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Preparation and Characterization of Mercapto-bridged Homo- and Hetero-binuclear Palladium Platinum Complexes

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Abstract

Reaction of $[Pd_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (R = Pr^n, Bu^n or Ph) with mercaptans in acetone yields dimercapto bridged binuclear palladium complexes, $[Pd_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ (R′ = Et or Pr^i) (**I**), which on treatment with $[M_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (M = Pd or Pt) in chloroform affords homo- or hetero-binuclear complexes of the type $[PdM(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ (M = Pd (**II**) or Pt (**III**)). In addition to **III**, homobinuclear complexes, $[Pt_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$, $[Pd_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ and $[M_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ were also formed. Treatment of **III** with R′SH in acetone yields another series of stable hetero-binuclear complexes, $[PdPt(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ (**IV**), (R = Pr^n or Bu^n; R′ = Et or Pr^i). The NMR data (^1H and $^{31}P\{^1H\}$) indicate that complexes **I** and **IV** exist in a *sym–cis* configuration while **II** and **III** have a structure in which phosphine ligands are *trans* to the bridging chloride. A few bridge cleavage reactions with pyridine, PPh_3, $AsPh_3$ have also been investigated by $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

Hetero-bimetallic complexes are of considerable current interest largely because of their relevance to catalysis [1–4]. The possibility exists of developing model systems in which two adjacent but different metal centers can jointly catalyse a desired chemical reaction. Such a combination of palladium and platinum would possess advantages. Although hetero-bimetallic complexes of palladium and platinum containing chelating ligands, such as dppm, have been reported in the last few years [1], only a few simple species have been fully characterized. Simple hetero-bimetallic complexes of the type $[PdPt(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ have been shown to exist in a dynamic equilibrium with symmetrical species $[M_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (M = Pd or Pt) [5]. Since the R′S group is a stronger bridging ligand than the chloride, a reaction between $[Pt_2(\mu\text{-}X)_2Cl_2(PR_3)_2]$ and $[Pd_2(\mu\text{-}X)_2Cl_2(PR_3)_2]$ (X = SR′ or Cl) would yield stable hetero-binuclear complexes. Similar reactions for the preparation of homo-binuclear platinum complexes have been reported [6]. In this communication the preparation and characterization of $[Pd_2(\mu\text{-}X)(\mu\text{-}SR')Cl_2(PR_3)_2]$ and $[PdPt(\mu\text{-}X)(\mu\text{-}SR')Cl_2(PR_3)_2]$ complexes are described.

Experimental

The complexes $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$, $[Pt_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$, $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ and $[Pd_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (R = Pr^n, Bu^n or Ph; R′ = Et or Pr^i) were prepared according to the literature methods [6–9]. Mercaptans were purchased from Fluka and phosphines were obtained from Strem Chemicals and all manipulations involving them were performed under a nitrogen atmosphere. Analtyical grade solvents were used in all reactions. The ^1H and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Varian FT-80A NMR spectrometer operating at 79.5 and 32.2 MHz, respectively. Chemical shifts are relative to the chloroform peak at δ 7.26 ppm (for proton) and external 85% H_3PO_4 (for ^{31}P); more positive shifts represent deshielding. Microanalyses were performed by Analytical Chemistry Division, BARC. Melting points were determined in capillary tubes and are uncorrected.

Preparation of $[Pd_2(\mu\text{-}SPr^i)_2Cl_2(PBu_3)_2]$

To an acetone solution (~25 ml) of $[Pd_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$ (179 mg, 0.24 mmol) excess of Pr^iSH (0.5 ml) was added. The reaction mixture was stirred for 3 h at room temperature. The solvent was stripped off under vacuum leaving a yellow solid which after washing with hexane (20 ml) recrystallized from a chloroform ethanol mixture in 76% yield.

Similarly other dimercapto bridged complexes were prepared. Pertinent data are summarized in Table I.

Preparation of $[Pd_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPh_3)_2]$

To a chloroform solution of $[Pd_2(\mu\text{-}SPr^i)_2Cl_2(PPh_3)_2]$ (79 mg, 0.08 mmol), solid $[Pd_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ (73 mg, 0.08 mmol) was added and

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TABLE I. Physical and Analytical Data for $[PdM(\mu\text{-SR}')(\mu\text{-Cl})Cl_2(PR_3)_2]$ and $[PdM(\mu\text{-SR}')_2Cl_2(PR_3)_2]$

Complex	Solvent for recrystallization (Yield %)	Melting point (°C)	Analyses: found(calc.) (%)		
			C	H	S
$[Pd_2(\mu\text{-SEt})_2Cl_2(PPr^n_3)_2]$	$CHCl_3$/EtOH (88)	129–131	36.20 (36.37)	10.36 (7.21)	8.47 (8.82)
$[Pd_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PPr^n_3)_2]$	$CHCl_3$/EtOH (79)	117–118	34.23 (34.28)	6.73 (6.76)	4.50 (4.57)
$[Pd_2(\mu\text{-SPr}^i)_2Cl_2(PPr^n_3)_2]$	$CHCl_3$/EtOH (84)	154–156	37.94 (38.20)	7.49 (7.48)	9.20 (8.50)
$[Pd_2(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PPr^n_3)_2]$	$CHCl_3$/EtOH (86)	198–200	35.10 (35.29)	6.81 (6.91)	4.55 (4.48)
$[Pd_2(\mu\text{-SEt})_2Cl_2(PBu^n_3)_2]$	$CHCl_3$/EtOH (82)	114	41.68 (41.49)	8.06 (7.96)	8.38 (7.91)
$[Pd_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu^n_3)_2]$	$CHCl_3$/EtOH (76)	145	40.13 (39.78)	7.93 (7.58)	4.97 (4.08)
$[Pd_2(\mu\text{-SPr}^i)_2Cl_2(PBu^n_3)_2]$	$CHCl_3$/EtOH (76)	139	42.93 (42.96)	8.26 (8.17)	7.92 (7.65)
$[Pd_2(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PBu^n_3)_2]$	$CHCl_3$/EtOH (72)	140–141	40.21 (40.59)	7.44 (7.70)	4.50 (4.01)
$[Pd_2(\mu\text{-SEt})_2Cl_2(PPh_3)_2]$	$CHCl_3$/EtOH (45)	238–240[a]	51.18 (51.63)	4.13 (4.33)	6.96 (6.89)
$[Pd_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PPh_3)_2]$	$CHCl_3$ (69)	256–258[a]	50.05 (50.44)	3.76 (3.90)	3.25 (3.53)
$[Pd_2(\mu\text{-SPr}^i)_2Cl_2(PPh_3)_2]$	$CHCl_3$/EtOH (56)	225–228[a]	52.57 (52.62)	4.49 (4.63)	6.87 (6.69)
$[Pd_2(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PPh_3)_2]$	$CHCl_3$ (92)	252–255[a]	52.45 (50.98)	3.97 (4.06)	4.36 (3.49)
$[PdPt(\mu\text{-SEt})_2Cl_2(PPr^n_3)_2]$	$CHCl_3$/MeOH (80)	132–134	32.23 (32.42)	6.10 (6.43)	–
$[PdPt(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PPr^n_3)_2]$	$CHCl_3$/MeOH (62)	205–207	30.33 (30.43)	5.75 (6.00)	–
$[PdPt(\mu\text{-SPr}^i)_2Cl_2(PPr^n_3)_2]$	$CHCl_3$/MeOH (95)	148–150	34.53 (34.19)	6.66 (6.69)	7.85 (7.60)
$[PdPt(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PPr^n_3)_2]$	$CHCl_3$/MeOH (52)	197–200	31.49 (31.39)	6.00 (6.15)	4.10 (3.99)
$[PdPt(\mu\text{-SEt})_2Cl_2(PBu^n_3)_2]$	$CHCl_3$/MeOH (71)	112–113	33.06 (37.40)	6.93 (7.17)	6.85 (7.13)
$[PdPt(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu^n_3)_2]$	$CHCl_3$/MeOH (50)	142–143	36.09 (35.74)	6.99 (6.81)	3.84 (3.67)
$[PdPt(\mu\text{-SPr}^i)_2Cl_2(PBu^n_3)_2]$	$CHCl_3$/MeOH (78)	153–155	39.52 (38.86)	7.60 (7.39)	6.65 (6.91)
$[PdPt(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PBu^n_3)_2]$	$CHCl_3$/MeOH (36)	138–139	37.93 (36.53)	7.44 (6.93)	4.05 (3.61)

[a] Decomposed.

heated under reflux for 4 h during which time all $[Pd_2(\mu\text{-Cl})_2Cl_2(PPh_3)_2]$ dissolved. After cooling the solution was filtered and the filtrate was set aside for recrystallization. The crystals thus obtained were washed with chloroform and dried under vacuum (yield 90%).

Reaction of $[Pd_2(\mu\text{-SEt})_2Cl_2(PPr^n_3)_2]$ with $[Pt_2(\mu\text{-Cl})_2Cl_2(PPr^n_3)_2]$

To a chloroform solution (3 ml) of $[Pd_2(\mu\text{-SEt})_2Cl_2(PPr^n_3)_2]$ (202 mg, 0.28 mmol) a solution of $[Pt_2(\mu\text{-Cl})_2Cl_2(PPr^n_3)_2]$ (235 mg, 0.28 mmol) was added and the resulting solution was left at room temperature (30–35 °C) for 3–4 h. To this solution 15 ml methanol was added and then it was kept in a freezer for 20–24 h. Yellow needle shaped crystals separated which were filtered out, washed with methanol and dried under vacuum (yield 275 mg, 62%). Other complexes of this series were prepared in a similar manner.

Dimercapto bridged hetero-bimetallic complexes were prepared in a manner similar to the preparation of $[Pd_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ as described above.

Reaction between $[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PBu_3)_2]$ *and* $[Pd_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PBu_3)_2]$ *in Chloroform*

Solutions of $[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PBu_3)_2]$ (67.5 mg, 0.07 mmol) and $[Pd_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PBu_3)_2]$ (56.3 mg, 0.07 mmol) in $CDCl_3$ were mixed in an NMR tube and the progress of the reaction was studied by $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction between $[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PBu_3)_2]$ *and* $[Pd_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$

Solutions of $[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PBu_3)_2]$ (80 mg, 0.08 mmol) and $[Pd_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$ (61.3 mg, 0.08 mmol) in $CDCl_3$ (~4 ml) were mixed in an NMR tube and the progress of the reaction was investigated by $^{31}P\{^1H\}$ NMR spectroscopy.

Cleavage Reactions of $[Pd_2(\mu\text{-}X)(\mu\text{-}SR')Cl_2(PR_3)_2]$ *(X = Cl or SR')*

(a) With pyridine

A 10 fold excess of pyridine was added to a solution of $[Pd_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PBu_3)_2]$ (80 mg) in $CDCl_3$ and the solution was examined spectroscopically immediately after mixing and after 4 days.

(b) PPh_3, $AsPh_3$

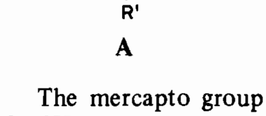
Two equivalents of ligand were added to a solution of the dimer $[Pd_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PBu_3)_2]$ and $[Pd_2(\mu\text{-}SR')_2Cl_2(PBu_3)_2]$ (60–90 mg) in $CDCl_3$ and the resulting solution was examined by $^{31}P\{^1H\}$ NMR spectroscopy.

Results and Discussion

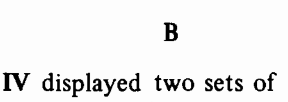
Treatment of chloro-bridged dinuclear palladium complexes, $[Pd_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$, with mercaptans in acetone affords yellow coloured dimercapto bridged palladium complex, $[Pd_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ (I) ($R = Pr^n$, Bu^n or Ph; $R' = Et$ or Pr^i). The latter complexes react with one equivalent of tetrachloro dipalladium complexes, $[Pd_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ in chloroform to yield chloro-mercapto bridged dipalladium complexes, $[Pd_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ (**II**). A similar reaction of **I** with $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$, on the other hand, is complex and yields a mixture of homo- and hetero-binuclear complexes. The products identified by ^{31}P NMR spectra (Table II) are $[PdPt(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ (**III**), **II**, $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$, $[Pd_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ and $[Pt_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$. The latter two complexes which are formed in small concentrations can be removed by recrystallization while **II** and its platinum analogue could not be removed completely from **III** as they appear to have more or less the same solubilities in the solvents from which they were recrystallized. Surprisingly, the reaction of $[Pt_2(\mu\text{-}SR')_2Cl_2(PBu^n_3)_2]$ with $[Pd_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$ in chloroform was extremely slow and even after 8 weeks the reactants were present in the solution.

Reaction of **III** with mercaptans in acetone yields stable dimercapto bridged hetero-bimetallic complexes, $[PdPt(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ (**IV**). Since **III** was contaminated with 25–30% symmetrical products $[M_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ (M = Pt or Pd), corresponding dimercapto bridged complexes were also formed in the same proportions as they were in **III**. Although a relative percentage of symmetrical dimers can be altered by repeated recrystallizations, in no case **IV** was free from them.

Of the two possible isomers A and B, only *sym–cis* isomer A (M = Pd) exists in solution for I as the ^1H NMR spectra in $CDCl_3$ displayed two sets of SR′ proton resonances. The $^{31}P\{^1H\}$ NMR spectra displayed a single resonance for tertiary phosphine ligands which was shielded considerably with respect to the one in the corresponding tetra chloro complexes.



A



B

The mercapto group of **IV** displayed two sets of S–CH< proton resonances and appeared as a complex multiplet due to overlapping with the resonances of symmetrical species. The ^{31}P NMR spectra of these complexes displayed resonances assignable to **IV** and the corresponding homo-binuclear complexes. Resonances due to the latter complexes can be identified by comparing them with the spectra of authentic samples. A $^{31}P\{^1H\}$ NMR spectrum of $[PdPt(\mu\text{-}SEt)_2Cl_2(PPr_3)_2]$ is shown in Fig. 1. Because of magnetic non-equivalence, resonances due to Pd–P and Pt–P in **IV** appeared as a doublet (^4J(P–P) ~ 6 Hz); the palladium bound phosphorus resonance showed ^3J(Pt–P) of the order of 12–19 Hz. The ^3J(Pt–P) values for the corresponding homobinuclear platinum complexes have been reported in the range 15–20 Hz for *cis* and ~50 Hz for *trans* isomers [7]. These data indicate that for **IV** only

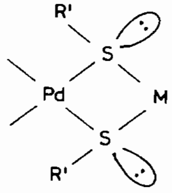
TABLE II. ^1H and $^{31}P\{^1H\}$ NMR Data for $[PdM(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ and $[PdM(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ (M = Pd or Pt) Complexes in $CDCl_3$ at Room Temperature

Complex	^1H NMR Data[a] δ SR′		$^{31}P\{^1H\}$ NMR Data				
	$-S-CH<$	$S-C<^{Me}$	δ(Pd–P)	δ(Pt–P)	^1J(Pt–P)	^3J(Pt–P)	^4J(P–P)
$[Pd_2(\mu\text{-}Cl)_2Cl_2(PPr^n{}_3)_2]$			38.0				
$[Pd_2(\mu\text{-}SEt)_2Cl_2(PPr^n{}_3)_2]$	2.55(Q, 7 Hz) 2.82(Q, 7 Hz)	[b]	15.0				
$[Pd_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$	2.95(Q, 7 Hz)	[b]	30.0				
$[Pd_2(\mu\text{-}SPr^i)_2Cl_2(PPr^n{}_3)_2]$	3.22(m) 3.70(m)	[b]	13.2				
$[Pd_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$	3.87(m)	[b]	29.6				
$[Pd_2(\mu\text{-}Cl)_2Cl_2(PBu^n{}_3)_2]$			39.4				
$[Pd_2(\mu\text{-}SEt)_2Cl_2(PBu^n{}_3)_2]$	2.56(Q, 7 Hz) 2.85(Q, 7 Hz)	[b]	15.9				
$[Pd_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PBu^n{}_3)_2]$	2.95(Q, 7 Hz)	[b]	30.8				
$[Pd_2(\mu\text{-}SPr^i)_2Cl_2(PBu^n{}_3)_2]$	3.25(m) 3.75(m)	[b]	14.3				
$[Pd_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PBu^n{}_3)_2]$	3.82(m)	[b]	30.2				
$[Pd_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$			[c]				
$[Pd_2(\mu\text{-}SEt)_2Cl_2(PPh_3)_2]$	3.11(Q, 7 Hz) 1.72(Q, 7 Hz)	1.53(t, 7 Hz) 0.48(t, 7 Hz)	16.7[d]				
$[Pd_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PPh_3)_2]$	1.83(Q)	0.70(t, 7 Hz)	32.0				
$[Pd_2(\mu\text{-}SPr^i)_2Cl_2(PPh_3)_2]$	4.00(m) 2.90(m)	1.84(d, 6.8 Hz) 0.70(d, 6.8 Hz)	16.2				
$[Pd_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPh_3)_2]$	3.40(m)	0.76(d, 6.8 Hz)	32.0				
$[PdPt(\mu\text{-}SEt)_2Cl_2(PPr^n{}_3)_2]$	2.65(Q) 3.00(m)	[b] [b]	13.4	1.4	3144	19	~6
$[PdPt(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$	2.95(m)	[b]	29.5	1.3	3951		
$[PdPt(\mu\text{-}SPr^i)_2Cl_2(PPr^n{}_3)_2]$	3.25(m) 4.00(m)	[b]	11.6	−0.3	3114	12	~6
$[PdPt(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$	3.82(m)	[b]	28.8	0.8	3975	11	
$[PdPt(\mu\text{-}SEt)_2Cl_2(PBu^n{}_3)_2]$	2.65(m) 3.00(m)	[b]	14.1	1.77	3142	18	6
$[PdPt(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PBu^n{}_3)_2]$	3.03(m)	[b]	23.8	−4.7	3956	8	
$[PdPt(\mu\text{-}SPr^i)_2Cl_2(PBu^n{}_3)_2]$	3.25(m) 4.00(m)	[b]	12.6	0.21	3117		6
$[PdPt(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PBu^n{}_3)_2]$	3.80(m)	[b]	29.5	1.20	3980	10	

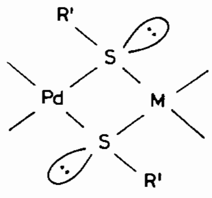
[a] m = multiplet, Q = quartet, t = triplet, d = doublet. [b] Merged in PR_3 resonances. [c] Insoluble in $CDCl_3$. [d] Small peak at 19.3 ppm appeared.

the *sym–cis* isomer **A** (M = Pt) is present in solution. The magnitude of ^1J(Pt–P) for **IV** is less than that of the corresponding *cis*-$[Pt_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$.

The dimercapto bridged complexes may exist in *syn* and *anti* configurations depending on the rearrangement of R′ groups with respect to each other (**C**, **D**). The X-ray structural analysis of *cis*-$[Pt_2(\mu\text{-}SEt)_2Cl_2(PPr^n{}_3)_2]$ has shown that the complex has an *anti* configuration with a non-planar central PtS_2Pt bridge [10]. In some cases isomerization of *syn* and *anti* forms is fast and involves inversion at sulfur atom(s) [11–14]. The rate of inversion has been shown to be dependent on the nature of ligands and on the method of preparation. Possibly due to such a fast inversion process *syn* and *anti* isomers for **I** and **IV** could not be detected by ^1H and $^{31}P\{^1H\}$



syn **C**

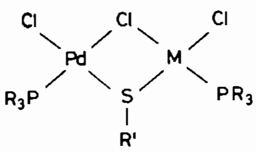


anti **D**

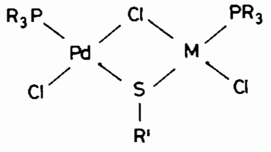
NMR spectroscopy, and also no CD bands for **IV** could be observed in the CD spectra, in spite of chiral sulfur centres.

Like chloro-mercapto bridged diplatinum complexes [6], analogous dipalladium, **II** and **III** complexes can exist in three configurations (**E**, **F**, **G**). Since dipalladium complexes, **II**, displayed single resonance in the $^{31}P\{^{1}H\}$ NMR spectra, the *sym–trans* isomer **G** does not exist in solution. Differentiation between **E** and **F** can not be made unambiguously in the absence of valuable coupling informations, yet the configuration **E** can be suggested as is observed for diplatinum complexes. A similar configuration has been reported for $[Pd_2(\mu\text{-SMe})(\mu\text{-Cl})Cl_2(EMe_3)_2]$ (E = P or As) [15]. The ^{1}H NMR spectra of **II** displayed a single set of SR' proton resonances.

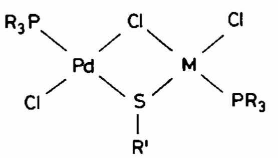
The ^{31}P NMR spectra of chloro-mercapto bridged hetero-bimetallic complexes displayed resonances for **III** and for the corresponding symmetrical complexes which can be identified by comparing the spectra with those of the authentic samples. A $^{31}P\{^{1}H\}$ NMR spectrum of $[PdPt(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PPr_3)_2]$ is shown in Fig. 2. Unlike dimercapto complexes of the type **IV**, ^{4}J(P–P) for **III** could not be resolved and appears to be smaller than digital resolution (2.5 Hz). In some cases ^{3}J(Pt–P) (~7 Hz) could be resolved while in others the base of the palladium-bound phosphorus signal broadened. The magnitude of ^{3}J(Pt–P) for **III** indicates that the phosphine ligands are *trans* to bridging chloride [6]. It is interesting to note that in **III** and **IV** the platinum bound phosphorus resonance is deshielded while the palladium bound phosphorus resonance is shielded with respect to the corresponding homo-binuclear complexes.



E



F



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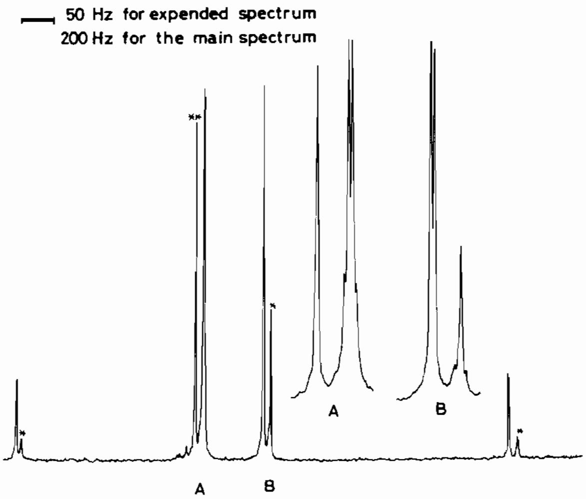

Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum of $[PdPt(\mu\text{-SEt})_2Cl_2(PPr_3)_2]$ in $CDCl_3$. Expansions for the regions A and B are shown in the Figure and are labelled respectively. *Due to $[Pt_2(\mu\text{-SEt})_2Cl_2(PPr_3)_2]$. **Due to $[Pd_2(\mu\text{-SEt})_2Cl_2(PPr_3)_2]$.

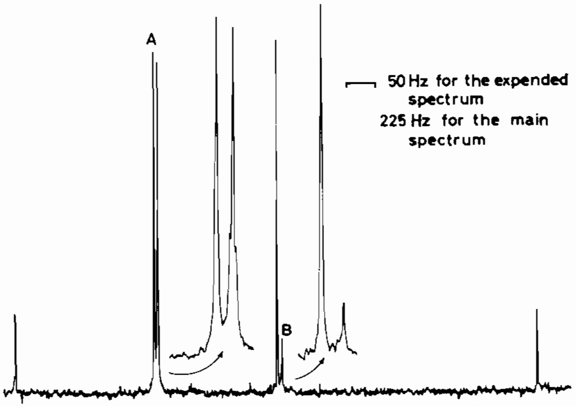

Fig. 2. $^{31}P\{^{1}H\}$ NMR spectrum of $[PdPt(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PPr_3)_2]$ in $CDCl_3$. Signals labelled A and B are due to $[Pd_2(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PPr_3)_2]$ and $[Pt_2(\mu\text{-SPr}^i)(\mu\text{-Cl})Cl_2(PPr_3)_2]$, respectively.

The reaction between $[Pd_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu_3)_2]$ and $[Pt_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu_3)_2]$ in chloroform was investigated with the hope that disproportionation of these dimers would yield **III** quantitatively. The $^{31}P\{^{1}H\}$ NMR spectrum, obtained just after mixing $CDCl_3$ solutions containing 1:1 stoichiometric quantities of $[Pd_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu_3)_2]$ and $[Pt_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu_3)_2]$, showed additional resonances assignable to $[Pd_2(\mu\text{-Cl})_2Cl_2(PBu_3)_2]$ and $[Pt_2(\mu\text{-SEt})_2Cl_2(PBu_3)_2]$ which were formed in small concentrations. Over a period of time the concentration of the latter two dimers increased and after a week all four dimers were present in approximately

1:1:1:1 ratio. Subsequently another species began to form whose resonances were attributable to [PtPd(μ-SEt)(μ-Cl)Cl_2(PBu_3)$_2$]. On keeping the solution for another week the concentration of **III** increased and attained its maximum value as no further noticeable change in signal intensities as well as integrations could be seen on keeping the solution over a period of the next few days. It is reasonable to conclude from these observations that the following equilibrium is attained:

$$[Pd_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu_3)_2] + [Pt_2(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu_3)_2]$$

$$\rightleftharpoons$$

$$[Pd_2(\mu\text{-Cl})_2Cl_2(PBu_3)_2] + [Pt_2(\mu\text{-SEt})_2Cl_2(PBu_3)_2]$$

$$\rightleftharpoons$$

$$[PdPt(\mu\text{-SEt})(\mu\text{-Cl})Cl_2(PBu_2)_2]$$

A similar equilibrium was established over a period of 6–8 weeks when a reaction of [Pt_2(μ-SPr^i)$_2$$Cl_2$($PBu_3$)$_2$] with [$Pd_2$($\mu$-Cl)$_2$$Cl_2$($PBu_3$)$_2$] was carried out in chloroform solution.

A few bridge cleavage reactions of dipalladium complexes with donor ligands were studied and were found to be facile. In contrast similar reactions of corresponding diplatinum complexes have been reported to be slow [5–7]. Reactions of [Pd_2(μ-SPr^i)(μ-Cl)Cl_2(PBu_3)$_2$] with pyridine, PPh_3 or $AsPh_3$ were found to be fast. Reaction with pyridine gave two products [$PdCl_2$(py)(PBu_3)] (δ(^{31}P) 27.2 ppm) and [Pd_2(μ-SPr^i)$_2$$Cl_2$($PBu_3$)$_2$]. The dimer is probably formed via an intermediate [PdCl(SPr^i)(py)(PBu_3)] (δ(^{31}P) 17.0 ppm). A small amount of [$PdCl_2$(PBu_3)$_2$] was formed on keeping the solution at room temperature for 2–3 days. The reaction with triphenylarsine in a 1:2 stoichiometry proceeds similarly. Initially [$PdCl_2$($AsPh_3$)(PBu_3)] (δ(^{31}P) 21.5 ppm), [Pd_2(μ-SPr^i)$_2$$Cl_2$($PBu_3$)$_2$] and [Pd($SPr^i$)Cl($AsPh_3$)($PBu_3$)] ($\delta$(^{31}P) 17.0 ppm) were formed, but after 2–3 days the former two complexes and [$PdCl_2$(PBu_3)$_2$] were the only phosphorus containing species left in solution. Reaction with triphenylphosphine proceeds smoothly and yields a complex mixture of mononuclear palladium complexes and ~5% [Pd_2(μ-SPr^i)$_2$$Cl_2$($PBu_3$)$_2$]. Reaction of triphenylphosphine with [Pd_2(μ-SPr^i)$_2$$Cl_2$($PBu_3$)$_2$] is slow at room temperature and generates a ^{31}P NMR spectrum similar to that observed for the above reaction.

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