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

NEW σ-BONDED ARYL DERIVATIVES OF PALLADIUM(II)

S. SERGI, F. FARAONE, L. SILVESTRO AND R. PIETROPAOLO
Istituto di Chimica Generale ed Inorganica, Università di Messina (Italy)

(Received June 2nd, 1971)

SUMMARY

A new series of organopalladium complexes of the type *trans*-[PdL_2RX] ($L=SeEt_2$, $TeEt_2$; R=aryl group; X=halogen) containing σ-bonded organic substituents has been obtained from *trans*-[PdL_2X_2] complexes and the appropriate Grignard reagents. Analogous aryl derivatives could not be obtained from *trans*-[PdL_2X_2] complexes ($L=SEt_2$ or SPh_2).

The properties of the new compounds are reported and discussed. Their stabilities vary with the size of the neutral ligand and the position of substitution on the benzene ring.

INTRODUCTION

We previously described the synthesis and characterization of some new aryl–platinum(II) derivatives stabilized by the presence of sulphur or selenium ligands[1]. More recently, a study of the analogous tellurium compounds has shown that there is no significant difference between the Group VI ligands in stabilizing the aryl–platinum(II) compounds[2].

In this paper we report an extension of the previous research to the analogous palladium(II) compounds. The main interest in this work is the energetic splitting between the d_{xy} non-bonding and the $d_{x^2-y^2}$ antibonding metal orbital which seems to be more critical for palladium(II) than for platinum(II).

EXPERIMENTAL

Apparatus

Infrared spectra (Nujol mulls) were recorded with a Perkin–Elmer 457 grating spectrometer and with a Beckman IR-11 spectrometer. Analyses were carried out by Alfred Bernhardt, Mülheim Germany. Molecular weights were determined osmometrically on a Knauer vapor pressure osmometer. Melting points (uncorrected) were determined on a Fisher–Jones hot stage apparatus.

Preparations

All the reactions were carried out under nitrogen.

trans-Bis(diethyltelluride)dichloropalladium(II) was prepared as reported[3].

TABLE 1

PHYSICAL PROPERTIES, ANALYTICAL DATA AND MOLECULAR WEIGHTS

Complex	Colour	M.p. (°C)	Analyses (%)						Mol.wt.	
			Found			Calcd.			Found in C_6H_6	Calcd.
			C	H	X	C	H	X		
trans-$[Pd(TeEt_2)_2(Ph)Br]$	Yellow orange	88–92	26.29	3.92	12.33	26.47	3.90	12.59	608	634
trans-$[Pd(TeEt_2)_2(Ph)I]$	Pale yellow	87–90	24.89	3.59	18.86	24.66	3.58	18.60		
trans-$[Pd(TeEt_2)_2(o\text{-}Tol)Br]$	Yellow	97–102	28.04	4.34	12.09	27.76	4.19	12.32		
trans-$[Pd(TeEt_2)_2(p\text{-}Tol)I]$	Yellow	87	26.06	4.03	18.11	25.87	3.91	18.23	682	696
trans-$[Pd(TeEt_2)_2(Mes)Br]$	Yellow	97–100	30.35	4.89	12.69	30.16	4.60	12.74	657	627
trans-$[Pd(TeEt_2)_2(o\text{-}ClC_6H_4)Br]$	Yellow orange	69–71	24.94	3.57	5.20[a] 11.91[b]	25.03	3.60	5.30 11.79	689	712
trans-$[Pd(TeEt_2)_2(p\text{-}ClC_6H_4)Cl]$	Yellow	99–106	26.96	4.00	10.92	26.73	3.84	11.27	619	625
trans-$[Pd(TeEt_2)_2(p\text{-}ClC_6H_4)Br]$	Yellow	112–124 dec.	24.92	3.66	4.99[a] 11.61[b]	25.03	3.60	5.30 11.79	641	669
trans-$[Pd(TeEt_2)_2(p\text{-}FC_6H_4)Br]$	Pale yellow	110–115	26.00	3.84	2.92[c] 12.62[b]	25.70	3.70	2.90 12.20	648	652
trans-$[Pd(SeEt_2)_2(Ph)Cl]$	White	60–64	34.11	5.28	7.08	34.09	5.21	7.19		
trans-$[Pd(SeEt_2)_2(Ph)Br]$	White	73–75	31.58	4.47	15.00	31.31	4.69	14.87	566	536
trans-$[Pd(SeEt_2)_2(Mes)I]$	Yellowish green	100–110 dec.	32.68	5.08	20.49	32.50	4.96	20.20		
trans-$[Pd(SeEt_2)_2(p\text{-}ClC_6H_4)Cl]$	Pale yellow	75 dec.	32.04	4.62	13.38	31.87	4.58	13.44		
trans-$[Pd(SeEt_2)_2(p\text{-}ClC_6H_4)Br]$	Pale yellow	88–91	29.59	4.26	5.78[a] 13.87[b]	29.38	4.32	6.19 13.95	580	572
trans-$[Pd(SeEt_2)_2(p\text{-}FC_6H_4)Br]$	Pale yellow	95–103 dec.	30.56	4.35	3.33[c] 14.32[b]	30.30	4.36	3.40 14.30	580	555

[a] For Cl. [b] For Br. [c] For F.

All other complexes PdL_2Cl_2 (where $L=SeEt_2$, SEt_2, SPh_2) were prepared similarly by addition of the ligands to aqueous solutions of potassium tetrachloropalladate(II), and were characterized by elemental analyses, molecular weights and IR spectra. Bromo and iodo derivatives were prepared by metathetical replacement from PdL_2Cl_2 with LiX salts in methyl alcohol. Analytical data and physical properties are reported in Table 1.

trans-Bis(diethyl selenide)bromo(phenyl)palladium(II), $Pd(SeEt_2)_2(Ph)Br$. A solution of $Pd(SeEt_2)_2Br_2$ (500 mg, 0.92 mmoles) in ether (80 ml) was cooled to −78° and phenylmagnesium bromide (1.85 mmoles) in ether was added with stirring. The reaction mixture was stirred for 30 min at −78°, during which it slowly turned black, owing to formation of elemental palladium. It was allowed to warm to 0° and hydrolyzed. Evaporation of the ether phase left a residue, which was taken up in ether. The solution was filtered to remove finely divided metallic palladium and cooled to −78° to give crystals. Repetition of this procedure gave the colourless complex.

trans-Bis(diethyl selenide)chloro(phenyl)palladium(II), $Pd(SeEt_2)_2(Ph)Cl$. This compound was prepared similarly from PhMgCl in THF and *trans*-$Pd(SeEt_2)_2Cl_2$ (molar ratio 2/1).

trans-Bis(diethyl telluride)bromo(phenyl)palladium(II), $Pd(TeEt_2)_2(Ph)Br$. To an ethereal solution of $Pd(TeEt_2)_2Br_2$ (500 mg, 0.78 mmoles) phenylmagnesium bromide (3.14 mmoles) was added dropwise during 30 min at −78°. Working-up as above gave *trans*-$Pd(TeEt_2)_2(Ph)Br$ as colourless needles from pentane.

trans-Bis(diethyl telluride)iodo(phenyl)palladium(II), $Pd(TeEt_2)_2(Ph)I$, and trans-bis(diethyl telluride)chloro(phenyl)palladium(II), $Pd(TeEt_2)_2(Ph)Cl$. These compounds were similarly prepared from the reaction of *trans*-$Pd(TeEt_2)_2I_2$ and *trans*-$Pd(TeEt_2)_2Cl_2$, respectively, with the appropriate phenylmagnesium halide (molar ratio 1/2). No analytical data are reported for the *trans*-$Pd(TeEt_2)_2(Ph)Cl$ (m.p. 32–33°) because it is very unstable in the air. It was characterized by its IR spectrum.

trans-Bis(diethyl telluride)bromo(o-tolyl)palladium(II), $Pd(TeEt_2)_2(o\text{-}Tol)Br$. No reaction was apparent when *o*-tolylmagnesium bromide (1.57 mmoles) in ether was added to $Pd(TeEt_2)_2Br_2$, (500 mg, 0.88 mmoles) in ether (30 ml) at −78°. The mixture was allowed to warm to room temperature and became dark. After about 1 h it was hydrolyzed, and evaporation of the ether layer gave an oil which was crystallized from ether/pentane to give yellow crystals.

trans-Bis(diethyl telluride)bromo(o-chlorophenyl)palladium(II), $Pd(TeEt_2)_2(o\text{-}Cl\text{-}C_6H_4)Br$. To the dibromide, $Pd(TeEt_2)_2Br$, (500 mg, 0.78 mmoles) in ether (30 ml) at −78° was added (*o*-chlorophenyl)magnesium iodide (1.57 mmoles) in ether. After 1 h at −78° the mixture was allowed to warm to room temperature and then slowly darkened. After hydrolysis at 0°, evaporation of the ether phase gave an oil which was treated with methanol to give an orange-coloured solid.

trans-Bis(diethyl selenide) iodo(mesityl)palladium(II), $Pd(SeEt_2)_2(Mes)I$. To $Pd(SeEt_2)_2I_2$ (500 mg, 0.79 mmoles) in ether (50 ml) at −78° was added mesitylmagnesium bromide (1.6 mmoles). The mixture was then allowed to warm to room temperature and more mesitylmagnesium bromide (1.6 mmoles) was added with cooling. No reaction was apparent at −78° but the solution rapidly darkened at room temperature. After hydrolysis with ice, evaporation of the organic layer left a residue. This was dissolved in benzene, and the solution was filtered and evaporated to dryness. The oil obtained was treated with ether to give a yellowish-green solid.

trans-Bis(diethyl telluride)bromo(mesityl)palladium(II), $Pd(TeEt_2)_2(Mes)Br$. To $Pd(TeEt_2)_2Br_2$, (500 mg, 0.78 mmoles) in ether (50 ml) at −78° was added mesitylmagnesium bromide (3.1 mmoles). No reaction appeared to take place below −10°, but the mixture darkened as it warmed to room temperature. After hydrolysis at 0°, the crude product obtained was dissolved in ether, and the filtered solution was concentrated and was cooled at −78° to give a yellow solid.

trans-Bis(diethyl telluride)iodo(p-tolyl)palladium(II), $Pd(TeEt_2)_2(p\text{-}Tol)I$. To $Pd(TeEt_2)_2I_2$ (500 mg, 0.68 mmoles) *p*-tolylmagnesium iodide (1.36 mmoles) was added dropwise at −78° during 30 min. The mixture was then allowed to warm to room temperature and more *p*-tolylmagnesium iodide was added with cooling. No reaction was apparent at −78° after addition of 2.72 mmoles, but the solution rapidly darkened at room temperature. After hydrolysis at 0°, evaporation of the ether phase left a residue which was crystallized from ether/pentane to give a yellow solid.

trans-Bis(diethyl selenide)bromo(p-fluorophenyl)palladium(II), $Pd(SeEt_2)_2(p\text{-}F\text{-}C_6H_4)Br$. To a suspension of $Pd(SeEt_2)_2Cl_2$ (400 mg, 0.9 mmoles) in ether (50 ml) at −78° was added *p*-fluorophenylmagnesium bromide (0.9 mmoles). The mixture rapidly darkened. After hydrolysis at 0°, evaporation of the ether phase gave the crude complex, which was dissolved in ether, and the filtered solution was concentrated to a small volume. Cooling gave a colourless solid.

trans-Bis(diethyl selenide)chloro(p-fluorophenyl)palladium(II), $Pd(SeEt_2)_2(p\text{-}F\text{-}C_6H_4)Cl$. This compound was prepared from the *trans*-$Pd(SeEt_2)_2(p\text{-}FC_6H_4)Br$ and LiCl in methyl alcohol (m.p. 85–95° dec.). No analytical data are reported because the product is very unstable in the air.

trans-Bis(diethyl telluride)bromo(p-fluorophenyl)palladium(II), $Pd(TeEt_2)_2(p\text{-}FC_6H_4)Br$. To a suspension of $Pd(TeEt_2)_2Cl_2$ (500 mg, 0.9 mmoles) in ether (50 ml) at −78° was added (*p*-fluorophenyl)magnesium bromide (0.9 mmoles). Working-up as above gave a pale-yellow complex from pentane.

trans-Bis(diethyl selenide)bromo(p-chlorophenyl)palladium(II), $Pd(SeEt_2)_2(p\text{-}ClC_6H_4)Br$. The dibromide $Pd(SeEt_2)_2Br_2$, (500 mg, 0.92 mmoles) was similarly treated with an ethereal solution of (*p*-chlorophenyl)magnesium bromide (1.85 mmoles). Working-up as above gave a colourless complex from ether/pentane.

trans-Bis(diethyl selenide)chloro(p-chlorophenyl)palladium(II), $Pd(SeEt_2)_2(p\text{-}ClC_6H_4)Cl$. This compound was prepared by addition of (*p*-chlorophenyl)magnesium chloride (1.76 mmoles) in THF to a suspension of *trans*-$Pd(SeEt_2)_2Cl_2$ (400 mg, 0.88 mmoles) in ether. Working-up as above gave *trans*-$Pd(SeEt_2)_2(p\text{-}ClC_6H_4)Cl$ as pale-yellow needless from ether.

trans-Bis(diethyl telluride)bromo(p-chlorophenyl)palladium(II), $Pd(TeEt_2)_2(p\text{-}ClC_6H_4)Br$. To $Pd(TeEt_2)_2I_2$ (500 mg, 0.68 mmoles) in ether (40 ml) was added (*p*-chlorophenyl)magnesium bromide (3.5 mmoles). No reaction was apparent at −78°, but the solution darkened at room temperature. The mixture was stirred for 30 min at room temperature, cooled to 0°, and hydrolyzed. Evaporation of the ether phase gave a crude product containing some starting material. Crystallization from ether/pentane gave the desired complex as pale yellow crystals.

trans-Bis(diethyl telluride)chloro(p-chlorophenyl)palladium(II), $Pd(TeEt_2)_2(p\text{-}ClC_6H_4)Cl$. The dichloride, $Pd(TeEt_2)_2Cl_2$, in ether was similarly treated with (*p*-chlorophenyl)magnesium chloride (molar ratio 1/2). Working-up as above gave a yellow product from ether.

RESULTS AND DISCUSSION

Few organometallic derivatives of palladium(II) containing Pd–C σ-bonds have been previously described. Methyl derivatives[4] have been reported in complexes containing neutral ligands (such as tertiary phosphines and arsines, 1,5-cyclooctadiene and bidentate ligands such as bipyridine, 1,2-bis(diphenylphosphino)ethane, 1,2-bis-(methylthio)ethane, *o*-phenylenebis(dimethylarsine), [*o*-(dimethylarsino)phenyl]diethylphosphine), but σ-aryl–palladium(II) compounds are known only in complexes containing tertiary phosphines[4–6].

A variety of behaviour was observed on treating complexes of the type *trans*-PdL_2X_2 (L=$TeEt_2$, $SeEt_2$, SEt_2, SPh_2; X=halogen) with arylmagnesium halides. When L=$TeEt_2$, aryl derivatives of the type *trans*-$Pd(TeEt_2)_2XR$ were always obtained, often in low yield. When *trans*-$Pd(SeEt_2)_2X_2$ was used as starting material the corresponding aryl derivatives were successfully obtained only with phenylmagnesium halide, *o*-tolylmagnesium halide, mesitylmagnesium halide, (*p*-fluorophenyl)magnesium halide and (*p*-chlorophenyl)magnesium halide; with *p*-tolylmagnesium halide or (*o*-chlorophenyl)magnesium halide the substrate was reduced and metallic palladium was formed. Finally, compounds containing the neutral ligands SEt_2 and SPh_2 were always reduced to metallic palladium; this has been reported by others for the complex with L=SEt_2[4].

Attempts were also made to use organolithium reagents but a fast reduction was observed in every case, even at low temperature (−78°).

The use of an excess of the Grignard reagent never gives species of the type *trans*-PdL_2R_2. Aryl–platinum(II) derivatives containing Group VIB ligands, on the contrary, are well known[1,2].

All attempts to obtain σ-methyl–palladium(II) derivatives from CH_3MgX (X=Br, I) were unsuccessful. However, reduction does not occur in these cases, and the starting complexes can be completely recovered.

As can be expected from the general tendency of palladium(II) to form complexes containing monodentate ligands, all the new complexes have a *trans*-planar structure, as can be seen from the infrared spectra summarized in Table 2. The frequency of the single stretching vibration Pd–X has been used by several authors to determine the geometry of complexes of this type.

The ν(Pd–Cl) and ν(Pd–Br) stretching vibrations are shifted to values which are low compared with those of the *trans*-PdL_2X_2 compounds, in agreement with a structure in which the halogen ligand is *trans* to the organic group. From the data reported in Table 2 there seems to be no simple relationship between the Pd–X stretching frequency and the nature of the organic aryl group. It was not possible for any complex to assign a value for the ν(Pd–I) vibration. However, because of the analogous behaviour of the compounds containing the other halogens it seems reasonable to assign a *trans* configuration to the iodo derivatives also. The ν(Pd–C) gives a very weak band, which makes its assignment difficult and tentative.

The stability of the *trans*-PdL_2RX compounds synthetized is limited and, with the exception of the *p*-chloro and *p*-fluoro derivatives, which are relatively stable, they undergo decomposition to metallic palladium slowly at room temperature in solution and even in the solid state. When the halogen is varied the stability increases in the order Cl < Br < I. This sequence of stability in respect to reduction is surprising when

TABLE 2

IR DATA

In cm^{-1}; nujol mull.

Complex	ν(Pd–C)	ν(Pd–Cl)	ν(Pd–Br)
trans-[Pd(TeEt$_2$)$_2$(Ph)Cl]	483 w	281 s	
trans-[Pd(TeEt$_2$)$_2$(Ph)Br]	481 w		
trans-[Pd(TeEt$_2$)$_2$(Ph)I]	479 w		
trans-[Pd(TeEt$_2$)$_2$(*o*-Tol)Br]	515 w		
trans-[Pd(TeEt$_2$)$_2$(Mes)Br]			165 vs
trans-[Pd(TeEt$_2$)$_2$(*p*-FC$_6$H$_4$)Br]	521 m		173 s
trans-[Pd(TeEt$_2$)$_2$(*p*-ClC$_6$H$_4$)Cl]		281 s	
trans-[Pd(TeEt$_2$)$_2$(*o*-ClC$_6$H$_4$)Br]			160 m
trans-[Pd(SeEt$_2$)$_2$(Ph)Cl]		282 s	
trans-[Pd(SeEt$_2$)$_2$(*p*-FC$_6$H$_4$)Cl]	526 m	278 s	
trans-[Pd(SeEt$_2$)$_2$(*p*-FC$_6$H$_4$)Br]	524 m		172 vs
trans-[Pd(SeEt$_2$)$_2$(*p*-ClC$_6$H$_4$)Cl]	508 w	280 m	
trans-[Pd(SeEt$_2$)$_2$(*p*-ClC$_6$H$_4$)Br]	505 w		166 vs

one considers that I^- is the halide ion which most easily undergoes oxidation. However, the sequence can be explained if one bears in mind the importance of polarizability ("softness") in determining the stability of palladium(II) compounds, since Pd^{II} is a typical "class b" metal ion ("soft acid")[7].

The monophenyl complex, *trans*-Pd(TeEt$_2$)$_2$(C$_6$H$_5$)Br, undergoes exchange reactions; for example, potassium thiocyanate gives *trans*-Pd(TeEt$_2$)$_2$(C$_6$H$_5$)SCN. Attempts to prepare a nitro derivative resulted in decomposition.

As for the effect on the stability of the nature of the organic group, those σ-aryl derivatives in which there is an electron-withdrawing *para*-group are more stable than analogous compounds containing electron-donor *para*-groups[4,5].

In the case of L = SeEt$_2$, (*p*-fluorophenyl)magnesium halide or (*p*-chlorophenyl)-magnesium halide gave the corresponding monoaryl derivatives, whereas with *p*-tolylmagnesium halide only metallic palladium was recovered. This is consistent with results reported in the literature[8,9]. On the other hand, when L = TeEt$_2$ it was possible also to obtain the relatively unstable *p*-tolyl derivative. This shows the importance of the nature of the neutral ligand on the stability. *o*-Substituted aryl derivatives have previously been reported to be more stable than the corresponding phenyl compounds, a result which was explained in terms of an *ortho*-effect[10]. However, we found that the *o*-chlorophenyl derivatives are much less stable than the corresponding phenyl and *o*-tolyl compounds, and attempts to prepare Pd(SeEt$_2$)-(*o*-ClC$_6$H$_4$)X, always resulted in the formation of metallic palladium. It seems that the *ortho*-effect mentioned above is a steric one, and thus should be present in our case also, because rotation about the Pd–C bond is probably hindered in the presence of the bulky *o*-chloro substituent. It seems reasonable to ascribe the observed instability to electronic factors.

The reported results indicate clearly the large difference in the ability of SEt$_2$, SeEt$_2$ and TeEt$_2$ ligands to stabilize aryl–palladium(II) derivatives. The stability increases in the order $SEt_2 < SeEt_2 < TeEt_2$, *i.e.* with increasing atomic number of the donor atom. A similar trend was observed in platinum(II) chemistry for Group VB donors ($PPh_3 < AsPh_3 < SbPh_3$)[9], but for the platinum(II) compounds no significant difference was reported for Group VIB donors[1,2]. The observed trend is probably related to the polarizability of the donor atoms. In addition, π-bonding between palladium and sulphur (in thio ethers) has been reported to be insignificant[11], whereas overlap between the filled 4*d* orbitals of palladium(II) and the empty 4*d* and 5*d* orbitals of selenium and tellurium respectively seems to be important. The view that π-interaction is more important in the Pd–Te than in the Pd–Se bond is supported by the work of Pluscec and Westland[12].

ACKNOWLEDGEMENTS

We thank Professor L. Cattalini for discussions during the preparation of this article and the Italian National Research Council (C.N.R. Rome) for financial assistence.

REFERENCES

1 S. Sergi, V. Marsala, R. Pietropaolo and F. Faraone, *J. Organometal. Chem.*, 23 (1970) 281.
2 S. Sergi, F. Faraone and L. Silvestro, *J. Inorg. Nucl. Lett.*, in press.
3 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, (1957) 2351.
4 G. Calvin and G. E. Coates, *J. Chem. Soc.*, (1960) 2008.
5 M. D. Rausch and F. E. Tibbetts, *J. Organometal. Chem.*, 21 (1970) 487.
6 J. Hopton, A. J. Rest, D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc. A*, (1966) 1326.
7 St. Ahrland, *Structure and bonding*, Vol. 1, Springer-Verlag, Berlin, 1966, p. 207.
8 C. R. Kistner, J. H. Hutchinson, J. R. Doyle and J. C. Storlie, *Inorg. Chem.*, 2 (1963) 1255.
9 C. R. Kistner, J. D. Blackman and W. C. Harris, *Inorg. Chem.*, 8 (1969) 2165.
10 M. L. H. Green, in G. E. Coates, M. L. H. Green and K. Wade (Eds.), *Organometallic compounds*, Vol. II, Methuen, London, 1968, p. 225.
11 L. Cattalini, in J. O. Edwards (Ed.), *Inorganic Reaction Mechanisms*, Vol. 13, Interscience, New York, 1970, p. 263.
12 J. Pluscec and A. D. Westland, *J. Chem. Soc.*, (1965) 5371.