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Novel Palladium(II)-Tin and Palladium(II)-Germanium Complexes

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Novel palladium(II) derivatives containing metal-metal bonds of the type trans–$[Pd(RNC)_2(M'X_3)_2]$ *and* $[Pd(C_6H_5NC)(L)(M'Cl_3)Cl]$ *(RNC = phenyl, cyclohexyl- and* p*-nitrophenylisocyanide; L = triphenylphosphine and triphenylarsine; M' = Sn and Ge; X = Cl and Br) have been prepared. These compounds have been characterized by elemental analysis, molecular weight measurements, i.r. spectra, X-ray powder diffraction patterns and cleavage of the Pd–Sn and Pd–Ge bonds by reaction with iodine. Their structure was assigned, where possible, on the basis of i.r. data. An attempt to identify the Pd–Sn and Pd–Ge stretching frequencies has been made: the* $\nu(Pd{-}SnCl_3)$ *appears to fall in the range 199-226 cm*$^{-1}$*;* $\nu(Pd{-}SnBr_3)$ *in the range 156-180 cm*$^{-1}$*, and* $\nu(Pd{-}GeCl_3)$ *in the range 228-240 cm*$^{-1}$*.*

Introduction

In the last few years there has been an ever-growing interest in the chemistry of compounds containing metal-metal bonds,[1-4] but to the best of our knowledge little has been done on palladium(II)-metal derivatives. Only a few compounds with Pd–Ge,[5,6] Pd–Sn,[7,11] and Pd–Pb[12] bonds have been reported in the literature so far, and they are in general fairly unstable. Some of the tin derivatives have not been completely characterised, like $[Pd(SnCl_3)_2Cl]_2^{4-}$, where the palladium atom should be in the formal Pd^I oxidation state,[7] some others have been prepared in very low yield, such as $[Pd(CO)(SnCl_3)_2Cl]^-$,[8] and others are cluster compounds, such as $[Pd_3(C_8H_{12})_3(SnCl_3)_2]$.[9] Only a very few compounds, such as the allyl derivative $[Pd(C_3H_5)(P(C_6H_5)_3)(SnCl_3)]$, have been fully characterized.[10,11] So far no Pd–GeCl$_3$ compound has been reported. The lack of information about complexes of the type $[Pd(L)_2(GeCl_3)_2]$ and $[Pd(L)_2(SnCl_3)_2]$ (L = neutral ligand), which is probably due to the instability of such systems, is ascribed by us mainly to the choice of the ligand L.

It is well known[1,2] that compounds with a σ bond between a transition metal and Group IV metal are characterized by the fact that the transition metal is coordinated to ligands having good π-acceptor properties: carbon monoxide (the most widely used), cyclopentadienyl and allyl groups, tertiary phosphines, diolefins etc. It is also known that isocyanides are rather good π-acceptor ligands which are able to stabilize zero-valent palladium derivatives.[13] All these facts led us to use the complexes $[Pd(RNC)_2Cl_2]$ (RNC = phenyl-, cyclohexyl-, and *p*-nitrophenylisocyanide as the starting materials for the preparation of novel palladium(II)–GeCl$_3$ and –SnCl$_3$ derivatives. Our choice was supported by a recent paper reporting the preparation of a series of Fe^{II}–SnCl$_3$ compounds having isocyanides coordinated to the iron atom.[14] In this way we have prepared both complexes of the type $[Pd(RNC)_2(M'X_3)_2]$ (M' = Ge and Sn; X = Cl and Br) and the mixed derivatives $[Pd(C_6H_5NC)(L)(M'Cl_3)Cl]$ (L = triphenylphosphine and triphenylarsine) either by insertion reactions of SnX$_2$ across the Pd–Cl bond or metathetical reactions with CsGeCl$_3$. We wish to report here these preparations together with a discussion of the structure of the reaction products on the basis of their i.r. spectra. A tentative assignment of Pd–Ge and Pd–Sn stretching frequencies is also presented.

Experimental Section

The starting compounds $[Pd(RNC)_2Cl_2]$ and $[Pd(RNC)(L)X_2]$ (L = $P(C_6H_5)_3$ and $As(C_6H_5)_3$) were prepared according to the methods already described.[15,16] $SnCl_2 . 2H_2O$ and $CsGeCl_3$ were commercial grade reagents; $SnBr_2 . 2H_2O$ was prepared by metathetical reaction.

1. *Preparation of the complexes* $[Pd(RNC)_2(SnX_3)_2]$ *(X = Cl, Br).* 1 mmole of $[Pd(RNC)_2Cl_2]$,

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suspended or dissolved in 10 ml of CH_2Cl_2, was treated with an excess of $SnX_2 . 2H_2O$, dissolved in the minimum amount of ether with stirring (Pd/Sn = 1/3—1/10). The insertion reaction takes place immediately, as observed by a sharp change of colour of the mixture. The reaction mixture was stirred for 1-2h, and then was taken to dryness under reduced pressure. The solid residue was extracted twice with CH_2Cl_2 (50 ml each time), and the extract treated with charcoal. The resultant clear solution was concentrated under reduced pressure and the product precipitated by adding a mixture of ether/petroleum ether (2:1). It was filtered off, washed several times with ether, and dried under vacuum.

The complex $[Pd(C_6H_{11}NC)_2(SnCl_3)_2]$ precipitated satisfactorily pure during the addition of $SnCl_2 . 2H_2O$ so that it does not require further purification. Also $[Pd(pO_2N—C_6H_4NC)_2(SnCl_3)_2]$ precipitates during the reaction: it is only slightly soluble in CH_2Cl_2 and in the common organic solvents, thus preventing a better purification. The yields vary from 50 to 87% (see Table I). Molecular weight for $[Pd(C_6H_5NC)_2(SnCl_3)_2]$: Calcd. 762, Found 780. The molecular weights of the $SnBr_3$ derivatives could not be measured because they are insufficiently soluble in 1,2-dichloroethane.

2. *Preparation of the complexes $[Pd(C_6H_5NC)(L)(M'Cl_3)Cl]$ (M' = Sn and Ge).* a) $[Pd(C_6H_5NC)(L)(SnCl_3)Cl]$ (L = $P(C_6H_5)_3$ and $As(C_6H_5)_3$). 1 mmole of $[Pd(C_6H_5NC)(L)Cl_2]$, partially dissolved in 15 ml of CH_2Cl_2, was treated with $SnCl_2 . 2H_2O$ dissolved in a large volume of ether (Pd/Sn = 1/3). The insertion products precipitate on forming. The reaction mixture was stirred for 30 min. The products were filtered off, washed several times with ether, and dried under vacuum. They are already sufficiently pure, although they can be further purified by dissolving in a large volume of CH_2Cl_2 and precipitating with a mixture of ether/petroleum ether (2:1). Yields: 80-96%. Molecular weight for $[Pd(C_6H_5NC)(P(C_5H_5)_3)(SnCl_3)Cl]$: Calcd. 732, Found 740.

b. $[Pd(C_6H_5NC)(P(C_6H_5)_3)(GeCl_3)Cl]$. 1 mmole of $[Pd(C_6H_5NC)(P(C_6H_5)_3)Cl_2]$ dissolved in 50 ml of CH_2Cl_2 was treated with 1.1 mmole of $CsGeCl_3$ suspended in 10 ml of acetone. The reaction mixture was stirred for 1 h, then treated with charcoal and filtered. The clear solution was concentrated under reduced pressure and the product precipitated with ether-petroleum ether (2:1). No further purification is required. Yield 80%.

3. *Preparation of the complexes $[Pd(RNC)_2(GeCl_3)_2]$.* $[Pd(C_6H_5NC)_2(GeCl_3)_2]$ was prepared by the same method as $[Pd(C_6H_5NC)(P(C_6H_5)_3(GeCl_3)Cl]$, by using a Pd/Ge ratio of 1-2.5 and a reaction time of 2 h. Yield 60%.

$[Pd(C_6H_{11}NC)_2(GeCl_3)_2]$ was prepared by the same method, although in this case benzene was used as solvent. Yield 65%. The molecular weight of these compounds could not be measured since they decompose or react with the solvent.[5,6]

4. *Reactions with Iodine.* a) Complexes $[Pd(RNC)_2(M'Cl_3)_2]$ (RNC = phenyl- and cyclohexylisocyanide; M' = Sn and Ge). 0.5 mmoles of $[Pd(RNC)_2(M'Cl_3)_2]$ dissolved in CH_2Cl_2 were treated with stirring with a solution of I_2 in CCl_4 0.1 *M* (10 ml of this solution were used: ratio Pd/I_2 = 1/2). After 15 minutes the reaction mixture was concentrated to a small volume under reduced pressure. The products $[Pd(RNC)_2I_2]$ were precipitated by dilution with a mixture of ethanol/ether (1:10). The yields were almost quantitative (90-95%). The iodo-derivatives were identified by comparing their i.r. spectra and melting points with authentic samples.[15,16]

b. Complex $[Pd(C_6H_5NC)(P(C_6H_5)_3)(SnCl_3)Cl]$. 370 mg (≃0.5 mmoles) of this compound dissolved in CH_2Cl_2 were treated with stirring with 5 ml of a solution of I_2 in CCl_4 0.1 *M* (Pd/I_2 = 1/1). After 30 minutes the solution was concentrated to a small volume and the product precipitated with ether. 216 mg (≃0.3 mmoles) of a compound, identified as $[Pd(C_6H_5NC)(P(C_6H_5)_3)I_2]$ were obtained. The filtrate was again concentrated to a small volume and diluted with a mixture of ether/petroleum ether (10/1). A second product was obtained, which was identified as $[Pd(C_6H_5NC)(P(C_5H_5)_3)Cl_2]$. The amount of this product was 82 mg (≃0.15 mmoles). Since these products are very likely formed by rearrangement of the unstable intermediate $[Pd(C_6H_5NC)(P(C_5H_5)_3)ClI]$, one would expected a molar ratio 1:1. This is not the case, but the yield of the iodo-derivative is higher than the theoretical one (0.3 mmoles instead of 0.25). Clearly the chloro-derivative undergoes a further metathetical reaction with the iodotin products of the cleavage reaction.

Molecular weight measurements. A Mechrolab thermoelectric molecular weight apparatus was used in all cases. The solvent was 1,2-dichloroethane and the temperature 37°C.

Infrared Spectra. Infrared spectra were recorded in the region 4000-250 cm^{-1} with a Perkin-Elmer model 621 instrument and with a Beckman I.R. 11 in the region 400-140 cm^{-1}. From 4000 to 1300 cm^{-1} hexachlorobutadiene mulls and NaCl plates were used; from 1700 to 250 cm^{-1} Nujol mulls and CsI plates were used. Nujol mulls and thin polythene sheets were used from 400 to 80 cm^{-1}. Calibration was performed against the carbon monoxide rotational spectrum, polystyrene film and the water vapour rotational spectrum. Accuracy is believed to be better than ±1 cm^{-1}.

Results and Discussion

The palladium-tin derivatives have been prepared according to the following insertion reactions in the presence of an excess of $SnX_2 . 2H_2O$:

$$cis\text{—}[Pd(RNC)_2Cl_2] \xrightarrow[\text{excess}]{SnX_2\,.\,2H_2O} trans\text{—}[Pd(RNC)_2(SnX_3)_2] \quad (1)$$

$$cis\text{—}[Pd(C_6H_5NC)(L)Cl_2] \xrightarrow[(Pd/Sn=1/3)]{SnCl_2\,.\,2H_2O} [Pd(C_6H_5NC)(L)(SnCl_3)Cl] \quad (2)$$

Table I. Analytical and physical data for $[Pd(RNC)(L)(M'X_3)_{2-n}X_n]$ (RNC = phenyl-, cyclohexyl- and *p*-nitrophenylisocyanide; L = . RNC, $P(C_6H_5)_3$ and $As(C_6H_5)_3$; M′ = Sn and Ge; X = Cl and Br)

Complex	Colour	C		H		N		X		Melting[a] points (°C)	Ratio Pd/M′ used in the preparations. Yields are given in the brackets
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
$[Pd(C_6H_5NC)_2(SnCl_3)_2]$	orange-brick	22.04	22.2	1.32	1.4	3.67	3.8	27.89	27.4	Dark 170° Dec. 247°	1/10 (87%)
$[Pd(C_6H_5NC)_2(SnBr_3)_2]$	yellow	16.33	16.5	0.98	1.0	2.72	2.8	46.57	46.2	167 dec.	1/8 (65%)
$[Pd(C_6H_5NC)_2(GeCl_3)_2]$	yellowish	25.08	25.2	1.50	1.6	4.18	4.2	31.72	31.4	228 dec.	1/2.5 (60%)
$[Pd(C_6H_5NC)(P(C_6H_5)_3)(SnCl_3)Cl]$	orange	41.00	40.5	2.75	2.7	1.91	1.9	19.36	20.3	210 dec.	1/3 (96%)
$[Pd(C_6H_5NC)(P(C_6H_5)_3)(GeCl_3)Cl]$	deep yellow	43.76	44.0	2.94	3.0	2.04	2.1	20.66	20.3	181 dec.	1/1.1 (80%)
$[Pd(C_6H_5NC)(As(C_6H_5)_3)(SnCl_3)Cl]$	orange-brick	38.68	38.2	2.60	2.6	1.80	1.9	18.27	18.4	205 dec.	1/3 (80%)
$[Pd(C_6H_{11}NC)_2(SnCl_3)_2]$	dark-red	21.70	21.3	2.86	2.9	3.62	3.5	27.45	27.7	230 dec.	1/3 (70%)
$[Pd(C_6H_{11}NC)_2(SnBr_3)_2]$	yellow	16.14	16.2	2.13	2.2	2.69	2.7	46.03	46.1	225 dec.	1/6 (50%)
$[Pd(C_6H_{11}NC)_2(GeCl_3)_2]$	yellow-orange	24.63	24.8	3.25	3.3	4.10	4.2	31.16	31.0	205 dec.	1/2.5 (65%)
$[Pd(p{-}O_2NC_6H_4NC)_2(SnCl_3)_2]$	dark-red	19.72	20.3	0.95	1.1	6.57	6.8	24.94	24.5	>270	1/4 (70%)
$[Pd(p{-}O_2NC_6H_4NC)_2(SnBr_3)_2]$	orange	15.02	15.0	0.72	0.8	5.00	4.9	42.83	43.0	210 dec.	1/6 (50%)

[a] All melting points are uncorrected.

Table II. Characteristic i.r. absorptions (cm^{-1}) of the complexes $[M(RNC)(L)(M'X_3)_{2-n}X_n]$ (M = Pd and Pt)

Complex	ν(NC)	ν(M′–X)	ν(M–M′)	δ(M′–X)
$[Pd(C_6H_5NC)_2(SnCl_3)_2]$	2206 vs, 2172 sh	330 vs, br	214 mw	133 s, 120 s
$[Pd(C_6H_5NC)_2(SnBr_3)_2]$	2202 vs, 2168 sh	250 s, 229 s, 215 s	156 m	89 m, br
$[Pd(C_6H_5NC)_2(GeCl_3)_2]$	2214 vs, 2180 sh	380 vs, br	240 w	158 s, 150 sh
$[Pd(C_6H_5NC)(P(C_6H_5)_3)(SnCl_3)Cl]$	2200 vs, 2160 sh	342 vs, 336 s, 316 vs[a]	226 ms or 206 ms	124 ms, br
$[Pd(C_6H_5NC)(P(C_6H_5)_3)(GeCl_3)Cl]$	2202 vs, 2160 sh	384 vs, 360 vs, 338 sh[a]	228 ms	155 m, br
$[Pd(C_6H_5NC)(As(C_6H_5)_3)(SnCl_3)Cl]$	2199 vs, 2160 sh	340 vs, 324 vs[a]	212 ms or 199 ms	118 m
$[Pd(C_6H_{11}NC)_2(SnCl_3)_2]$	2231 vs, 2200 sh	335 vs, 321 vs	208 mw	128 s, 120 sh
$[Pd(C_6H_{11}NC)_2(SnBr_3)_2]$	2230 vs, 2200 sh	257 s, 239 s, 229 s	178 s	87 m
$[Pd(C_6H_{11}NC)_2(GeCl_3)_2]$	2236 vs, 2200 sh	370 vs, br	233 mw	155 s
$[Pd(p{-}O_2NC_6H_4NC)_2(SnCl_3)_2]$	2207 vs, 2170 sh	331 vs, br	211 mw	128 ms br
$[Pd(p{-}O_2NC_6H_4NC)_2(SnBr_3)_2]$	2203 vs, 2160 sh	255 s, 242 s, 231 s	180 m	90 m, br
$[Pt(C_6H_{11}NC)_2(SnCl_3)_2]$	2237 s[b]	333 vs, 323 sh[b]	190 m	126 s
$[Pt(p{-}CH_3OC_6H_4NC)_2(SnCl_3)_2]$	2210 s[b]	346 vs, br[b]	206 m, 200 sh	134 sh, 124 s

[a] These bands include or cover the ν(Pd–Cl). [b] These values and the corresponding compounds have been kindly given to us by drs. F. Bonati and G. Minghetti (University of Milan), who have prepared them while this work was in progress.[23]

The formation of $SnBr_3$ derivatives by reaction [1] is due to exchange of the chloride in the group $SnBr_2Cl$, which is the first product of the insertion, with the bromide of the excess of $SnBr_2 . 2H_2O$.

The palladium-germanium derivatives have been prepared by metathetical reactions with $CsGeCl_3$, as described in the experimental section.

Reaction [2] gives definite, well characterized products only with phenylisocyanide derivatives, while with cyclohexylisocyanide it gives intensely coloured product of variable composition, very difficult to purify and identify. It does not occur with *p*-nitrophenylisocyanide derivatives, presumably because of steric and/or electronic factors related to the *p*-nitro group and triphenylphosphine. Analytical and physical data for all complexes are reported in Table I. The last column of this table shows the Pd/M′ ratio used in the preparation of each compound and the corresponding yield, since in the experimental section only the general methods of preparation are described. The molecular weights of some representative compounds are also reported in the experimental section and they are in a good agreement with the proposed compositions.

Thin-layer chromatography was not helpful for checking the purity of the new compounds, owing in many cases to the low solubility of the products, and, in other cases to decomposition both on silica gel and aluminium oxide. A few compounds, such as $[Pd(C_6H_5NC)(P(C_6H_5)_3)(SnCl_3)Cl]$, are so strongly absorbed that no separation was observed.

The starting materials $SnCl_2 . 2H_2O$, $CsGeCl_3$, $[Pd(C_6H_5NC)(P(C_6H_5)_3Cl_2]$ and the final products $[Pd(C_6H_5NC)(P(C_6H_5)_3)(M'Cl_3)Cl]$ were investigated also by X-ray powder diffractions. The comparison of the diffraction paterns clearly shows that the final products are new definite compounds. Moreover the similarity of the patterns of $[Pd(C_6H_5NC)(P(C_6H_5)_3)(SnCl_3)Cl]$ and its germanium analogue indicates that they are probably isomorphous.

All the complexes with a few exceptions are moderately soluble in halogenated solvents. They are stable in the solid state, but tend to decompose to some extent in solution.

Fortunately the decomposition is not so fast as to prevent purification of the products by reprecipitation and , in certain cases, the determination of molecular weight. It was in fact this measurement which indicated that the Pd–Ge derivatives decompose more rapidly than the corresponding Pd–Sn ones in 1,2-dichloroethane. The decomposition in solution may occur through a reaction with the halogenated solvent in the same way as reported by Brooks and Glockling for some Pd–Ge compounds.[5,6] The mixed complexes $[Pd(C_6H_5NC)(L)(SnCl_3)Cl]$ appear to be the most stable in solution.

The palladium-metal bond in these compounds is readily split by iodine. This reaction occurs under very mild conditions and affords reliable chemical evidence of the presence of Pd–Ge and Pd–Sn bonds. Complexes of the type *trans*–$[Pd(RNC)_2(M'Cl_3)_2]$ yield almost quantitatively the corresponding *trans*–$[Pd(RNC)_2I_2]$. The Sn^{IV} compounds, which are formed in the reaction, were not isolated but the presence of tin in the residue was detected (qualitatively). The reaction of I_2 on the mixed complex $[Pd(C_6H_5NC)(P(C_6H_5)_3(SnCl_3)Cl]$ gives $[Pd(C_6H_5NC)(P(C_6H_5)_3)I_2]$ and $[Pd(C_6H_5NC)(P(C_6H_5)_3)Cl_2]$ as products.

As far as the structure of the complexes of Table I is concerned, all the $[Pd(RNC)_2(M'X_3)_2]$ derivatives have a *trans* configuration, as revealed by the presence of only one very strong ν(NC) band in the region 2199-2237 cm^{-1} (asymmetric stretching).

This band shows a minor shoulder at lower frequency, which is probably due to the heavier carbon isotope ^{13}C. This shoulder cannot be attributed to the N–C symmetric stretching since it is present also in $[Pd(C_6H_5NC)(L)(M'Cl_3)Cl]$, where there is only one isocyanide molecule, both in the solid state and in 1,2-dichloroethane solution.

I.r. spectroscopy is of little help in assigning a probable structure to the latter compounds. Even the ν(Pd–Cl) band cannot be located with certainty because of the strong absorptions of the ν(Sn–Cl) bands in the region 300-350 cm^{-1} and ν(Ge–Cl) in the region 350-400 cm^{-1}.

The position of the ν(NC) bands deserves further comment. It is known that these bands are greatly influenced by the electron density on the palladium atom, in the sense that a higher electron density would cause a higher back-donation with a consequent lowering of the N–C stretching frequency.[15]. In our case, the ν(NC) frequencies fall in the range 2199-2237 cm^{-1} and the highest values occur for cyclohexylisocyanide derivatives. They are shifted to higher frequency by some 75-102 cm^{-1} from the values of the free isocyanides. These shifts are of the same order of magnitude as for $[Pd(RNC)_2X_2]$ derivatives.[16] This implies a relatively low electron density on the palladium atom and, consequently, a small extent of π-bonding in the Pd-isocyanide bond. On the other hand, the Pd–$M'X_3$ bond is likely to have some π-bonding of the type d_π–d_π, as found in the Co–Ge and Co–Sn bonds for complexes of the type $X_3M'Co(CO)_4$ by means of nuclear quadrupole resonance studies.[17] It was also found that the σ bond order for the $(C_6H_5)_3M'$ derivatives is greater than that for the X_3M' derivatives. This may be responsible of the low value of 2130 cm^{-1} for ν(NC) found in a preliminary study on *trans*–$[Pd(C_6H_5NC)_2(Sn(C_6H_5)_3)_2]$.

The Sn–Cl stretching frequencies fall in the range 316-342 cm^{-1}, the Sn–Br in the range 215-257 cm^{-1}, and the Ge–Cl in the range 360-384 cm^{-1}. They are considerably shifted to higher frequency upon coordination if compared to those of the free ions:[18,19] for instance in $[Pd(C_6H_5NC)(P(C_6H_5)_3)(GeCl_3)Cl]$ they are at 384(a_1) and 360(e) cm^{-1}, while in $GeCl_3^-$ the a_1 type is at 320 cm^{-1} and the e type at 253 cm^{-1}. Such a shift is typical for compounds containing a metal-$M'X_3$ bond and is indicative of an increased oxidation state of M'.[20]

For the $[Pd(RNC)_2(M'Cl_3)_2]$ derivatives the ν(M'–Cl) vibrations give rise to strong absorptions, usually merged into one very intense broad band. On the contrary, the corresponding $SnBr_3$ derivatives are characterized by three strong and well separated ν(Sn–Br) bands. The bending vibrations of the $M'X_3$ groups (see TableII) are not affected by coordination. In fact, their values are not different from those of the free ions.[18,19] In Table II a tentative assignment of the metal-metal stretching frequencies is reported. These bands, which are usually of low intensity, appear to fall in the ranges 199-226 cm^{-1} for ν(Pd–$SnCl_3$), 156-180 cm^{-1} for ν(Pd–$SnBr_3$), 228-240 cm^{-1} for ν(Pd–$GeCl_3$) and 190-206 cm^{-1} for ν(Pt–$SnCl_3$). They cannot be considered of course as pure stretching modes because of the coupling which may occur with other vibrational modes of the molecule in the low frequency region. However, in the absence of any theoretical calculation, they can be roughly described as M–M' stretching vibrations. Such bands are not present in the spectra of the free ligands RNC or in those of the parent compounds $[Pd(RNC)_2Cl_2]$ and $[Pd(C_6H_5NC)(L)Cl_2]$. We have based our assignment on the fact that in compounds of the type $[M(RNC)(L)(M'X_3)_{2-n}X_n]$ many factors, which may influence the metal-metal stretch, can be changed. In this way, we have found that a change of RNC does not alter appreciably the position of ν(M–M'). The only exception is the low value (156 cm^{-1}) of ν(Pd–Sn) in *trans*–$[Pd(C_6H_5NC)_2(SnBr_3)_2]$ compared to those of the other $SnBr_3$ derivatives (178 and 180 cm^{-1}). On passing from $SnCl_3$ to $SnBr_3$ compounds (change of X) the corresponding ν(M–M') are lowered by 30-58 cm^{-1}, while on passing from $SnCl_3$ to $GeCl_3$ derivatives (change of M') ν(M–M') are increased by *ca.* 25 cm^{-1}. It seems also that the platinum complexes have ν(Pt–$SnCl_3$) a little lower than the corresponding palladium ones. Literature data on complexes of the type $Cl_3M'Co(CO)_4$ report ν(Co–Ge) at 240 cm^{-1} and ν(Co–Sn) at 204 cm^{-1},[21] which confirms our assignment of ν(Pd–$GeCl_3$) and ν(Pd–$SnCl_3$). On the other hand, the value of 209.8 cm^{-1} for ν(Pt–$SnCl_3$) in $[Pt(SnCl_3)_5]^{3-}$ [22] is in a good agreement with those we have found for the platinum derivatives, even though the structures are different.

The assignment of ν(Pd–$SnCl_3$) in the complexes $[Pd(C_6H_5NC)(L)(SnCl_3)Cl]$ is complicated by the occurence of two bands in the same spectral region ($\sim$200 cm^{-1}), one of which is probably due to some deformation of the Pd–Cl bond. Even the complex $[Pd(C_6H_5NC)(P(C_6H_5)_3)(GeCl_3)Cl]$ has another additional band at 180 cm^{-1}, but in this case there is little uncertainty in assigning the band at 228 cm^{-1} to ν(Pd–$GeCl_3$) by comparing with the ν(Pd–Ge) values of the other germanium derivatives.

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