolylamino)(cyclohexylamino)carbene]dichloro-platinum(II) (V)

To a chloroform solution of *cis*-bis(cyclohexyl isocyanide)dichloroplatinum (II) (0.5 g) *p*-toluidine was added (0.107 g). As no reaction was apparent after 24 h, the solution was refluxed for 3 days under nitrogen, and then evaporated to dryness. The oily residue was stirred with petroleum ether to give a whitish solid, which was crystallized twice from $CHCl_3$/petroleum ether to give the analytical sample of (V).

(p-Tolyl isocyanide)[bis(p-tolylamino)carbene]bis(trichlorotin)platinum(II) (VIII)

Compound (VII) (323 mg) was stirred with dry, sublimed tin(II) chloride (190 mg) in presence of chloroform (30 ml). Petroleum ether was added to precipitate crude (VIII), which was purified from CH_2Cl_2/ether and CH_2Cl_2/pentane.

Compound (VI) was prepared analogously from compound (V), but the reaction time was six days; it was crystallized from $CHCl_3$/petroleum ether and ether/hexane.

(Cyclohexyl isocyanide)[(methoxy)(cyclohexylamino)carbene]bis(trichlorotin)platinum(II) (X)

Compound (IX)[2] (105 mg) and dry, sublimed tin(II) chloride (70 mg) were stirred two days under chloroform (20 ml). The solution was filtered and evaporated to dryness. The oily residue was washed with petroleum ether and then dissolved in CCl_4; product (X) (75 mg) was precipitated by careful addition of petroleum ether.

(Cyclohexyl isocyanide)[(ethoxy)(cyclohexylamino)carbene]dichloroplatinum(II) (XI)

cis-Bis(cyclohexyl isocyanide)dichloroplatinum(II)[2] (480 mg) was refluxed in ethanol (10 ml) for 5 h. The solution was evaporated to dryness; the oily residue solidified on treating with diethyl ether and evaporating off the solvent. The crude product (XI) (327 mg) was crystallized from $CHCH_3$/hexane.

ACKNOWLEDGEMENTS

NMR spectra were recorded by Dr. P. C. Fantucci, whom we thank. Financial support by Consiglio Naz. delle Ricerche is acknowledged.

REFERENCES

1 L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Wiley, London, 1969.
2 F. Bonati and G. Minghetti, *J. Organometal. Chem.*, 24 (1970) 251.
3 B. Crociani, T. Boschi and U. Belluco, *Inorg. Chem.*, in the press.
4 E. M. Badley, J. Chatt, R. L. Richards and G. A. Sim, *J. Chem. Soc. D*, (1969) 1322 and references therein.
5 (a) R. Pietropaolo, M. Graziani and U. Belluco, *Inorg. Chem.*, 8 (1969) 1506;
(b) R. Pietropaolo, G. Dolcetti, M. Giustiniani and U. Belluco, *Inorg. Chem.*, 9 (1970) 549.
6 F. Bonati, S. Cenini, D. Morelli and R. Ugo, *J. Chem. Soc. A*, (1966) 1052 and references therein.
7 B. Crociani, T. Boschi and U. Belluco, *Inorg. Chim. Acta*, submitted for publication.
8 F. Bonati and G. Minghetti, to be published.
9 T. L. Brown, P. A. Edwards, C. B. Harris and J. L. Kirsh, *Inorg. Chem.*, 8 (1969) 763.
10 D. F. Shriver and M. P. Johnson, *Inorg. Chem.*, 6 (1967) 1265.
11 L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, (1962) 407.
12 (a) K. L. Watters, J. N. Brittain and W. M. Risen, Jr., *Inorg. Chem.*, 8 (1969) 1347;
(b) D. M. Adams and P. J. Chandler, *Chem. Ind. (London)* (1965) 269.