Journal of Organometallic Chemistry, 317 (1986) C23–C24
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

A ROUTE FOR THE SYNTHESIS OF NOVEL ASYMMETRIC BINUCLEAR PENTAFLUOROPHENYL DERIVATIVES OF PALLADIUM(II)

GREGORIO LOPEZ*, GABRIEL GARCIA, CONCEPCION DE HARO, GREGORIO SANCHEZ and JOAQUIN GARCIA

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Murcia, 30001 Murcia (Spain)

(Received September 10th, 1986)

Summary

Binuclear halogen-bridged complexes of the type $(C_5F_5)_2Pd(\mu\text{-}Cl)_2ML_2$ (M = Ni, Pd (L_2 = dpe), Pt (L = PEt_3)] have been prepared by reaction of *cis*-$Pd(C_6F_5)_2(PhCN)_2$ with the corresponding halo complexes, MCl_2L_2, in dichloromethane. IR and NMR structural data are discussed.

Neutral binuclear organo complexes of palladium(II) of the type $L(C_6F_5)Pd(\mu\text{-}Cl)_2Pd(C_6F_5)L$ are known compounds which can be prepared by reaction between $Pd(C_6F_5)_2L_2$ and $PdCl_2$ [1]. However, to our knowledge no method has been described for the synthesis of neutral binuclear pentafluorophenyl derivatives in which the metal atoms have different coordination environments. Such a method requires the availability of a labile organometallic palladium complex that can react with a halo-complex, $PdCl_2L_2$ to give the desired product, $(C_6F_5)_2Pd(\mu\text{-}Cl)_2PdL_2$.

The labile complexes $Pd(C_6F_5)_2$(dioxane) [2] and $Pd(C_6F_5)_2(PhCN)_2$ [3] have been shown to be good precursors for the synthesis of several pentafluorophenyl derivatives of palladium(II) [3,4]. We now report that $Pd(C_6F_5)_2(PhCN)_2$, an organometallic analogue of the so-called "soluble palladium chloride", $PdCl_2(PhCN)_2$, can be used as starting material for the preparation of homo- and hetero-nuclear bimetallic complexes of the required type.

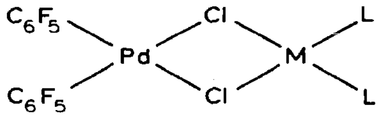
TABLE 1

^{1}H-, ^{31}P- AND ^{19}F-NMR DATA FOR COMPOUND 3 (solvent $CDCl_3$)

^{1}H (ppm vs. $SiMe_4$)	2.02 (m, 12H), 1.25 (m, 18H)
^{31}P (ppm vs. H_3PO_4)	11.64; $J(^{195}Pt-^{31}P)$ 3514.5 Hz
^{19}F (ppm vs. $CFCl_3$)	−116.12 (*o*-F), −162.00 (*p*-F), −164.92 (*m*-F)

When *cis*-$Pd(C_6F_5)_2(PhCN)_2$ and the appropriate chloro complex, MCl_2L_2 (molar ratio 1/1) are allowed to react in dichloromethane the binuclear complexes **1**–**3** are formed according to eq. 1. Compounds **1**–**3** can be readily isolated by precipitation with hexane (yields higher than 80%). Satisfactory analyses have been obtained for the complexes. All three are pale yellow (Pd, Pt) or orange (Ni) air-stable solids, and thermogravimetric analysis shows that they decompose above 100 °C. Their acetone solutions are non-conducting. Their infrared spectra show the two absorptions in the 800 cm^{-1} region which are characteristic of the *cis*-$Pd(C_6F_5)_2$ fragment [4]. That the non-organometallic compound is linked to the organometallic moiety is demonstrated by the absence of infrared bands in the $\nu(C{\equiv}N)$ region as well as by the fall (ca. 15 cm^{-1}) observed for the $\nu(M{-}Cl)$ frequencies on going from Cl_2ML_2 to $(C_6F_5)_2Pd(\mu\text{-}Cl)_2ML_2$ (**1**: 320, 305; **2**: 275, 265; **3**: 280, 265 cm^{-1}).

$$cis\text{-}Pd(C_6F_5)_2(PhCN)_2 \;+\; cis\text{-}MCl_2L_2 \xrightarrow[-2\,PhCN]{in\ CH_2Cl_2}$$



(1)

(**1** : M = Ni, L_2 = dpe;
2 : M = Pd, L_2 = dpe;
3 : M = Pt, L = PEt_3)

NMR data for compound **3** are listed in Table 1. The chemical shifts of the ^{19}F resonances are normal for bis(pentafluorophenyl) derivatives of palladium(II) [5], but the ^{31}P resonance is clearly influenced by the coordination of $Cl_2Pt(PEt_3)_2$ to the *cis*-$Pd(C_6F_5)_2$ moiety. Thus a downfield coordination chemical shift of 21.24 ppm is found for $Cl_2Pt(PEt_3)_2$ [Data for $Cl_2Pt(PEt_3)_2$ are: δ −9.60 ppm, $J(^{195}Pt{-}^{31}P)$ 3520 Hz [6].]

The synthetic method described herein, which is seemingly of general application, should allow the study of the interaction of the $(C_6F_5)_2Pd$ fragment with various halogeno complexes MX_2L_2.

The Dirección Regional de Universidad e Investigación de la Comunidad Autónoma de Murcia is thanked for financial support.

References

1 R. Usón, J. Forniés, R. Navarro and M.P. García, Inorg. Chim. Acta, 33 (1979) 69.
2 G. García and G. López, Inorg. Chim. Acta, 52 (1981) 87.
3 C. de Haro, G. García, G. Sánchez and G. López, J. Chem. Res., (S), (1986) 119, (M), (1986) 1128.
4 G. López, G. García, C. de Haro, G. Sánchez and M.C. Vallejo, J. Organomet. Chem., 263 (1984) 247.
5 G.B. Deacon and I.L. Grayson, Transition Met. Chem., 8 (1983) 131.
6 S.O. Grim, R.L. Keiter and W. McFarlane, Inorg. Chem., 6 (1967) 1113.