Journal of Organometallic Chemistry, 439 (1992) 231–235
Elsevier Sequoia S.A., Lausanne
JOM 22861

Synthesis and characterization of dinuclear palladium(II) complexes containing both chloro and organochalcogenides as bridging ligands

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(Received March 13, 1992)

Abstract

Dinuclear palladium(II) complexes of the type $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}EAr)(PR_3)_2]$ (E = S, Se, Te; Ar = Ph, C_6H_4OMe-4, C_6H_4OEt-4; PR_3 = PBu_3 and PMe_2Ph) have been prepared and characterized. These complexes adopt a *sym–cis* structure in which phosphine ligands are *trans* to the bridging chloride.

Introduction

A wide variety of dinuclear palladium(II) and platinum(II) complexes containing a bridging thiolato group $[M_2X_2(\mu\text{-}Y)(\mu\text{-}SR)L_2]$ have been synthesized and characterized [1–18]. Subtle variation in the nature of X, Y, R, and L leads to diversity in the structural features and also influences the chemical reactivity of such complexes. For example, mixed chloro/thiolato bridged complexes of platinum showed much higher catalytic activity than the corresponding dithiolato-bridged complexes [10,12]. Recently we have reported arylselenolato [19] and aryltellurolato [20–22] bridged dinuclear platinum complexes. To our knowledge, the dinuclear palladium(II) complexes containing RSe^- or RTe^- ligands reported so far are $[Pd_2Cl_2(\mu\text{-}SePh)_2(PPh_3)_2]$ [23], $[Pd_2Cl_2(\mu\text{-}TeAr)_2(PPh_3)_2]$ (Ar = C_6H_4OMe-4, C_6H_4OEt-4) [24] and $[Pd_2(TeR)_2(\mu\text{-}TeR)_2(PPh_3)_2]$ [25]. The present study aims at the synthesis of dinuclear palladium(II) complexes containing both chloro and organochalcogenide (RE^-; E = S, Se, Te) as the bridging ligands.

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Results and discussion

Treatment of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with $Pb(SPh)_2$ or NaEAr at room temperature gave dinuclear complexes of the type $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}EAr)(PR_3)_2]$ (eqs. 1 and 2).

$$[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + 1/2Pb(SPh)_2 \rightarrow [Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PR_3)_2] + \tfrac{1}{2}PbCl_2 \quad (1)$$

$$[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2] + NaEAr \rightarrow [Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}EAr)(PR_3)_2] + NaCl \quad (2)$$

where E = Se, Te; Ar = Ph, C_6H_4OMe-4, C_6H_4OEt-4; $PR_3 = PBu_3$, PMe_2Ph.

All these complexes are yellow or orange crystalline solids. They were recrystallized from a dichloromethane/ethanol mixture in 37–90% yield.

The $^{31}P\{^1H\}$ NMR spectra of these complexes displayed single resonances suggesting the predominance of a *cis* form in solution. The $^{31}P\{^1H\}$ signal for these complexes is shielded from the corresponding resonance for $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$. As is evident from Table 1, there is little dependence of the ^{31}P chemical shifts with the changes in EAr group. This indicates that the phosphine ligands are *trans* to the bridging chloride. Recent X-ray structural analyses of $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SR')(PR_3)_2]$ (M = Pd or Pt) [14,17,18] and $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(PBu_3)_2]$ [21] have revealed the *cis* structures with phosphine ligands *trans* to the bridging chloride for all these complexes.

The ^1H NMR spectra exhibited expected peak multiplicities and integration. Only one set of EAr proton resonances has been observed. The complexes containing dimethylphenylphosphine showed either a single doublet or two doublets for PMe_2 protons. This may be attributed to the subtle structural differences leading to equivalence or non-equivalence of PMe_2 methyl protons. For example, dinuclear palladium complexes with alkylthiolato bridges adopt a bent structure [14,17] while those with arylthiolato bridges exhibit a planar conformation.

Experimental

The palladium complexes, $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ [26] and diaryldittellurides [27] were prepared according to the literature methods. The phosphines (Strem Chemicals), Ph_2Se_2 (Aldrich), PhSH (Fluka) and $PdCl_2$ (Johnson Matthey) were obtained from commercial sources. Analytical grade solvents were used in all reactions. Proton NMR spectra were recorded on a Bruker AC 200 or Varian FT-80A NMR spectrometer in $CDCl_3$. Chemical shifts are relative to an internal chloroform peak (δ 7.26 ppm). ^{31}P NMR spectra were obtained on a Varian FT-80A NMR spectrometer operating at 32.203 MHz in $CDCl_3$ and chemical shifts are relative to external 85% H_3PO_4. Microanalyses were carried out by the Analytical Chemistry Division of this research centre.

Preparation of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PBu_3)_2]$

To an acetone solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ (81 mg, 0.107 mmol) was added solid $Pb(SPh)_2$ (26 mg, 0.061 mmol), prepared from $Pb(OAc)_2$ and thiophe-

Table 1

Melting points, analyses and NMR data ($CDCl_3$) for $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}EAr)(PR_3)_2]$ complexes

Compound	m.p. (°C)	Found (calc.) (%)		$^{31}P\{^1H\}$ NMR data (δ)	^1H NMR data [a] (δ)
		C	H		
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PBu_3)_2]$	118	42.8 (43.3)	6.8 (7.1)	36.5 [b]	0.85–1.75 (br, m, 54H, Bu); 7.10–7.30 (m), 8.15 (m, 5H, Ph)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PMe_2Ph)_2]$	195	37.3 (37.5)	3.8 (3.9)	10.5	1.78 (d, 12.5 Hz, 12H, PMe); 6.95–7.80 (m, 15H, Ph)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SePh)(PBu_3)_2]$	130	40.6 (41.0)	6.9 (6.8)	29.5	0.85–1.80 (br, m, 54H, Bu); 7.15–7.30 (m), 8.15 (m, 5H, Ph)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SePh)(PMe_2Ph)_2]$	220 dec.	34.6 (35.2)	3.6 (3.6)	10.1	1.64 (d, 12.5 Hz, 6H, PMe); 1.80 (d, 12.4 Hz, 6H, PMe); 6.97–7.37 (m, 15H, Ph)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(PBu_3)_2]$	128 dec.	38.4 (38.8)	6.9 (6.4)	30.5	0.80–1.70 (br, m, 54H, Bu); 7.15–7.35 (m), 8.10 (m, 5H, Ph)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeC_6H_4OMe\text{-}4)(PBu_3)_2]$	138 dec.	38.0 (38.8)	6.2 (6.4)	30.2	0.84–1.87 (br, m, 54H, Bu); 3.82 (s, 3H, OMe); 6.83 (d, 8.4 Hz, 2H, C_6H_4); 8.13 (d, 8.4 Hz, 2H, C_6H_4)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeC_6H_4OEt\text{-}4)(PBu_3)_2]$	135 dec.	39.5 (39.5)	6.8 (6.5)	30.0	0.85–1.80 (br, m, 57H, Bu + Me); 4.00 (q, 2H, $-CH_2O$); 6.75 (d, 8Hz, 2H, C_6H_4); 8.05 (d, 8 Hz, 2H, C_6H_4)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TePh)(PMe_2Ph)_2]$	140 dec.	33.4 (33.0)	3.4 (3.4)	10.4	2.14 (d, 12.4 Hz, 12H, PMe); 6.90–7.50 (m, 15H, Ph)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeC_6H_4OMe\text{-}4)(PMe_2Ph)_2]$	143 dec.	33.2 (33.3)	3.7 (3.5)	10.4	1.70 (d, 12.5 Hz, 6H, PMe); 1.93 (d, 12.5 Hz, 6H, PMe); 3.80 (s, 3H, OMe); 6.40 (d, 8 Hz, 2H, C_6H_4); 7.15–7.35 (m, 12H, Ph + C_6H_4)

[a] d, doublet; t, triplet; m, multiplet; s, singlet; br, broad.

[b] Recorded in acetone-d_6.

nol, and stirred at room temperature for 3 h. Lead chloride was filtered off and the filtrate was concentrated *in vacuo*. The residue was recrystallized from dichloromethane/ethanol (80 mg, 90%) as a yellow crystalline solid. In the case of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PMe_2Ph)_2]$, the product precipitated during the reaction. The solvent was removed *in vacuo*, and the residue was extracted with dichloromethane and recrystallized.

Preparation of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SePh)(PBu_3)_2]$

To a solution of Ph_2Se_2 (31 mg, 0.1 mmol) in benzene/methanol (1:3 v/v, 4 ml), a dilute methanolic solution of $NaBH_4$ was added with vigorous stirring under nitrogen. Addition of $NaBH_4$ was stopped when a colorless solution of NaSePh was obtained. To this, an acetone solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ (150 mg, 0.190 mmol) was added and the mixture was stirred for 3 h. The solvents were evaporated *in vacuo* and the residue was extracted with dichloromethane and passed through a Florisil column. Volume was reduced to 1 ml and a few drops of ethanol were added to give an orange crystalline solid (125 mg, 72%). $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SePh)(PMe_2Ph)_2]$ was prepared similarly.

Preparation of $[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}TeC_6H_4OMe\text{-}4)(PBu_3)_2]$

Dianisylditelluride (31 mg, 0.066 mmol) was dissolved in a benzene/methanol mixture (1:3 v/v, 4 ml) and was reduced to $NaTeC_6H_4OMe$-4 by addition of a dilute methanolic solution of $NaBH_4$. To this, an acetone solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ (104 mg, 0.137 mmol) was added and the mixture was stirred at room temperature for 3 h under nitrogen. The solution turned blackish-orange during the course of the reaction. The solvents were removed *in vacuo*. The residue was dissolved in dichloromethane and treated with activated charcoal and filtered. The filtrate was passed through a Florisil column to give a yellow solution. The solvent was reduced to 1 ml and ethanol (1 ml) was added to give orange crystals (70 mg, 53%). Other aryltellurolato-bridged complexes were prepared, similarly.

Acknowledgments

The authors thank Drs. J.P. Mittal and D.D. Sood for their keen interest throughout this work. We are thankful to the Analytical Chemistry Division for performing the microanalyses.

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