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# HYDROCONDENSATION OF $CO_2$

## III *. REACTION OF CARBON DIOXIDE AND HYDROGEN WITH COPPER AND PALLADIUM BIS(DIPHENYLPHOSPHINO)-METHANE COMPLEXES

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### Summary

New bis(diphenylphosphino)methane, (dpm) complexes of palladium have been prepared from $PdCl_2dpm$, either by borohydride reduction or halide abstraction in the presence of added ligand. The catalytic activities of these and other polynuclear palladium and copper complexes in the $CO_2/H_2$ reaction have been tested. The results confirm the catalytic formation of alkyl formate and dialkyl formamide, but the juxtaposition of two or more metal centres does not appear to promote the catalytic formation of $C_2$-compounds (oxalate).

### Introduction

Low-valent transition metal aggregates are of current interest not only as models of surface catalysis but also as novel catalytic systems in their own right. The metal carbonyls have received particular attention [2 and 3 and refs cited therein], but there are numerous other complexes wherein the metal centres are held in juxtaposition by one or more constraining ligands. Thus not only does the ligand bis(diphenylphosphino)methane (dpm) form stable polynuclear complexes with several transition metals (e.g. Cu, Pd, Pt, Rh [4—8]), but also in certain cases the metal is present formally in an unusual oxidation state (e.g. $Pd^I$, $Pt^I$). In addition certain dpm complexes have the property of coordinating small molecules, generally in A-frame type structures [9].

The catalytic hydrogenation of carbon dioxide on Ni-, Fe- and Cu-based contact masses leads to a variety of products (methane, methanol and their homologues) in which the oxygen atoms of the $CO_2$ are wholly or in part lost as $H_2O$

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* For part II see ref. 1.

[10]. The most economic exploitation of $CO_2$ as a source of chemical carbon, however, involves syntheses in which the oxygen atoms are retained (e.g. formate, oxalate, esters, etc...). Formates and formamides may be obtained catalytically from $CO_2/H_2$ with several transition metal compounds [11—17], whereas oxalates may be obtained by the reductive dimerisation of $CO_2$ (electrode processes, amalgams [10]). We therefore undertook the present study of the hydrogenation of $CO_2$ with polynuclear Cu- and Pd-dpm complexes with the idea that the juxtaposition of two or more low-valent transition metal centres might promote the reductive dimerisation of $CO_2$.

## Results and discussion

### *Syntheses of complexes*

Bis(diphenylphosphino)methane forms mono- and poly-nuclear complexes with numerous transition metal compounds, but the latter are normally the more stable. The structures of several of these complexes, including the tetra- and tri-nuclear $Cu^I$ complexes $[(CuCl)_2dpm]_2$, $[Cu_3Cl_2dpm_3]Cl$ [4,5] the dinuclear $Pd^I$ compound $(PdBrdpm)_2$ [8] and the monomeric $Pd^{II}$, $PdCl_2dpm$ [18], have been established by single crystal X-ray structure analyses. We have attempted to extend the group of known palladium-dpm complexes to include $Pd^0$ and coordinatively unsaturated $Pd^I$ and $Pd^{II}$ compounds, using either borohydride reduction or halogen abstraction [19].

*Sodium borohydride reductions.* Sodium borohydride reduction of both I and II in the presence of an equivalent of dpm gave the $Pd^0$ complex III, eq. 1. The same compound may be obtained by borohydride reduction of $PdCl_2(PhCN)_2$ in the presence of 2 equivalents of dpm, eqn. 1.

$$\left.\begin{array}{l}\underset{(I)}{(\mathrm{PdCldpm})_2}\\[1ex] \underset{(II)}{\mathrm{PdCl_2dpm}}\end{array}\right\} \xrightarrow[\mathrm{dpm}]{\mathrm{NaBH_4}} \underset{(III)}{\mathrm{Pd(dpm)_2}} \xleftarrow[\mathrm{dpm}]{\mathrm{NaBH_4}} \mathrm{PdCl_2(PhCN)_2} \tag{1}$$

In the absence of added ligand, the borohydride reduction of II, gave an insoluble product analysing for $[\mathrm{Pddpm}]_n$.

Under an atmosphere of carbon monoxide the sodium borohydride reduction of II gives the known chlorocarbonyl IV in acetone/ethanol mixtures, and the carbonyl V in ethanol, eq. 2.

$$\underset{(V)}{[\mathrm{Pddpm}]_2\mathrm{CO}} \xleftarrow[\mathrm{ethanol}]{\mathrm{CO/NaBH_4}} \underset{(II)}{\mathrm{PdCl_2dpm}} \xrightarrow[\substack{\mathrm{ethanol}\\ \mathrm{acetone}}]{\mathrm{CO/NaBH_4}} \underset{(IV)}{[\mathrm{PdCldpm}]_2\mathrm{CO}} \tag{2}$$

It is of interest to note that the $Pd^0$ complex III reacts smoothly with $PdCl_2(PhCN)_2$ to give the dinuclear complex I, eq. 3 thus providing a much simplified synthesis of the latter.

$$\underset{(III)}{\mathrm{Pd(dpm)_2}} + \mathrm{PdCl_2(PhCN)_2} \rightarrow \underset{(I)}{(\mathrm{PdCldpm})_2} + 2\ \mathrm{PhCN} \tag{3}$$

Copper(II) chloride reacts with III to give a copper-palladium complex analysing for ($Pd_2Cu_2Cl_6dpm_3$).

*Halogen abstraction reactions.* Treatment of acetone or methanol solutions of dichloropalladium(II)-dpm (II) with $AgBF_4$ led to quantitative precipitation of AgCl and formation of clear orange-red solutions. It was not possible to isolate any stable crystalline solids from these solutions. The presence of solvated cationic entities was inferred, however, from the observations that subsequent treatment with dpm or $PPh_3$ permitted the isolation of the respective coordinatively saturated complexes VI or VII, eq. 4, S = acetone or methanol

$$\mathrm{PdCl_2dpm} \xrightarrow[\mathrm{S}]{\mathrm{AgBF_4}} [\mathrm{PddpmS}_x](\mathrm{BF_4})_2 \left[ \begin{array}{l} \mathrm{dpm} \rightarrow [\mathrm{Pd(dpm)_2}](\mathrm{BF_4})_2 \\ \qquad\qquad \text{(VI)} \\ \mathrm{PPh_3} \rightarrow [\mathrm{Pddpm(PPh_3)_2}](\mathrm{BF_4})_2 \\ \qquad\qquad \text{(VII)} \end{array} \right. \qquad (4)$$

## *Catalytic reactions*

Preliminary catalytic tests (numbers 1 and 2 Table 1) with the solvent systems $EtOH/C_6H_6$ and $EtOH/Et_3N$ and $CO_2/H_2$ (1/1) mixtures confirmed the superiority of the latter for ethyl formate formation [16]. The results of comparative tests under standard conditions (not optimised) with the different palladium and copper complexes (Table 1) indicate that the products consist essentially of ethyl formate, methane, and sometimes small quantities of diethyl oxalate.

The activity of the palladium catalysts in ethyl formate formation is influenced by the nature of the ligand as well as by the coordination and oxidation states of the metal centre. Thus, all the dpm systems (numbers 2 to 7) are

TABLE 1

HYDROGENATION OF $CO_2$, $EtOH/Et_3N$ [a]

| Experiment number | Catalyst ($\mu$-mol metal) | Products ($\mu$-mol) | | |
|---|---|---|---|---|
| | | $CH_4$ | HCOOEt | $(COOEt)_2$ |
| 1 | $(PdCldpm)_2$ [b] (340) | 250 | 5 | 0 |
| 2 | $(PdCldpm)_2$ (520) | 800 | 2000 | 1 |
| 3 | $Pd(dpm)_2$ (440) | 40 | 4000 | 0.4 |
| 4 | $[Pddpm(EtOH)_x](BF_4)_2$ (420) | 60 | 1000 | 1 |
| 5 | $(Pddpm)_n$ (320) | 200 | 500 | 0.2 |
| 6 | $PdCl_2dpm$ (480) | 300 | 250 | 1 |
| 7 | $Pd_2Cu_2Cl_6dpm_3$ (460) | 440 | 2000 | 0.6 |
| 8 | $Pd(dpe)_2$ (400) | 40 | 560 | 0 |
| 9 | $PdCl_2dpe$ (710) | 0 | 150 | 0 |
| 10 | $Pd(PPh_3)_4$ (480) | 20 | 200 | 0 |
| 11 | $PdCl_2(PPh_3)_2$ (480) | 0 | 350 | 0.3 |
| 12 | $[(CuCl)_2dpm]_2$ (340) | 0 | 30 | 0 |
| 13 | $[Cu_3Cl_2dpm_3]Cl$ (410) | 0 | 12 | 0 |
| 14 | $(PdCldpm)_2$ [c] (420) | 40 | $HCONEt_2$, 1080 | $(CONEt)_2$, 0 |

[a] Reaction conditions, $CO_2$ (15 bar), $H_2$ (15 bar), EtOH (50 ml), $Et_3N$ (10 ml), 120°C, 24 h. [b] solvent $C_6H_6$ (50 ml), EtOH (5 ml). [c] solvent $C_6H_6$ (40 ml), $Et_2NH$ (10 ml).

more active than the diphos (numbers 8 and 9) and triphenylphosphine ones (number 10 and 11); the solvato complex (number 4) is more active than the parent dichlorocomplex (number 6); the most active system is that derived from the palladium(0) complex (number 3). These observations are consistent with the combined effect of the stabilizing influence of the dpm ligand and the electrophilic nature of $CO_2$, which requires an electron-rich nucleophilic metal centre [17,20].

The palladium are all much more active than the copper catalysts (numbers 12 and 13). It is of interest to note however that the mixed Pd/Cu system (number 7) has an activity similar to that of the palladium(I) complex (number 2).

The dinuclear palladium(I) compound $(PdCldpm)_2$ in diethylamine/benzene transforms $CO_2/H_2$ into diethyl formamide; none of the corresponding $C_2$ product (oxamide) could be detected in the products.

The present results confirm that alkyl formates and dialkyl formamides can be formed catalytically from $CO_2/H_2$ mixtures [10,17]. However, the juxtaposition of low valent palladium or copper centres does not seem to promote the catalytic formation of $C_2$ products, although oxalates are formed in less than stoichiometric quantities.

The presence of both formate and oxalate amongst the products raises the question of whether they originate in common or in different intermediates. Formate formation has been interpreted in terms of metal-formato, metal-alkoxy carbonyl- and metal-bicarbonato intermediates [1,10,12—15,17] and that of oxalates in terms of alkoxycarbonyl intermediates [1,21]. Formato and carbamido complexes seem to be unlikely intermediates [1,22] in the formation of alkyl formates and dialkyl formamides, and we are investigating the possible roles of alkoxycarbonyl- and carbonato-metal compounds as possible intermediates in these syntheses.

## Experimental

Unless otherwise stated the preparations of the organometallic compounds were carried out under dry argon. The infrared spectra were obtained with a Perkin-Elmer 580 instrument; characteristic infrared adsorptions in the 800 to 450 $cm^{-1}$ region are given in Table 2. The $^1H$ NMR spectra ($CDCl_3$ solutions, with TMS as internal standard) were recorded on a Varian XL 100 instrument. The microanalyses are by the C.N.R.S. Microanalytical Centre, Solaize, France.

The catalyses tests were carried out in a stainless steel Autoclave Engineers 300 ml Magnedrive unit with commercial grade $CO_2$ and $H_2$. The commercial

TABLE 2

CHARACTERISTIC INFRARED ABSORPTIONS IN THE 800 TO 450 $cm^{-1}$ REGION

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Pd(dpm)_2$ | 775 | 735 | | | | 690 | 513 | | 480 | 470 | | |
| $(Pddpm)_n$ | 775 | 732 | | 713 | | 690 | 515 | | 505 | 480 | 460 | |
| $(Pddpm)_2CO$ | 779 | 739 | | 720 | | 690 | 518 | | 503 | 475 | | |
| $(PdCldpm)_2$ | 780 | 740 | | | | 690 | 518 | | 505 | 487 | | |
| $Pd_2Cu_2Cl_6dpm_3$ | 780 | 739 | | 715 | | 690 | 550 | | 518 | 505 | 477 | 460 |
| $[Pd(dpm)_2](BF_4)_2$ | 752 | 740 | | 718 | | 688 | 530 | | 502 | 470 | 460 | |
| $[Pd(dpm)(PPh_3)_2](BF_4)_2$ | 784 | 762 | 748 | 740 | 712 | 690 | 545 | 529 | 510 | 498 | 480 | 472 |

grade solvents were distilled before use. The gaseous organic products were analysed by vapour phase chromatography on Carbosieve B and Porapack R and Q columns, the liquid products, after distillation on Porapack R and Silicone SE 30 columns. Published methods were used for the preparation of $[(CuCl_2)_2dpm]_2$ [23] $[Cu_3Cl_2dpm_3]Cl$ [23], $PdCl_2dpm$ [18], $PdCl_2dpe$ [18], $Pd(dpe)_2$ [24], $PdCl_2(PPh_3)_2$ [25], and $Pd(PPh_3)_4$ [24].

### *Preparation of $Pd(dpm)_2$, (III)*

Sodium borohydride (0.08 g, 2 mmol) was slowly added to a solution of dpm (0.39 g, 1 mmol) and $PdCl_2dpm$ (0.56 g, 1 mmol) in ethanol (20 ml). After stirring for 20 min at room temperature the orange product was filtered off, washed with EtOH, and recrystallised from $CH_2Cl_2$/EtOH,: yield, 0.62 g (70%). (Found: C, 67.5; H, 5.3; P, 14.2. $C_{50}H_{44}P_4Pd$ calcd., C, 68.6; H, 5.0: P, 14.2%), $\delta(CH_2) = 4.10$ ppm (2 protons).

### *Preparation of $(Pddpm)_n$*

The addition of sodium borohydride (0.08 g, 2 mmol) to a solution of $PdCl_2dpm$ (0.56 g, 1 mmol) in ethanol (20 ml) gave a purple precipitate after 10 mins and this was washed with EtOH and dried in vacuum. The product was insoluble in all the common organic solvents: yield 0.40 g (80%). (Found: C, 60.4; H, 4.6; P, 12.7. $C_{25}H_{22}P_2Pd$ calcd.: C, 61.2; H, 4.5; P, 12.6%).

### *Preparation of $(Pddpm)_2CO$ (V).*

Sodium borohydride (0.08 g, 2 mmol) was added to a solution of $PdCl_2dpm$ (0.56 g, 1 mmol) in ethanol (20 ml) under a stream of carbon monoxide. The clear red-brown solution was evaporated to dryness at room temperature. The residue was extracted with $CH_2Cl_2$, and the filtered extract slowly evaporated. The crystalline material so obtained was filtered off and dried in vacuum,: yield 0.3 g (60%). (Found: C, 59.9; H, 4.5; P, 11.9. $C_{51}H_{44}OP_4Pd$ calcd.: C, 60.7; H, 4.4; P, 12.3%), $\nu(CO)$ 1820 $cm^{-1}$.

### *Preparation of $(PdCldpm)_2$ (I)*

Solid $PdCl_2(PhCN)_2$ (0.19 g, 0.5 mmol) was added to a solution of $Pd(dpm)_2$ (0.44 g, 0.5 mmol) in $CH_2Cl_2$ (15 ml). After stirring at room temperature for 10 min, the clear red solution was concentrated (ca. 5 ml) and treated with methanol. The crude material thus obtained was crystallised from $CH_2Cl_2$/MeOH to give $(PdCldpm)_2$, identified by a direct comparison with an authentic specimen [26]: yield 0.42 g (80%).

### *Preparation of $Pd_2Cu_2Cl_6dpm_3$*

$CuCl_2$ (0.25 g, 1.8 mmol) was added to a stirred suspension of $Pd(dpm)_2$ (0.44 g, 0.5 mmol) in EtOH (30 ml). After 30 min the yellow precipitate was filtered, washed with EtOH and dried solid was recrystallised from $CH_2Cl_2/Et_2O$: yield 0.31 g (73%). (Found: C, 51.9; H, 3.8; P, 10.2; Cl, 13.3; Cu, 7.8; Pd, 12.1 $C_{75}H_{66}Cu_2Cl_6P_6Pd_2$ calcd.: C, 52.8; H, 3.9; P, 10.9; Cl, 12.5; Cu, 7.4; Pd, 12.5%) $\delta(CH_2) = 415$ ppm.

### *Preparation of $[PddpmS_x]^{2+}$ and related compounds*

The stoichiometric quantity of $AgBF_4$ (1.05 mmol) was added to a stirred suspension of $PdCl_2dpm$ (0.28 g, 0.5 mmol) in methanol or acetone. After a few minutes AgCl was formed and a clear orange-red supernatant solution obtained. Concentration of the filtered solutions led to orange-red solids which rapidly decomposed.

*$[Pd(dpm)_2](BF_4)_2$ (VI) and $[Pd(dpm)(PPh_3)_2](BF_4)_2$ (VII).* The addition of one equivalent of dpm or two equivalents of $PPh_3$ to the clear solutions of the cationic salts, prepared as above, resulted in the immediate precipitation of white and cream solids, respectively. (Found: C, 56.8; H, 4.1 P, 12.1. $C_{50}H_{44}B_2F_8P_4Pd$ (VI) calcd.: C, 57.3; H, 4.2; P, 11.8%. $\nu(BF_4)$ 1050 $cm^{-1}$). (Found: C, 60.1; H, 4.2; P, 10.5. $C_{61}H_{55}B_2F_8P_4Pd$ (VII) calcd.: 60.9; H, 4.4; P, 10.4%. $\nu(BF_4)$ 1050 $cm^{-1}$).

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