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CATALYSIS BY PALLADIUM SALTS
I. THE ROLE OF DIMETHYLFORMAMIDE AND RELATED SOLVENTS IN THE PALLADIUM–OLEFIN INTERACTION

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SUMMARY

The synthesis of π-allyl palladium(II) compounds, $[PdCl(C_nH_{2n-1})]_2$ from olefins and $PdCl_2$ under mild conditions is described.

The mechanism of the reaction and the role of the solvent are discussed with reference to some aspects of the catalytic activity of palladium(II) salts in non-aqueous solvents. The behaviour of $PtCl_2$ under similar reaction conditions is compared with that of $PdCl_2$.

INTRODUCTION

The interaction of olefins with palladium(II) salts has been the subject of many investigations[1a,1b] mainly prompted by the industrial interest in reactions such as olefin oxidation[2], carbonylation[3] and dimerisation[4], which are catalysed by palladium (II) salts. During these investigations some interesting, but not yet fully understood, salt and solvent effects were observed; for instance dimethylformamide (DMF) stabilises the palladium catalyst in the vinyl acetate synthesis[5] and in the homogeneous hydrogenation of dicyclopentadiene[6]. When studying the interaction and isomerisation of straight chain olefins with palladium chloride in dimethylformamide[7–9], we found[10] that π-allyl palladium(II) compounds are obtained under milder conditions than those usually reported[11] using other solvents, and we have now carried out a study of this behaviour in order to interpretate the role of the solvent, which is important in the homogeneous palladium catalysis of olefins.

Synthesis of π-allyl complexes of Pd^{II}

The isomerisation of α-olefins such as 1-butene, 1-pentene, 1-hexene, and 1-octene in the presence of $PdCl_2$ proceeded only partially in dimethylformamide at room temperature. For example, with an olefin to palladium ratio of about 4 the reaction stopped after a few hours at a 30–40% of olefin conversion. Two stable compounds could be recovered from the solution after evaporation of dimethylformamide.

One of them was yellow and soluble in light hydrocarbons; it varied with the olefin and its analysis, IR and NMR spectra were consistent with those of the known π-allyl compounds of the type $[PdCl(\pi\text{-}C_nH_{2n-1})]_2$[1b, 7, 11b].

The other product was brown, and insoluble in light hydrocarbons and in the common non-polar organic solvents, but it was very soluble in water. The absence of any absorption in the IR assignable to an olefinic moiety and the uniformity of analysis irrespective of the olefin used led to the conclusion that this compound must originate from the solvent. Its IR spectrum shows a broad carbonyl stretching band due to the amide at 1630 cm^{-1} and a broad absorption in the region 1600–600 cm^{-1} with strong "transmission windows"[12–14] not observed for compounds of formula $Pd(DMF)_2X_2$ (X=Cl, Br)[15]. This fact and the slight lowering of the frequency of the carbonyl absorption with respect to pure dimethylformamide[16] were consistent with the presence of the cation $[(DMF)_2H]^+$ formed by a hydrogen ion probably symmetrically bonded[17] between the two carbonyl groups.

Analysis agreed with the ionic formula $[(DMF)_2H]_2(Pd_2Cl_6)$ which was also confirmed by some physical investigations. Thus the conductivity in nitrobenzene over a range of concentrations was consistent with a 2/1 type electrolyte[18], and the presence of the $(Pd_2Cl_6)^{2-}$ anion was confirmed by presence of terminal and bridging Pd–Cl stretching frequencies in the IR spectrum and formation by cation exchange of $(AsPh_4)_2(Pd_2Cl_6)$, characterized by analysis and electronic spectra[19]. The recent report[20] that $(M_2X_6)^{2-}$ anions [*e.g.* $(Hg_2Br_6)^{2-}$] stabilise dimeric symmetrically hydrogen bonded species also supports the presence of the $[(DMF)_2H]^+$ cation. The same ionic complex can also be obtained by bubbling hydrogen chloride through a dimethylformamide solution of palladium chloride. In the palladium chloride–olefin interaction hydrogen chloride is formed, under mild conditions, by hydrogen abstraction from the allylic position of the olefin with consequent formation of π-allyl palladium compounds.

The general stoichiometry of the reaction seems to be:

$$2\,C_nH_{2n}+4\,PdCl_2+4\,DMF \rightarrow [PdCl(C_nH_{2n-1})]_2+[(DMF)_2H]_2(Pd_2Cl_6)$$

In agreement with this equation the yields of the π-allyl compounds are generally 30–35% (see Table 2) compared with a theoretical value of 50% (based on palladium). However, the yields of $(Pd_2Cl_6)^{2-}$ anion are generally higher than 50%, as a consequence of the presence of hydrogen chloride formed via oxidation of olefin to carbonyl compounds in the reaction medium, which is not completely anhydrous. The formal mechanism of the reaction is illustrated in Scheme 1.

SCHEME 1

SUGGESTED MECHANISM OF FORMATION OF π-ALLYL COMPOUNDS

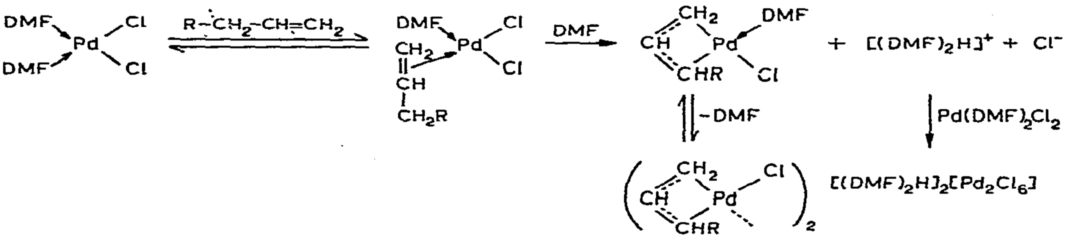
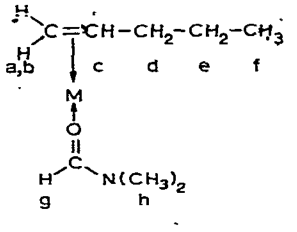
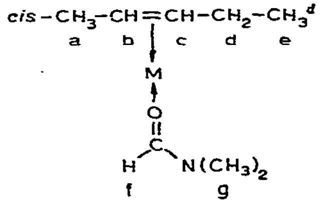


TABLE 1

NMR SPECTRA OF M(DMF)(π-PENTENE)Cl_2[a]

Compound	Hydrogen	Pd[b]	Pt[c]
	$H_{a,b}$	5.3 (complex m)	5.6 (complex m)
	H_c	3.9 (broad m)	4.7 (broad m)
	H_d	8.00 (m)	8.15 (broad m)
	H_e	8.40 (m)	
	H_f	9.18 (t, J 6–7 Hz)	8.9 (t, J 7–8 Hz)
	H_g	2.33 (s)	1.78 (s)
	H_h	7.91, 8.28 (s)	6.90, 7.00 (s)
	H_a	8.35 (d, J 5–6 Hz)	
	$H_{b,c}$	3.9 (complex m)	
	H_d	8.00 (broad m)	
	H_e	8.68 (t, J 8 Hz)	
	H_f	1.90 (s)	
	H_g	7.00, 7.12 (s)	

[a] Chemical shifts (τ values) referred to TMS at room temperature. [b] In $CD_3C_6H_5$ at −20°. [c] In CCl_4. [d] In $CDCl_3$.

The intermediate π-olefin complex of palladium(II) was obtained indirectly by treating $Pd(DMF)_2Cl_2$[15] with an excess of 1-pentene or *cis*-2-pentene at room temperature. The compounds Pd(olefin)(DMF)Cl_2, where the olefin is 1-pentene or *cis*-2-pentene, have low melting points and are only stable at low temperatures. They were characterized by their NMR spectra (Table 1). The reaction to give π-allyl complexes is general (see Table 2), and palladium bromide reacted like palladium chloride. In the presence of ethylene $[(DMF)_2H]_2(Pd_2Cl_6)$ was slowly formed with simultaneous separation of metallic palladium. The presence of acetaldehyde in the reaction mixture, due to nucleophilic reaction of traces of water in the solvent, accounts for the simultaneous formation of $[(DMF)_2H]_2(Pd_2Cl_6)$. No butene or π-allyl palladium(II) derivatives of butenes were isolated, contrary to results in other solvents[4].

The influence of the olefin on the structure of the π-allyl complexes was also investigated. With 1-pentene some olefin isomerization took place, but only the π-allyl derivative formed from a 1-pentene π-complex {*e.g.* $[C_2H_5(\pi\text{-}C_3H_5)PdCl]_2$} was isolated. This result is interesting, as a mixture of π-allyl isomers is generally obtained with the conventional thermal method[11]. The difference is explained by the fact that in the presence of *cis*-2-pentene in DMF solution no hydrogen abstraction takes place, and only the π-olefin complex of palladium (Table 1) is formed. This compound is rather labile in DMF solution as the π-coordinated olefin is easily displaced by the excess of the solvent.

When the investigation was extended to other aprotic solvents, dimethyl acetamide (DMA) behaved analogously, and π-allyl palladium complexes and

TABLE 2

π-ALLYL PALLADIUM COMPLEXES FROM OLEFINS[a]

Olefin	Solvent (ml)	$PdCl_2$ (mmole)	Time (h)	$[\pi\text{-allylPdCl}]_2$ (% yield)	$(L_2H)_2(Pd_2Cl_6)$ (% yield)	Ref.
Propene	DMF (30)	31.0	3	35	56	11a
1-Butene	DMF (100)	14.0	5	26	47	37
Isobutene	DMF (70)	14.0	16	30	59	11a
1-Pentene	DMA (10)	8.4	3	23	49	This work

[a] Excess olefins; temperature 20°; L = N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMA).
[b] Yields based on $PdCl_2$.

$[(DMA)_2H]_2(Pd_2Cl_6)$ were isolated (see Table 2). However, with less basic solvents, such as formamide, the π-allyl species were not obtained. In the case of dimethylsulphoxide only the known palladium(II)–sulphoxide complex[15b] was isolated.

Synthesis of π-olefin complexes of Pt^{II}

When platinum chloride was used under the same conditions as palladium chloride neither a π-allyl compound nor $[(DMF)H]_2(Pt_2Cl_6)$ were obtained. However, by treating $[Pt(DMF)_2Cl_2]$[15] with an excess of 1-pentene at room temperature a yellow compound of formula $[Pt(olefin)(DMF)Cl_2]$ was isolated. The presence of a π-bonded olefin in this compound, which is more stable than the analogous palladium complex, is confirmed by the IR spectrum [band at 1503 cm^{-1}, assigned to the $\nu(C{=}C)$ of coordinated olefin] and by the NMR spectrum (Table 1) at room temperature, which shows two series of peaks characteristic, respectively, of dimethylformamide and of 1-pentene coordinated to the metal. The three peaks of intensity 1/3/3 at τ 1.78, 6.90 and 7.00 were assigned to formyl and methyl protons of dimethylformamide, respectively. The olefin peaks of intensity 1/2/4/3 centered at $\tau = 4.70$ (broad), 5.6 (broad), 8.15 and 8.90 were assigned to the unsaturated methine and methylene, to the two saturated methylene, and to the methyl groups respectively. A broadening of the NMR resonances has previously been reported for some butene complexes of platinum[21], but not for some other such complexes[22,23]. Probably in our case we are close to the coalescence temperature of the olefin signals. The metal–olefin bonding is not very strong, as shown by the slow decomposition of the complex at room temperature.

By treating propylene with platinum chloride in dimethylformamide using more drastic conditions such as 100° and 10 atm, a very unstable green platinum compound was obtained. This compound, not yet fully investigated, shows a terminal carbonyl absorption at 2030 cm^{-1} probably due to carbon monoxide abstraction from dimethylformamide, as previously found under similar conditions[24,25].

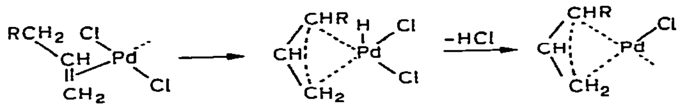
DISCUSSION

The conditions under which π-allyl palladium(II) compounds are formed in the presence of dimethylformamide seem to be unusually mild in comparison to those known for the one-step synthesis from olefins and palladium chloride in the absence of basic solvents[11]. Recently it has been shown that other basic substances such as acetate ion in acetic acid[26] or Na_2CO_3[27] facilitate formation of π-allyl palladium complexes in high yields. The effect of the basic dimethylformamide could possibly be regarded as simply favouring hydrogen abstraction from the olefins by shifting the equilibrium[11,26,27]:

$$[PdCl_2(C_nH_{2n})]_2 \rightleftharpoons [PdCl(C_nH_{2n-1})]_2 + 2\,HCl$$

However, the role of basic species such as dimethylformamide or acetate ion may be more important than that of just shifting this equilibrium. It could, for example, be that of directly making the hydrogen abstraction in the allylic position of the π-bonded olefin more favourable. Using Saville's[28] concepts of hard and soft interactions, the breaking (or ionisation to carbanion) of the carbon–hydrogen bond of the olefin must be easier in the presence of hard bases such as dimethylformamide. The role of the metal in the mechanism should be that of assisting C–H ionisation by supplying, within the initial π-complex, a soft coordination position ready to accept the electrons of the C–H bond, thus favouring the olefin deprotonation. The behaviour of other basic ligands, which can form hydrogen bonded cations, must be considered from this point of view. Stable species such as $[(DMSO)_2H]^+$ are readily formed when dry HCl is bubbled into a DMSO solution of $PdCl_2(DMSO)_2$, but no formation of the π-allyl palladium complex from $PdCl_2(DMSO)_2$ and olefins (1-pentene, 1-butene) has been detected. This different behaviour is probably due to the fact that DMSO is too strongly bonded to palladium to allow any interaction of the olefin with the palladium atom. This is also indirectly confirmed by the lack of isomerisation of 1-pentene in a solution of $[PdCl_2(DMSO)_2]$ in DMSO at 50°.

Our results are not wholly consistent with this simple interpretation. Many "soft" metal ions, such as Pt^{II}, could be expected to give rise to the same type of reaction, but we have found that they do not abstract hydrogen from the allylic position of an olefin under mild conditions, and it is well known that palladium(II) salts easily catalyse[29] olefin isomerisation whilst platinum(II) salts require more drastic conditions or the presence of a cocatalyst[30]. A delicate electron balance in the metal–olefin bond seems to be required for the hydrogen abstraction, which could also proceed via a metal–hydrogen bond:



The influence of dimethylformamide could be not only that associated with its basic properties but might also involve stabilization of the hydrido intermediate, so avoiding the reduction to palladium metal; the stabilising power of this solvent has indeed been noted in the hydrogenation of dicyclopentadiene in presence of noble metal salts[6].

An interesting feature is that the olefin isomerisation does not proceed further once π-allyl derivatives are formed, confirming that these species stabilise the palladium catalytic centre and lead to the inhibition of the isomerisation reaction[31]. However, π-allylic palladium compounds can catalyse olefin isomerisation under more drastic conditions, for example, 1-octene is isomerized at 100° [32] under nitrogen. Under these conditions metallic palladium slowly separates, but the isomerisation cannot be attributed to the metallic palladium[32,33]. It can, however, be attributed to a second hydrogen abstraction from the homoallylic position of the coordinated olefin with the formation of a conjugated diene and palladium hydride. As already noted by some of us[34] these hydridic species are rather unstable, and metallic palladium can separate with the formation of conjugated dienes.

CONCLUSION

Our results, along with previously published data[26,27], show that basic substances can favour formation of π-allyl or pseudo π-allyl structures, which may be intermediates in some olefin reactions catalysed by palladium salts. There is in fact such experimental evidence to show that olefin reactivity in the presence of palladium(II) salts is greatly changed when a basic cocatalyst is present in the medium. For instance, the lack of any appreciable olefin isomerisation by $PdCl_2$ at 20° in the presence of potassium acetate, compared with the extensive isomerisation in the presence of lithium acetate[24] could be ascribed to the fact that in aprotic solvents potassium acetate is more basic than lithium acetate. Moreover, in the reaction of 1-olefins and acetic acid to form alkenyl esters in dimethylformamide at 100°, linear esters are mainly formed in the presence of potassium acetate, whilst with lithium acetate nearly equal amounts of linear and branched alkenyl esters are obtained[35]. The influence of these basic substances has been the subject of much discussion and is still controversial[10]. It may be that in some cases in solution basic substances favour formation of asymmetric pseudo π-allyl intermediates differing in reactivity from intermediates formed from normal π-olefin palladium complexes, as has already been tentatively suggested by other authors[36].

EXPERIMENTAL

The olefins were obtained commercially; peroxides were removed from liquid olefins before use. The solvents were commercial products, and were distilled and dried before use.

IR spectra were recorded with a Perkin–Elmer 227 instrument, electronic spectra with a Beckman D.K.A., conductivities with a Philips instrument, and NMR spectra with a Perkin–Elmer 60-A or Varian 100 instrument.

All the melting points are uncorrected.

Analyses were carried out in the analytical laboratory of the Bollate Research Centre of Montecatini–Edison.

Isomerisation of olefins by $PdCl_2$ in dimethylformamide

A mixture of 5.6 mmoles of palladium(II) chloride, 50 mmoles of 1-pentene, and 5 ml of *N,N*-dimethylformamide was stirred at 80° for 22 h. After this time the olefin composition was as follows: 1-pentene 80.1%, *trans* 2-pentene 15.9%, *cis*-2-pentene 4.0%. This composition did not change further during two days.

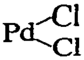
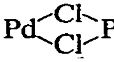
Similar results were obtained with other olefins.

Preparation of π-allyl palladium(II) chloride compounds in dimethyl formamide

A mixture of palladium dichloride and dimethylformamide was stirred at 20° in presence of 1 atm of gaseous or liquid olefin. After 6 h the red-brown solution was filtered from some palladium metal. The brown residue obtained by evaporation of the solvent at 0.1 mm was extracted with ethyl ether. From the ether, after washing with water and drying over sodium sulphate, a yellow crystalline product having an analysis and NMR spectrum of the expected bis[π-allylpalladium(II) chloride] derivative (see Table 2), was obtained.

The brown crystalline compound, insoluble in ethyl ether (m.p. 95° decompn.) analysed as $[(DMF)_2H]_2(Pd_2Cl_6)$. (Found: C, 19.76; H, 4.10; Cl, 29.5; N, 7.53. $C_6H_{15}Cl_3N_2O_2Pd$ calcd.: C, 19.9; H, 4.16; Cl, 29.5; N, 7.77%.)

The nature of the anion in this salt was confirmed by an exchange reaction to form tetraphenylarsonium tetrachloro-μ-dichlorodipalladate(II). When an ethanolic solution of tetraphenylarsonium chloride was added to an ethanolic solution of $[(DMF)_2H]_2(Pd_2Cl_6)$ the light brown precipitate, after washing with ethanol, gave the expected analysis for $(AsPh_4)_2(Pd_2Cl_6)$ ($\lambda_{max}=425$ nm in ethanol)[19]. (Found: C, 48.08; H, 3.39; Cl, 17.78; Pd, 17.89. $C_{24}H_{20}AsCl_3Pd$ calcd.: C, 48.3; H, 3.35; Cl, 17.9%.)

The IR spectrum in Nujol of $[(DMF)_2H]_2(Pd_2Cl_6)$ shows a broad absorption band at 1630 cm^{-1} and large transmission windows at 855 and 630 cm^{-1}. The far IR spectrum shows two Pd–Cl stretching frequencies at 345 and 354 cm^{-1} due to the  $Pd\genfrac{}{}{0pt}{}{\diagup Cl}{\diagdown Cl}$ moiety and two bands at 277 and 268 (sh) cm^{-1} due to the bridging  $Pd\genfrac{}{}{0pt}{}{\diagup Cl \diagdown}{\diagdown Cl \diagup}Pd$ moiety.

Conductivity of $[(DMF)_2H]_2(Pd_2Cl_6)$

The conductivities were measured in nitrobenzene at various concentrations in the range 10^{-3}–10^{-4} *M*. The equivalent conductivity Λ_e was plotted as a function of $\sqrt{c}$, where c is the equivalent concentration and $\Lambda_0=79$ (ohm$^{-1}\cdot$cm^2) was obtained by extrapolation to infinite dilution. By plotting $\Lambda_0-\Lambda_e$ against $\sqrt{c}$ the slope 445 was obtained in agreement with that observed for 2/1 ion type electrolytes[18].

Dichloro(N,N'-dimethylformamide)(1-pentene)palladium(II)

A mixture of 2.0 g of dichlorobis(*N*,*N*-dimethylformamide)palladium(II)[15], 10.0 ml of toluene, and 10.0 ml of 1-pentene was stirred at −20° for 15 min under nitrogen in anhydrous conditions. The yellow suspension was filtered and the precipitate was cooled to −78° and treated with 30 ml of n-pentane at −78°. The yellow solid (0.35 g) obtained was filtered off, washed with n-pentane, and dried at −20° in nitrogen; it melted above 0°. Its nature was established from its NMR spectrum at low temperature (Table 1).

Dichloro(N,N'-dimethylformamide)(cis-2-pentene)palladium(II)

A mixture of 1.0 g of dichlorobis(*N*,*N*-dimethylformamide)palladium(II)[15], and 6.4 g of *cis*-2-pentene was stirred at 0° for 3 h under nitrogen. The yellow-green solid was filtered off, washed with n-pentane, and dissolved in 10 ml of dry toluene. On cooling the solution to −78° and adding 30 ml of n-pentane cooled to −78°, 0.35 g of a light yellow compound with a m.p. below 0° was obtained. The nature of the compound was established from its NMR spectrum, details of which are given in Table 1.

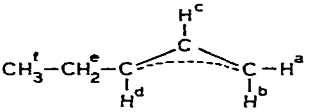
Dichloro(N,N'-dimethylformamide)(1-pentene)platinum(II)

A mixture of 1.0 g of dichlorobis(*N,N*-dimethylformamide)platinum(II)[15], and 6.5 g of 1-pentene was stirred at 20° overnight. From the yellow solution cooled to −78°, 0.15 g of a yellow crystalline compound, m.p. 65°, was obtained. The brown residue was washed with ether to remove the excess of dimethylformamide, and dried in a nitrogen stream, and 6.5 g of 1-pentene was added to give a further 0.25 g of product, the residue being the starting material. The IR spectrum in Nujol shows a very strong band at 1660 cm^{-1} due to the ν(C=O) of bonded DMF and a weak band at 1493 cm^{-1} due to ν(C=C) of the π-bonded olefin. (Found: C, 22.8; H, 4.8; N, 3.3. $C_8H_{17}Cl_2NOPt$ calcd.: C, 23.4; H, 4.25; N, 3.42%.)

Preparation of μ-dichlorobis(1-ethyl-π-allyl)dipalladium(II) in dimethylacetamide

A mixture of 1.5 g of palladium dichloride, 1.5 g of 1-pentene and 10 ml of *N,N*-dimethylacetamide was stirred at 20° for 3 h. The brown solution was filtered from the palladium metal (0.18 g) and then concentrated under vacuum (0.1 mm) to 2 ml. The red-brown residue was extracted with 30 ml of ethyl ether, and the extract was washed with water, dried, and evaporated to give a yellow compound (0.40 g), m.p. 74–76°. (Found: C, 28.9; H, 4.20; Cl, 16.4. C_5H_9ClPd calcd.: C, 28.5; H, 4.27; Cl, 16.8%.)

The IR spectrum shows a band at 1505 cm^{-1} due to the allylic group. The NMR spectrum indicates that the compound is (1-ethyl-π-allyl)palladium chloride (I) [multiplet at τ 4.70, area 1 (H^c); multiplet at τ 6.10, area 2 (H^a, H^d); doublet at 7.18, area 1 (H^b); multiplet at τ 8.30, area 2 (H^e); triplet at 8.88 area 3 (H^f); $J_{bc} \simeq J_{cd} =$ 11.0 Hz, $J_{ac} = 6.0$ Hz]. The brown crystalline compound insoluble in ethyl ether (decompn. 112°) analysed as $[(DMA)_2H]_2(Pd_2Cl_6)$. (Found: C, 25.3; H, 4.8; Cl, 27.9; N, 7.2. $C_8H_{19}Cl_3N_2O_2Pd$ calcd.: C, 24.7; H, 4.89; Cl, 27.4; N, 7.21%.)



(I)

The dimeric nature of the anion was confirmed by the formation of $(AsPh_4)_2(Pd_2Cl_6)$ in an exchange reaction with $AsPh_4Cl$. The IR spectrum shows a broad carbonyl stretching band at 1650 cm^{-1} and a large "transmission window" at 960 cm^{-1}; the far IR spectrum shows two Pd–Cl stretchings at 343 and 332 cm^{-1} due to the $\mathrm{Pd}\langle^{\mathrm{Cl}}_{\mathrm{Cl}}$ moiety and two bands at 280 and 270 cm^{-1} due to the bridging $\mathrm{Pd}\langle^{\mathrm{Cl}}_{\mathrm{Cl}}\rangle\mathrm{Pd}$ moiety.

Direct preparation of $[(DMF)_2H]_2(Pd_2Cl_6)$

Gaseous HCl was bubbled through a solution of 1.8 g of $Pd(DMF)_2Cl_2$[15] in 40 ml of DMF at 25°. After 1 h the brown-red solution was poured into 100 ml of ethyl ether. The oil initially obtained was converted into a brown powder by vigorous scratching with a glass rod; the product was identical with an authentic sample of $[(DMF)_2H]_2(Pd_2Cl_6)$.

Direct preparation of $[(DMSO)_2H]_2(Pd_2Cl_6)$

Gaseous HCl was bubbled in a suspension of 0.30 g of $Pd(DMSO)_2Cl_2$[15b] in 10 ml of ethanol at 25°. The initially yellow suspension immediately turned to a clear red-orange solution. After evaporation of the ethanol and washing with ethyl ether a red-orange compound (m.p. 45–47°) was obtained. (Found: C, 13.3; H, 3.5; Cl, 26.2. $C_4H_{13}Cl_3O_2PdS_2$ calcd.: C, 13.0; H, 3.51; Cl, 28.7%.)

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