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CHLORIDE-BRIDGED METHYLPALLADIUM(II) DIMERS. PREPARATION, CARBONYLATION AND BRIDGE-SPLITTING REACTIONS WITH TERTIARY PHOSPHINES

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Summary

$[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ (L = PEt_3, PBu_3 or PMe_2Ph) reacts with $AlMe_3$ in ether, THF or a mixture of these solvents depending on L to give $[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$ in high yield, which has been characterized by IR and NMR spectroscopy as well as elemental analysis. Treatment of $[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$ with CO yields $[Pd_2(\mu\text{-}Cl)_2(COMe)_2L_2]$, while its reaction with L leads to *trans*-$[PdClMeL_2]$. The preparative method and the characteristic data of these complexes are discussed in comparison with the earlier work on the analogous aryl and aralkyl complexes.

Introduction

Halide-bridged complexes of palladium(II) and platinum(II) have been widely used as starting materials for the syntheses of organometallic and coordination compounds [1]. Complexes of the type $[Pt_2(\mu\text{-}Cl)_2R_2L_2]$ (R = aryl; L = tertiary phosphine) have been prepared from *cis*-$[Pt(C_2H_4)Cl_2L]$ and $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$ by using $SnRMe_3$ [2] and HgR_2[3], respectively, as arylating agents. HgR_2 (R = alkyl or aryl) also reacted with *cis*-$[PtCl_2(CO)L]$ to produce acyl or aroyl complexes of the same type, but no insertion products were isolated when LiR (R = Me or Ph) was used [3,4].

Only a few isolated examples of halide-bridged organopalladium(II) complexes such as $[Pd_2(\mu\text{-}Cl)_2(CH_2Ph)_2(PPh_3)_2]$ [5] and $[Pd_2(\mu\text{-}Cl)_2R_2L_2]$ (R = C_6F_5 or C_6Cl_5) [6–8] had appeared until a general route to such complexes was described by Anderson [9]. Anderson tried to prepare aryl and aralkyl complexes of the type $[Pd_2(\mu\text{-}Cl)_2R_2L_2]$ by using HgR_2, but this method was not examined for the preparation of a simple alkyl analogue. To date, there have been no attempts to prepare halide-bridged methyl and other simple alkylpalladium(II) complexes, except one by Calvin and Coates [10].

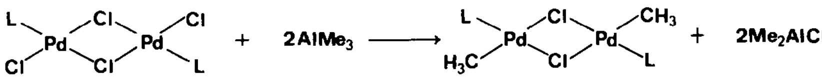
This paper presents the first example of chloride-bridged methylpalladium(II) complexes prepared by using $AlMe_3$ as an alkylating agent, and the reactions of these complexes with carbon monoxide and tertiary phosphines.

Results and discussion

Preparation and characterization of chloride-bridged methylpalladium(II) dimers

As mentioned above, the only previous attempt to make halide-bridged methylpallladium(II) complexes appears to be that by Calvin and Coates [10], who tried the direct alkylation of $[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ ($L = PBu_3$) with LiMe. However, the reaction proceeded to give metallic palladium, even at −45°C. The use of HgR_2 as an organic group transfer agent was accompanied by some decomposition in its reactions [9]. In some cases, it was necessary to resort to vacuum sublimation at high temperatures over 80°C in order to remove the by-product RHgCl. Thus, the procedure led to further decomposition and consequently resulted in low yields below 42%. To overcome this difficulty, we used $AlMe_3$ as an alkylating agent to obtain chloride-bridged methylpalladium(II) complexes, which are expected to be one of the most useful starting materials for organometallic synthesis.

Treatment of $[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ ($L = PEt_3$, PBu_3 or PMe_2Ph) with twice molar amounts of $AlMe_3$ in ethereal solvents produced the corresponding chloride-bridged methylpalladium(II) complexes $[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$ (I, $L = PEt_3$; II, $L = PBu_3$; III, $L = PMe_2Ph$) and Me_2AlCl according to eq. 1:



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These new dimeric complexes are colourless or pale yellow crystalline solids. I and II are stable to air, whereas III is rather unstable and decomposes slowly in air. II is readily soluble in most organic solvents and can be recrystallized from these, while III is soluble only in polar solvents such as ethers and haloalkanes, in which it decomposes slowly if air is included. The solubility of I is intermediate between these two. The dimeric nature of II was ascertained by molecular weight measurements both in non-polar and polar solvents (see Experimental section). The complexes were also characterized on the basis of IR and NMR spectroscopy and elemental analysis. The data are listed in Table 1.

As shown in Table 1, I–III showed an IR absorption assignable to δ(C–H) of the coordinated methyl group together with a Pd–C stretching vibration. These assignments were made by comparisons with the spectra of the corresponding tetrachloro dimers. The IR data obtained from *trans-* and *cis-*$[PdMe_2L_2]$ [11], *trans-*$[PdBrMe(PEt_3)_2]$ [10] and $[Pd_2(\mu\text{-}SEt)_2Me_2(PBu_3)_2]$ [10] were also referred to. The ^1H NMR spectra of I–III gave a doublet for the Pd–Me group with the ^3J(P–H) value comparable to that for the benzylic protons of $[Pd_2(\mu\text{-}Cl)_2(CH_2Ph)_2L_2]$ [9]. The $^{31}P\{^1H\}$ NMR spectra exhibited a single, but somewhat broadened, line (half-width values: 2.0, 2.7 and 2.7 Hz for I, II and III, respectively). The same situation has been encountered in the case of the aryl and aralkyl complexes $[Pd_2(\mu\text{-}Cl)_2R_2L_2]$, and the presence of only one line was attributed to rapid

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA FOR THE COMPLEXES $[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$ AND $[Pd_2(\mu\text{-}Cl)_2(COMe)_2L_2]$

Complex L	Found (calcd.) (%)		IR [a] (cm^{-1})			$^{31}P\{^1H\}$ and ^1H NMR [b]	
	C	H	δ(C–H)	ν(Pd–C)	ν(CO)	δ(P) (ppm)	$\delta(CH_3)$ (ppm)
$[Pd_2(\mu\text{-}Cl)_2Me_2L_2]$							
PEt_3 (I)	30.43 (30.57)	6.59 (6.60)	1170s	533m		32.6	0.59d (^3J(P,H) 2.0 Hz) (P–Et) 1.18 dt (^3J(P,H) 18 Hz, ^3J(H,H) 7 Hz)
PBu_3 (II)	43.32 (43.47)	8.44 (8.42)	1167m	460m		24.5	0.57d (^3J(P,H) 1.8 Hz)
PMe_2Ph (III)	36.47 (36.64)	4.77 (4.77)	1163m	440w		9.8	0.60d (^3J(P,H) 2.5 Hz), (P–Me) 1.70d (^2J(P,H) 11.0 Hz)
$[Pd_2(\mu\text{-}Cl)_2(COMe)_2L_2$							
PEt_3 (IV)	31.68 (31.71)	6.08 (5.99)			1688s, 1700s	25.2	2.45s, (P–Et) 1.20dt (^3J(P,H) 18 Hz, ^3J(H,H) 7 Hz)
PBu_3 (V)	43.80 (43.43)	8.03 (7.81)			1692s	17.3	2.44s
PMe_2Ph (VI)	37.25 (37.18)	4.36 (4.37)			1700s	−0.7	2.25d (^4J(P,H) 1.1 Hz), (P–Me) 1.67d (^2J(P,H) 11.0 Hz)

[a] On Nujol mulls (I–III) or in CH_2Cl_2 solutions (IV–VI). [b] The ^1H and ^{31}P chemical shifts were measured in ppm relative to Me_4Si and external H_3PO_4, respectively, in $CDCl_3$ solutions; s: singlet, d: doublet, dt: double triplet.

isomerization between the *cis* and *trans* isomers caused by a bimolecular process, because no products of phosphine and organic group mixing were detected on mixing $[Pd_2(\mu\text{-}Cl)_2Ph_2(PBu_3)_2]$ and $[Pd_2(\mu\text{-}Cl)_2(CH_2Ph)_2(PMePh_2)_2]$ in $CHCl_3$ solution [9]. Unfortunately, we could not examine a similar experiment since only complexes of the same alkyl group with different phosphines were obtained. However, mixing II and III in $CDCl_3$ caused the formation, after 30 min, of an equimolar mixture of the two reactants ($\delta(PBu_3)$ 24.5 ppm; δ (PMe_2Ph) 9.8 ppm) and $[(Bu_3P)MePd(\mu\text{-}Cl)_2PdMe(PMe_2Ph)]$ ($\delta(PBu_3)$ 24.8 ppm; $\delta(PMe_2Ph)$ 9.8 ppm; the latter resonance line was broadened to the half-width value of 4.0 Hz from 2.7 Hz in III only, because of overlapping).

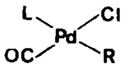
Carbonylation of the chloride-bridged methylpalladium(II) dimers

The dimeric complexes I–III reacted with carbon monoxide to produce the corresponding acetylpalladium(II) dimers, $[Pd_2(\mu\text{-}Cl)_2(COMe)_2L_2]$ (IV, L = PEt_3; V, L = PBu_3; VI, L = PMe_2Ph), which exhibit ν(CO) bands around 1700 cm^{-1} in their solution IR spectra and acetyl-methyl resonances in the range of δ2.25–2.45 ppm in their ^1H NMR spectra (Table 1). These complexes are pale or greyish yellow crystalline solids, which are stable to air for 1 or 2 months but decompose rapidly in solution if a CO gas is not bubbled through the solution.

When the carbonylation of II at ambient temperature and pressure was followed by ^1H NMR, the formation of V went to completion after 24 h in the coordinating solvent THF-d_8, whereas in CD_2Cl_2 its formation was 50% after 28 h and 80% even after 4 days. Therefore, all the synthetic studies were performed in THF. The reaction of II with CO in CH_2Cl_2 could also be monitored conveniently by IR measurements. In this case, the ν(CO) band at 1692 cm^{-1} increased in intensity as V was formed, and this was followed by the appearance, after 23 h, of new bands at 1995 and 2020 cm^{-1}, indicating some decomposition of V to terminal carbonyl species such as [PdCl(COMe)CO(PBu_3)].

Of the acetyl complexes isolated, only IV showed separate ν(CO) bands at 1688 and 1700 cm^{-1}, suggesting that the bimolecular exchange process is slow for this complex. For the other two, however, neither the IR nor the NMR spectrum showed any such evidence within our limited experimental data, although the $^{31}P\{^1H\}$ resonance lines were observed as somewhat broadened ones (half-width values: 2.7 and 1.5 Hz for V and VI, respectively) on the NMR time-scale.

The carbonylation mechanism for square-planar complexes of the type [$MClRL_2$] (M = Ni, Pd, Pt; R = organic group) has been shown by a detailed kinetic study [12] to proceed via two routes involving [MClR(CO)L_2], one of which requires direct insertion from the five-coordinate intermediate, while the other, often dominant, proceeds by initial L dissociation and subsequent R migration from the four-coordinate species [MClR(CO)L] [13]. In the present case, species **2** and/or **3** will be produced in the solution by initial bridge-splitting reactions of [$Pd_2(\mu\text{-}Cl)_2Me_2L_2$] with CO. In contrast with the platinum(II) case [3,14], the ready formation of the acetylpalladium(II) dimers IV–VI may be attributed to rapid isomerization of these species to **1**, which undergoes R migration to give the products.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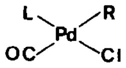
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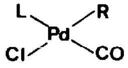
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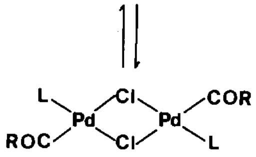

Bridge-splitting reactions of the methyl- and acetylpalladium(II) dimers with tertiary phosphines

The methyl- and acetyl-palladium(II) dimers I–VI underwent bridge-splitting reactions readily with stoichiometric amounts of L to produce *trans*-[$PdClMeL_2$] (VII, L = PEt_3; VIII, L = PBu_3; IX, L = PMe_2Ph) and *trans*-[PdCl(COMe)L_2] (XIII, L = PEt_3; XIV, L = PBu_3; XV, L = PMe_2Ph), respectively. The *trans* geometry was established by the equivalence of two phosphorus nuclei which was demonstrated by the single resonance observed in their $^{31}P\{^1H\}$ NMR spectra (Table 2) and the triplet resonance at δ 0.09 ppm for the Pd–Me protons in VIII, whose ^1H NMR spectrum was the only one examined.

To obtain complexes with four different ligands, bridge-splitting reactions of [$Pd_2(\mu\text{-}Cl)_2Me_2L_2$] with a different phosphine L′ were carried out. The following three combinations of complex and L′ were chosen: (i) II + $2PPh_3$; (ii) II + $2PMe_2Ph$; and (iii) I + $2PPh_3$.

TABLE 2

$^{31}P\{^1H\}$ NMR DATA FOR COMPLEXES OF THE TYPES *trans*-[PdClMeL$_2$], [PdClMeLL′], AND *trans*-[PdCl(COMe)L$_2$] [a]

Complex		L,L′	δ(P) (ppm)	^2J(P–P′) (Hz)
trans-[PdClMeL$_2$]	(VII)	PEt$_3$	16.2	
	(VIII)	PBu$_3$	7.8	
	(IX)	PMe$_2$Ph	−2.7	
[PdClMeLL′] [b]	(X) [c]	PEt$_3$, PPh$_3$	20.8, 27.0	428
	(XI)	PBu$_3$, PPh$_3$	12.1, 27.2	430
	(XII)	PBu$_3$, PMe$_2$Ph	9.3, −3.9	452
trans-[PdCl(COMe)L$_2$]	(XIII)	PEt$_3$	12.3	
	(XIV)	PBu$_3$	4.4	
	(XV)	PMe$_2$Ph	−10.9	

[a] The ^{31}P chemical shifts were measured in ppm relative to external H$_3$PO$_4$. [b] The *trans* arrangement of L and L′ followed from the ^2J(P–P′) values in AB quartets [15]. [c] See text on broadening.

In the first case (II + 2PPh$_3$), the reaction eventually attained equilibrium after 15 h of mixing, when the solution included *trans*-[PdClMe(PBu$_3$)$_2$, *trans*-[PdClMe(PPh$_3$)$_2$] (δ(P) 30.2 ppm) and [PdClMe(PBu$_3$)(PPh$_3$)] (see Table 2 for δ(P) and ^2J(P–P′)) in a mole ratio of ca. 1.3/1/3, based on the integral ratio for the $^{31}P\{^1H\}$ NMR resonances. The product ratio is clearly displaced from that in a statistical mixture [16] towards an increase in the PBu$_3$-containing species. These results can probably be attributed to the large difference in basicity between PBu$_3$ and PPh$_3$ [17], because in these products having a small alkyl group in the position *cis* to phosphines the steric bulkiness of PPh$_3$ (cone angle θ 145° [18]) is thought to have no influence on their relative thermodynamic stability. If more PPh$_3$ is added to the solution, the added PPh$_3$ is expected to exchange with the coordinated phosphines in these three products. Indeed, addition of PPh$_3$ caused the PPh$_3$ ligands in *trans*-[PdClMe(PPh$_3$)$_2$] and [PdClMe(PBu$_3$)(PPh$_3$)] to exchange rapidly whereupon all the resonance lines due to the PPh$_3$-containing species collapsed, but that due to *trans*-[PdClMe(PBu$_3$)$_2$] kept its sharpness.

When a more basic and less bulky phosphine, L′ = PMe$_2$Ph [17,18], was used for the reaction with II (the second case: II + 2PMe$_2$Ph), equilibrium was reached within 10 min of mixing, when the solution contained *trans*-[PdClMe(PBu$_3$)$_2$], *trans*-[PdClMe(PMe$_2$Ph)$_2$] and [PdClMe(PBu$_3$)(PMe$_2$Ph)] (see Table 2 for δ(P) and ^2J(P–P′)) in a mole ratio of ca. 1.8/1/2.7. The relative quantity of the mixed-phosphine complex and the sum of the two *trans*-bis(phosphine) complexes is almost in accord with that in a statistical mixture, although it is strange that much more of *trans*-[PdClMe(PBu$_3$)$_2$] was produced than *trans*-[PdClMe(PMe$_2$Ph)$_2$] despite the fact that the difference in basicity between PBu$_3$ and PMe$_2$Ph is not very large.

The third reaction (I + 2PPh$_3$), however, showed a feature different from the other two. In this case, even when a stoichiometric amount of PPh$_3$ was added to the solution of I, the resonance due to *trans*-[PdClMe(PPh$_3$)$_2$] appeared as a broadened line and that due to [PdClMe(PEt$_3$)(PPh$_3$)] as a coalesced one with the loss of coupling of two phosphorus nuclei to each other. It is conceivable that the PPh$_3$ ligand dissociated from [PdClMe(PEt$_3$)(PPh$_3$)] by the stronger *trans*-labilizing effect of PEt$_3$ than that of PBu$_3$ behaves as an excess phosphine. Therefore, we carried out the reaction of I with PPh_3 in the molar ratio 1/1 to obtain the correct $^2J(P-P')$ value for $[PdClMe(PEt_3)(PPh_3)]$ (see Table 2 for $\delta(P)$ and $^2J(P-P')$). The solution which attained equilibrium in 40 min after mixing included *trans*-$[PdClMe(PEt_3)_2]$, *trans*-$[PdClMe(PPh_3)_2]$ and $[PdClMe(PEt_3)(PPh_3)]$ in a mole ratio of ca. 4.1/1/7.1, together with an approximate half molar amount of unreactive dimer. Again, the product ratio is largely displaced towards an increase in the PEt_3-containing species, reflecting the largest difference in basicity between PEt_3 and PPh_3.

Experimental

All operations were carried out in an atmosphere of nitrogen unless otherwise stated. Ethers and hydrocarbon solvents were distilled over sodium under argon. Other solvents used were dried over calcium chloride and distilled under argon. Type 3A molecular sieves were used as the drying agent for ethyl alcohol.

The IR spectra were taken on Nujol mulls or in CH_2Cl_2 solutions on a JASCO DS-3 spectrophotometer. The ^1H (100 MHz) and $^{31}P\{^1H\}$-FT (24.2 MHz) NMR spectra were recorded on JEOL JNM MH-100 and FX-60Q instruments, respectively. Molecular weights were determined on a vapour pressure osmometer manufactured by Knauer, West Berlin, F.R.G. Melting points were determined on a Yanagimoto micro-melting point apparatus.

The starting materials $[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ (L = PEt_3 [7]; PBu_3 [19]; PMe_2Ph [20]) were prepared according to the literature.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2(PEt_3)_2]$ (I)

A commercially available hexane solution (19%) of $AlMe_3$ (1.97 cm^3, 3.38 mmol) was added dropwise to a suspension of $[Pd_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$ (1 g, 1.69 mmol) in ether/THF (1/2 vol%, 25 cm^3) with stirring at −50°C. The temperature was then raised gradually to 25°C and the mixture was stirred for 10 min to give a clear solution. Methanol was then added to solvolyse the aluminium by-product, causing the formation of white precipitates. The solvent was completely evaporated, the residue was extracted with THF, and then the extract was concentrated to dryness to leave a white powder, which was washed with a small volume of methanol and dried in vacuo. The yield was 95% (0.89 g). M.p.: 81–82.5°C.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2(PBu_3)_2]$ (II)

A hexane solution of $AlMe_3$ (1.54 cm^3, 2.64 mmol) diluted with ether (13 cm^3) was added carefully to a suspension of $[Pd_2(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$ (1 g, 1.32 mmol) in ether (10 cm^3) with stirring at −50°C. The temperature was then raised gradually to 0–5°C and the mixture was kept at this temperature for 30–60 min until it became clear. Subsequent operations were carried out analogously to those in the preparation of I, except for the use of pentane as an extracting reagent. The yield of the colourless crystalline solid was 76% (0.72 g). Another crop of crystalline solid was obtained from the methanol washing on standing it overnight in a refrigerator. The total yield was 94% (0.89 g). M.p.: 70–71°C. Mol. wt. Found: 700 (CH_2Cl_2, 28°C, $(1.03\text{–}1.68) \times 10^{-2}$ *M*), 755 (THF, 42°C, $(0.92\text{–}1.40) \times 10^{-2}$ *M*). $C_{26}H_{60}Cl_2P_2Pd_2$ calcd.: 718.4.

Preparation of $[Pd_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2]$ *(III)*

Likewise, a hexane solution of $AlMe_3$ (1.86 cm^3, 3.18 mmol) was added dropwise to a suspension of $[Pd_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$ (1 g, 1.59 mmol) in THF (15 cm^3) with stirring at −70°C. These reactants were then allowed to react for 30 min at −50°C. Methanol was added before the colour of the mixture began to darken; otherwise, metallic palladium deposited in substantial quantity, thus resulting in a low product yield. The solvent was completely evaporated, the residue was extracted with CH_2Cl_2, and then the extract was again concentrated to dryness. The pale yellow residue was washed with a small volume of methanol and dried in vacuo. The yield was 79% (0.74 g).

Preparation of $[Pd_2(\mu\text{-}Cl)_2(COMe)_2(PEt_3)_2]$ *(IV)*

A THF solution of I (0.4 g, 0.73 mmol) was stirred under 1 atm of CO at ambient temperature for 9 h. The small quantity of metallic palladium that deposited was filtered off, the filtrate was concentrated, and then pentane was added to the concentrate to precipitate a pale yellow solid. The solid was filtered off and dried in vacuo. The yield was 75% (0.33 g).

Preparation of $[Pd_2(\mu\text{-}Cl)_2(COMe)_2(PBu_3)_2]$ *(V)*

Similarly, II was allowed to react with CO for 24 h. After the deposited metallic palladium was removed, the solvent was evaporated to dryness. The residue was redissolved in pentane and allowed to stand overnight at −20°C to yield a pale yellow crystalline solid. The yield was not calculated.

Preparation of $[Pd_2(\mu\text{-}Cl)_2(COMe)_2(PMe_2Ph)_2]$ *(VI)*

Analogously, III was allowed to react with CO for 24 h. In this case, the acetyl product (VI) was insoluble in pentane, so the solution was concentrated, the concentrate was filtered, and then pentane was added to the filtrate. The yellow solution obtained was allowed to stand overnight at −20°C to deposit a greyish yellow crystalline solid. The yield was not calculated.

Bridge-splitting reactions were carried out by the addition of a neat tertiary phosphine to a solution of the complex in an NMR tube and the $^{31}P\{^1H\}$ NMR spectra of the products were examined in situ.

Work on the preparation of mononuclear methyl(η-allyl)palladium(II) complexes, using the methylpalladium(II) dimers as starting materials, is now in progress.

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