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REACTIONS OF HOMOBINUCLEAR PLATINUM AND PALLADIUM COMPLEXES WITH CARBON MONOXIDE

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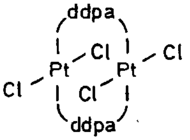
Summary

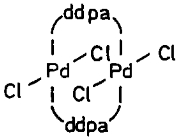
The reactivity of homobimetallic complexes of platinum(II) and palladium(II) containing diethyl(diphenylphosphinomethyl)amine (ddpa = $(C_6H_5)_2PCH_2N(C_2H_5)_2$) as a bridging ligand has been investigated. Carbon monoxide reacts reversibly with these complexes. The species formed are binuclear carbonyl-bridged derivatives, which can isomerize to ionic terminal carbonyl complexes. Reaction of $[PtCl_2(CO)]_2[(C_2H_5)_4N]_2$ with ddpa in dichloromethane gives the ionic platinum(I) complex $[Pt(ddpa)Cl_2]_2[(C_2H_5)_4N]_2$, which reacts with carbon monoxide. Still, homobimetallic derivatives of palladium(I) are unstable, and none have been isolated.

Introduction

There is increasing interest in the potential of ligands containing both nitrogen- and phosphorus-donor sites [1–5]. We have recently shown that platinum or palladium when complexed with diethyl(diphenylphosphinomethyl)amine (= ddpa, $(C_6H_5)_2PCH_2N(C_2H_5)_2$) forms some binuclear complexes [6] in which the ligand adopts a bridging role, **1** and **1′**.



(1)



(1′)

In this paper, we report on a study of the reactions of such complexes with carbon monoxide and also those of the homobimetallic derivatives of platinum(I) and palladium(I). Little is known about the reactivity of such platinum or palladium binuclear complexes containing a P– · · · –N linkage, although Balch et al. [7] recently reported the results of the reaction of carbon monoxide with $Pd_2(Ph_2$-

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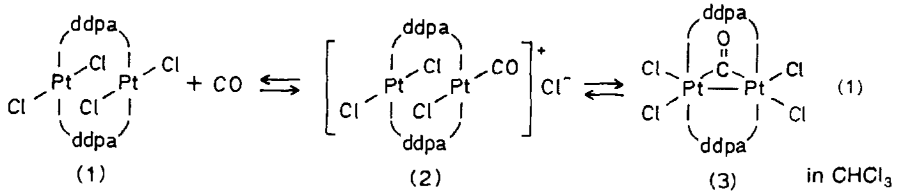
Ppy)$_2$Cl$_2$. However, the reactions of bis(diphenylphosphino)methane (= dppm) complexes of platinum [8] and palladium [9] have been described.

Results

Complexes of platinum(II) and palladium(II): [M(ddpa)Cl$_2$]$_2$-μ-CO, [M$_2$(dppa)$_2$-Cl$_3$CO]$^+$ Cl$^-$; M = Pt or Pd

Bubbling carbon monoxide through a trichloromethane solution of [Pt(ddpa)Cl$_2$]$_2$ (**1**) gives a carbonyl derivative, which was isolated as yellow crystals. The formula for this product, as deduced from analytical data, is Pt$_2$(ddpa)$_2$Cl$_4$(CO). It is diamagnetic ($\chi_M = -520 \times 10^{-6}$ cgs at 20°C). The IR spectra in trichloromethane solution and in the solid state show two CO bands, one at 1710 cm^{-1} which is assigned to a bridging carbonyl group, and the other at 2070 cm^{-1} which is assigned to a terminal carbonyl group (see Table 1). Consideration of the analytical and IR data suggests the presence of two species. Moreover, the conductivity value (45.2 Ω^{-1} cm^2 mol^{-1}) of the supposed mixture in nitromethane is too high for non-electrolyte complexes only, but is consistent with the presence of both an ionic species (probably with the terminal carbonyl group) **2** and molecular species (with the bridging carbonyl group) **3**. The addition of carbonyl monoxide is reversible, decarbonylation occurring readily under vacuum.



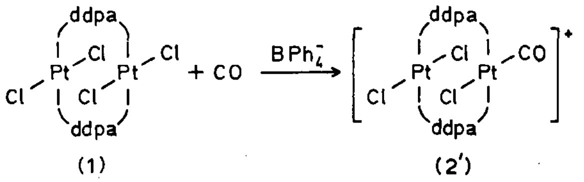
It is possible to obtain exclusively the ionic form by using the same process in acetone solution in the presence of NaBPh$_4$. Bubbling of carbon monoxide also

TABLE 1

INFRARED DATA (CM^{-1})

Complex		ν(CO) (cm^{-1})	Solvent
Pt^{II}			
[Pt(ddpa)Cl$_2$]$_2$-μ-CO	(3)	1710	Solid state CHCl$_3$
[Pt$_2$(ddpa)$_2$Cl$_3$CO]$^+$ Cl$^-$	(2)	2070	Solid state CHCl$_3$
[Pt$_2$(ddpa)$_2$Cl$_3$CO]$^+$ BPh$_4$$^-$	(2′)	2065	(CH$_3$)$_2$CO
Pd^{II}			
[Pd(ddpa)Cl$_2$]$_2$-μ-CO	(3′)	1715	CHCl$_3$
Pt^{I}			
[Pt$_2$(ddpa)$_2$-μ-COCl$_4$]$^{2-}$[(C$_2$H$_5$)$_4$N]$_2$$^+$	(6)	1665	CH$_2$Cl$_2$

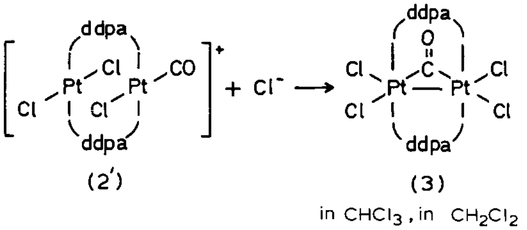
gives yellow crystals and the IR spectrum of a solution of these crystals in acetone shows only one band, at 2065 cm^{-1}, indicating the presence of a single species with terminal carbonyl group **2'**. The conductivity in acetone (90.6 Ω^{-1} cm^2 mol^{-1}) shows that this complex is a 1 : 1-electrolyte.



(2)

in CH_3COCH_3

Solutions of derivative **2'** in CH_2Cl_2 or $CHCl_3$ show only one IR band, but at 1700 cm^{-1}, indicating the presence of a single species with bridging carbonyl groups. This product can be tentatively identified as **3**, having regard for the fact the partial decomposition of the complex **2'** introduces extra chloride ligand into the solution and displaces the following equilibrium:

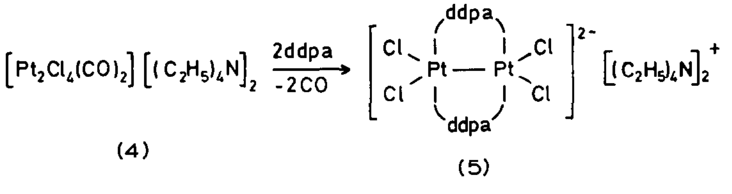


(3)

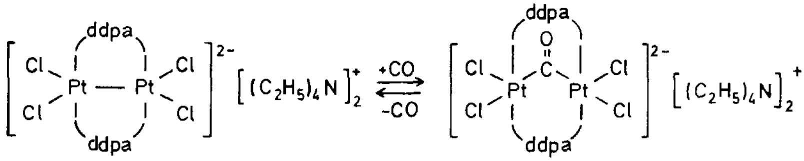
In the case of the palladium(II) complex, bubbling of carbon monoxide through a trichloromethane solution of $[Pd(ddpa)Cl_2]_2$ (**1'**) gives a carbonyl derivative, which was isolated as an imperfectly crystalline orange-yellow product. It cannot be isolated analytically pure, and has been characterized by means of spectroscopic data only. The IR spectrum in dichloromethane solution shows a band at 1715 cm^{-1} assignable to a bridging carbonyl group, which is consistent with the formulation $[Pd(ddpa)Cl_2]_2$-μ-CO (**3'**) analogous to **3** (Tab. 1).

Complexes of platinum(I) and palladium(I)

The action of $[PtCl_2(CO)]_2[(C_2H_5)_4N]_2$ (**4**) with diethyl(diphenylphosphinomethyl)amine leads to a yellow product **5**, whose elemental analysis is consistent with the formula $[Pt(ddpa)Cl_2]_2[(C_2H_5)_4N]_2$. Its conductivity (139.5 Ω^{-1} cm^2 mol^{-1}) in nitromethane is consistent with a 1 : 2-electrolyte. The reaction leads to a carbon-monoxide-free product, but bubbling the gas through a dichloromethane solution of **5** gives a yellow-white carbonyl derivative **6**, whose IR spectrum exhibits a CO frequency (ν(CO) 1665 cm^{-1}) characteristic of a bridging CO group.



(4)



(5) (6)

(5)

The conductivity (146.5 Ω^{-1} cm^2 mol^{-1}) in nitromethane shows complex **6** to be a 1 : 2-electrolyte. The complex is readily decarbonylated under vacuum to give **5**.

In the case of the palladium complexes the reaction of $[Pd(CO)Cl]_n$ with ddpa was performed in dichloromethane. After elimination of the unreacted initial reagent, this solution showed a bridging CO frequency (1715 cm^{-1}) and a progressive precipitation of palladium metal was observed. A dismutation is therefore a possibility, and the value of the CO frequency is consistent with complex **3′**. The bridging CO group is likely to belong to a palladium(II) complex.

The ^{31}P NMR measurements were not always carried out in the best conditions due to the difficulties in dissolving the complexes in appropriate solvents. The spectra of **1**, **2** and **3** only have been recorded in $CDCl_3$. Some changes occur in the NMR spectra during the spectrum accumulation period due to decomposition and oxidation. Because of the low solubility of complex **1**, the ^{31}P signal of phosphine oxide (recorded on type R10 Perkin–Elmer spectrometer) was previously [6] erroneously attributed to it.

We have recently been able to record the spectra on a Bruker WM 250 MHz spectrometer and to identify complexes **1**, **2** and **3** among other minor decomposition products. Thus, the proton-decoupled ^{31}P NMR spectrum of **1** (solvent: $CDCl_3$) gives a signal centred at −7.80 ppm (see Tab. 2). It exhibits satellites due to coupling of ^{195}Pt (34% natural abundance) with ^1J(P–Pt) 3580 Hz. The spectrum of the carbonyl derivative, assumed to be a mixture of **2** and **3**, gives a signal at −0.36 and a singlet at 7.65 ppm. The ^{31}P NMR spectrum of **2** is consistent with structure A but inconsistent with structure B, which should show two chemically distinct phosphorus atoms (Fig. 1). The fine structure of the ^{195}Pt satellites is not clearly resolved, but the values of the chemical shifts and coupling constants allow assignment of the signal at 7.65 ppm to complex **3** and that at −0.36 ppm to complex **2**.

TABLE 2

^{31}P {^1H} NMR DATA

Complex		δ (ppm) [a]	^1J(PPt) (Hz)
$[Pt(ddpa)Cl_2]_2$	(**1**)	−7.80 [b]	3580
$[Pt_2(ddpa)_2COCl_3]^+ Cl^-$	(**2**)	−0.36 [b]	3980
$[Pt(ddpa)Cl_2]_2$-μ-CO	(**3**)	7.65	2714

[a] External ref. H_3PO_4 in D_2O; solvent $CDCl_3$. [b] The signals show, in fact, two closed components (of separation around 0.13 ppm) suggesting the existence of two conformational isomers.

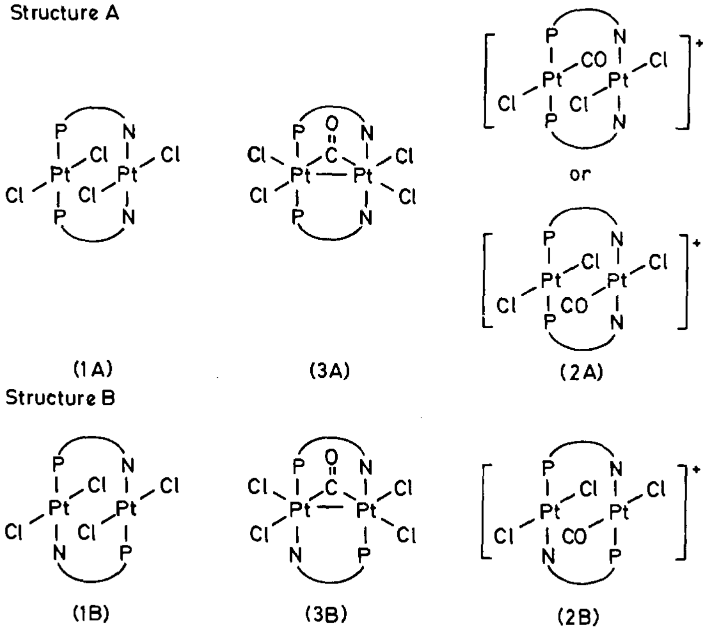


Fig. 1. Possible structures of compounds **1**, **2** and **3**.

Experimental section

The preparations of compounds, diethyl(diphenylphosphinomethyl)amine (ddpa) [6], $[PtCl_2(CO)]_2[(C_2H_5)_4N]_2$ [10], $[Pd(CO)Cl]_n$ [11], $[Pt(ddpa)Cl_2]_2$ [6], [Pd(ddpa)$Cl_2]_2$ [6] have been described previously. All reactions were carried out under argon using deoxygenated solvents.

[Pt(ddpa)Cl$_2$]$_2$-μ-CO. About 1 g (0.9 mmol) of [Pt(ddpa)$Cl_2]_2$ was dissolved in 20 cm^3 of trichloromethane. Carbon monoxide was slowly bubbled into the solution for 45 min. The solvent was evaporated and the product, which separated as yellow crystals, was vacuum dried. Anal. Found: C, 38.40; H, 4.02. $C_{35}H_{44}Cl_4N_2OP_2Pt_2$ calcd.: C, 38.12; H, 4.27%.

[Pt$_2$(ddpa)$_2$Cl$_3$CO]$^+$ BPh$_4$$^-$. 0.64 g (0.6 mmol) of [Pt(ddpa)$Cl_2]_2$ was added to a solution of $NaBPh_4$ in 15 cm^3 of acetone. Carbon monoxide was slowly bubbled into a solution for one hour. Then 5 cm^3 of n-propanol were added to the filtrate, and yellow crystals separated. They were collected but attempts to vacuum dry them gave black and brown material. Anal. Found: C, 50.27; H, 4.52, P, 4.56; Cl, 7.54. $C_{59}H_{64}BCl_3N_2OP_2Pt_2$ calcd.: C, 51.11; H, 4.65; P, 4.47; Cl, 7.67%.

[Pd(ddpa)Cl$_2$]$_2$-μ-CO. Carbon monoxide was slowly bubbled into a solution of about 0.5 g (0.6 mmol) of [Pd(ddpa)$Cl_2]_2$ in 5 cm^3 of trichloromethane. The solvent was evaporated and the product was recrystallized from dichloromethane, but could not be isolated analytically pure.

[Pt(ddpa)Cl$_2$]$_2$[(C$_2$H$_5$)$_4$N]$_2$. 0.45 g (0.7 mmol) of $[Pt_2Cl_4(CO)_2][(C_2H_5)_4N]_2$ in dichloromethane was added to a solution of ddpa (0.38 g) (1.4 mmol) in dichloromethane. The mixture was heated under reflux for one hour then cooled to

0°C. The crystals which separated were filtered off and vacuum dried. Repeated crystallizations from dichloromethane gave a yellow cristalline product containing no carbonyl groups. M.p. 135°C. Anal. Found: C, 44.31; H, 5.81. $C_{50}H_{84}Cl_4N_4P_2Pt_2$ calcd.: C, 44.94; H, 6.34%.

Reaction of $[Pd(CO)Cl]_n$ with ddpa. When 0.45 g of $[Pd(CO)Cl]_n$ was added to a solution of 0.73 g (2.7 mmol) of ddpa in 90 cm^3 of dichloromethane the solution became blood-red and carbon monoxide was evolved. The IR spectrum of the solution showed a band at 1715 cm^{-1}. The solution was filtered to remove unchanged $[Pd(CO)Cl]_n$ and a red solid was precipitated by addition of n-hexane. The brown-red precipitate was filtered off, washed with petroleum ether and dried under vacuum. The compound was very sensitive to air and moisture and decomposed rapidly at room temperature to give metallic Pd along with yellow crystals of the palladium(II) complex.

Conclusion

The reaction of $[M(ddpa)Cl_2]_2$ with carbon monoxide described here differ from those of complexes containing the symmetric ligand dppm (dppm = bis-(diphenylphosphino)methane or the dissymetric ligand Ph_2Ppy (Ph_2Ppy = 2-(diphenylphosphino)pyridine). The complexes of platinum(II) or palladium(II) with dppm are chelated [13,14]. $Pt(dppm)Cl_2$ is mononuclear in the solid state and the structure has been determined crystallographically [13]. $Pd(dppm)Cl_2$ has been shown to be mononuclear in $CHCl_3$ and the structure has been assigned on the basis of spectroscopic data [14]. Bridging by a diphosphine ligand occurs when the PMP angle which would be subtented by a chelating ligand exceeds 90° [15]. The complex of palladium(II) with Ph_2Ppy is a monodentate complex consistent with the formula $Pd(Ph_2PPy)_2Cl_2$ and uncoordinated by the pyridine nitrogen [7]. All the complexes we have studied are bridged binuclear, not mononuclear, complexes.

It is not surprising that the reactions of $[M(dppa)Cl_2]_2$ (complexes of M^{II} containing no metal–metal bond) with carbon monoxide are unlike those of binuclear complexes containing dppm or Ph_2Ppy ligands because the latter are M^I complexes containing a metal–metal bond. But it is surprising that the reaction of the platinum(I) complex $[Pt(CO)Cl_2]_2$ $[(C_2H_5)_4N]_2$ with ddpa does not form $[Pt(ddpa)Cl]_2$ or $[Pt(ddpa)Cl]_2$-μ-CO as observed by Brown et al. [8] for reactions with dppm, but instead gives $[Pt(ddpa)Cl_2]_2[(C_2H_5)_4N]_2$. In the case of $[M(dppm)Cl]_2$ (M = Pd [14], M = Pt [13]) molecular A-frame structures are formed by insertion of small molecules (CO, SO_2 $\cdots$) into the M–M bond. In the case of $[Pd(Ph_2Ppy)Cl]_2$ the Pd–Pd bond cannot open up to form an A-frame structure [7].

We tentatively attribute the result of the reaction of carbon monoxide with **1** and **1′** to the dibasic character of our ligand (like Ph_2Ppy) and to its flexibility (like dppm).

Finally, the presence or absence of a metal–metal bond in **2**, **3**, **5** and **6** has been postulated on the bases of simple electron counting. Confirmation of the proposals is needed especially in connection with the possible formation [1,3] or breaking [5] of the metal–metal bond as the result of CO bridging.

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