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# CATIONIC ORGANOCARBONYL PALLADIUM(II) COMPLEXES

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## Summary

The carbonylation under normal pressure, at 0°C, of organometallic perchlorato palladium(II) complexes in solution leads to the displacement of the perchlorato group and the formation of a series of cationic organocarbonyl palladium(II) compounds of the general formula $[CO(C_6F_5)PdL_2]ClO_4$, where $L_2$ are either two tertiary phosphine groups or a nitrogen chelate, such as 2,2′-bipyridine, 1,10-phenanthroline or *N,N,N′,N′*-tetramethylethylenediamine.

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## Introduction

The chemistry of palladium carbonyl derivatives is only slightly developed. $Pd(CO)_4$ is as yet unknown and the few reported carbonyl complexes correspond [1—3] to the types $[Pd(CO)X_2]_n$, $[Pd(CO)X_3]^-$ and $[Pd(CO)_2Cl_2]_n$. A single cationic carbonyl compound [*trans*-$Cl(CO)Pd(PEt_3)_2]BF_4$ has been described [4], and only one organometallic carbonyl has been prepared [5].

Herein we report a method for the preparation of a new type of compounds, cationic organocarbonyl palladium complexes, which contain, besides CO, a $C_6F_5$ group and different monodentate or bidentate ancillary ligands.

The method appears to be a general one but the ancillary ligands influence the stability of the resulting complexes and may therefore limit its scope.

## Results and discussion

### *(a) Preparation of the complexes*

Covalent perchlorates, obtained by the reaction of the corresponding chloroderivative with silver perchlorate according to eq. 1, are carbonylated to give the

$$Cl(C_6F_5)PdL_2 + AgClO_4 \rightarrow AgCl + O_3ClO(C_6F_5)PdL_2 \qquad (1)$$

$(L_2 = 2L \text{ or } L—L)$

cationic organocarbonyl palladium complexes as a consequence of the facile displacement of the perchlorato group from its coordination position [6—10].

$$O_3ClO(C_6F_5)PdL_2 + CO \rightleftharpoons [CO(C_6F_5)PdL_2]ClO_4 \qquad (2)$$

The starting perchlorato complex is in many cases soluble enough in the solvents used, which are generally non-donors, such as chloroform or toluene, so that the precipitated AgCl can be separated by filtration. The subsequently formed cationic complex can easily be isolated because it is insoluble in these solvents.

Whenever the initial perchlorato complex is insoluble and cannot be separated by filtration from the AgCl formed in reaction 1, acetone can be used as solvent so that the perchlorato complex goes in solution as $[(CH_3)_2CO(C_6F_5)PdL_2]ClO_4$. Once isolated and in chloroform suspension, carbonylation of the complex can be achieved, because the acetone (a better ligand than the perchlorato group) is also readily displaced by carbon monoxide.

The analytical data for the complexes are listed in Table 1.

### (b) Stability

At room temperature reaction 2 is an equilibrium which in the presence of an excess of CO is displaced towards the right, and can revert towards the left in its absence. Only in the case where L is $AsPh_3$ was it found that at room temperature reaction 2 was not displaced towards the right, but by passing the CO stream through a dry toluene solution of $O_3ClO(C_6F_5)Pd(AsPh_3)_2$ at −22°C the corresponding $[CO(C_6F_5)Pd(AsPh_3)_2]ClO_4$ was obtained as a white precipitate, which, after isolation at low temperature, liberated CO if the temperature was allowed to rise.

The other carbonyls are indefinitely stable below −28°C. Their decomposition with release of CO is quite rapid in $CHCl_3$ solution (those with nitrogen chelates

TABLE 1

ANALYTICAL DATA AND MOLAR CONDUCTIVITIES OF $[CO(C_6F_5)PdL_2]ClO_4$

| $L_2$ | Analysis found (calcd.) (%) | | | $\Lambda_M$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) | |
|---|---|---|---|---|---|
| | C | H | N | Acetone | Chloroform |
| $(PPh_3)_2$ | 54.90<br>(55.80) | 3.41<br>(3.34) | | 100.8 | 4.8 |
| $(PPhEt_2)_2$ | 44.51<br>(44.22) | 5.08<br>(4.09) | | 97.4 | 2.2 |
| $(PPh_2Me)_2$ | 48.05<br>(49.45) | 3.32<br>(3.24) | | 128.2 | 3.2 |
| $(PEt_3)_2$ | 35.40<br>(35.80) | 5.00<br>(4.71) | | 114.0 | 0.0 |
| (bipy) | 35.92<br>(36.63) | 1.47<br>(1.43) | 4.93<br>(5.02) | 120.8 | insoluble |
| (phen) | 39.72<br>(39.24) | 1.77<br>(1.37) | 4.83<br>(4.82) | 134.6 | insoluble |
| (tmen) | 29.22<br>(30.17) | 3.58<br>(3.09) | 5.05<br>(5.41) | 136.2 | insoluble |

are insoluble in this solvent) so that the band due to $\nu$(CO) could not be observed even in freshly-prepared solutions, except where L was $PEt_3$ in which case the solution is somewhat more stable.

The stability of the solids was studied by two diferent methods: (1) the temperature of a Nujol mull of the compound was gradually raised until the release of the CO bubbles was observed with the help of the microscope and the corresponding temperature was recorded; (2) the IR spectra of solid samples stored at room temperature were regularly recorded to determine the time (in days) until the band due to $\nu$(CO) had completely disappeared and the bands due to the $ClO_4^-$ group ($T_d$) were transformed into those which are characteristic for the $O_3ClO$ ($C_{3v}$) group. The results are collected in Table 2.

As may be seen, nitrogen ligands confirm higher stability than do phosphine ligands, indeed the triphenylarsine complex can be detected only at low temperatures. This is in general accordance with what is to be expected as characteristic of the M—CO bond; those ancillary ligands which increase the electron density on the metal atom also increase its capacity for back donation to the carbonyl group and must therefore be better $\sigma$ donors ($N > P > As$) but worse $\pi$ acceptors ($As > P > N$).

The small differences which are observed in the stabilities of complexes with similar ligands cannot be discussed in terms of bonding only since a number of other factors must also be operating.

Furthermore the chelate effect alone does not seem to account for the stabilization observed in complexes with nitrogen ligands, since the carbonylation of $O_3ClO(C_6F_5)Pd$(diphos), diphos = 1,2-bis(diphenylphosphino)ethane, cannot be accomplished at room temperature.

### *(c) Conductivities*

As mentioned above, chloroform solutions of the complexes release CO immediately and solutions of the perchlorato complexes are obtained. The measured conductivities are therefore not those expected for 1 : 1 electrolytes but those corresponding to non-conductors ($\Lambda_M$ = 0—4.8 $\Omega^{-1}$ cm$^2$ mol$^{-1}$). The conductivities which were measured in acetone solutions are nevertheless characteristic for 1 : 1 electrolytes ($\Lambda_M$ = 97—136 $\Omega^{-1}$ cm$^2$ mol$^{-1}$), not because

TABLE 2

STABILITY OF $[CO(C_6F_5)PdL_2]ClO_4$: DISAPPEARANCE OF CO STRETCHING VIBRATIONS

| $L_2$ | $T$ (°C) | Time for complete disappearance (days) |
|---|---|---|
| $(PPh_3)_2$ | 39 | 11 |
| $(PPhEt_2)_2$ | 65 | 170 |
| $(PPh_2Me)_2$ | 45 | 162 |
| $(PEt_3)_2$ | 32 | 15 |
| (bipy) | 142 | [a] |
| (phen) | 133 | [a] |
| (tmen) | 80 | [a] |

[a] No decrease in intensity after 5 months.

TABLE 3

ABSORPTIONS DUE TO $\nu$(CO) IN $[CO(C_6F_5)PdL_2]ClO_4$

| $L_2$ | $\nu$(CO) ($cm^{-1}$) |
|---|---|
| $(PPh_3)_2$ | 2143 |
| $(PPhEt_2)_2$ | 2146 |
| $(PPh_2Me)_2$ | 2147 |
| $(PEt_3)_2$ | 2132 |
| (bipy) | 2153 |
| (phen) | 2160 |
| (tmen) | 2163 |

the cationic complexes are stable in this solvent but because the CO released is replaced not by the perchlorato group but by a molecule of the solvent, according to eq. 3.

$$[CO(C_6F_5)PdL_2]ClO_4 \xrightarrow{(CH_3)_2CO} CO + [(CH_3)_2CO(C_5F_5)PdL_2]ClO_4 \qquad (3)$$

*(d) IR spectra*

All the spectra were taken with freshly-prepared samples in Nujol mulls. The complexes all show vibrations at 1100 and 620 $cm^{-1}$ characteristic of the $ClO_4^-$ group, [7] at 1635—1600 m, 1510—1490vs, 1460—1420vs, 1070—1050s, 960—950vs, 800—750s and 610w $cm^{-1}$ due to the $C_6F_5$ group [11,12], as well as those of the ancillary ligands. The $\nu$(CO) stretching vibrations in the complexes are located at very high frequencies, as may be seen from Table 3. This is not too surprising because of the high formal valency of the metal atom and the excess of positive charge in these cationic complexes.

*(e) Configuration*

Only complex $[(CO)(C_6F_5)Pd(PEt_3)_2]ClO_4$ was stable enough for its structure to be investigated by NMR spectroscopy.

The $^1$H NMR spectrum showed a quintuplet at $\tau$ 8.85 ppm for the $CH_3$ group, due to the strong coupling with both phosphorous nuclei, as has already been observed [13] for complexes of the *trans*-$X(C_6F_5)Pd(PEt_3)_2$ type.

## Experimental

IR spectra were recorded on a Beckman IR 20A spectrophotometer (over the range 4000—250 $cm^{-1}$) using Nujoll mulls between sodium chloride discs. Two-fold wave number scale expansions were used in the zone of the $\nu$(CO) stretching vibrations. Conductivities were measured in $\sim 5 \times 10^{-4}$ $M$ solutions with a Philips PW 9501/01 conductimeter. C, H and N analyses were made with a Perkin-Elmer 240 microanalyzer. Decomposition points (release of CO) were determined with a Reichert (Austria) apparatus provided with a microscope with polarizator.

The $^1$H NMR spectrum $[(CO)(C_6F_5)Pd(PEt_3)_2]ClO_4$ in $CDCl_3$ solution was registered with a Perkin—Elmer R-12B, 60 MHz spectrograph, and showed resonances at $\tau$ 8.35 (unresolved multiplet, $CH_2$) and 8.85 (quintuplet, $CH_3$) ppm.

The starting complexes were prepared as described elsewhere [14—16]. Dry CO was obtained from commercial sources in steel cylinders (under 150 atm, 99.97% purity).

All the preparations were carried out under anhydrous conditions and protected against light.

### $[CO(C_6F_5)Pd(PPh_3)_2]ClO_4$ (I)

To a solution of 0.72 g (0.9 mmol) of chloropentafluorophenylbis(triphenylphosphine)palladium(II) in 30 ml of toluene was added 0.20 g (0.9 mmol) of $AgClO_4$ and the mixture stirred for 30 min at room temperature. The precipitated AgCl was filtered off and a CO stream at 0°C was passed through the yellow solution for 30 min. The resulting white complex I was filtered off (85% yield).

### $[CO(C_6F_5)Pd(bipy)]ClO_4$ (II)

To a solution of 0.4 g (0.9 mmol) of chloropentafluorophenyl-2,2'-bipyridinepalladium(II) in 30 ml of acetone was added 0.2 g (0.9 mmol) of $AgClO_4$ and the mixture stirred for 1 h at room temperature. The precipitated AgCl was filtered off. After partially concentrating the filtrate and adding a few ml of chloroform a yellow product was obtained which was heated to 60°C for 48 h. A CO stream was bubbled for 30 min at 0°C through the suspension of the product in 50 ml of chloroform. The white complex II was separated by filtration (90% yield).

### $[CO(C_6F_5)Pd(PPh_2Me)_2]ClO_4$ (III)

To a solution of 0.8 g (1.2 mmol) of chloropentafluorophenylbis(diphenylmethylphosphine)palladium(II) in 20 ml of chloroform was added 0.25 g (1.2 mmol) of $AgClO_4$ and the mixture stirred for 1 h at room temperature. After filtering off the AgCl the yellow filtrate was partially evaporated and a few ml of hexane were added. CO was passed through the solution at 0°C for 30 min to give the white complex III, which was filtered off (67.5% yield).

### $[CO(C_6F_5)Pd(PEt_3)_2]ClO_4$ (IV)

To a solution of 0.6 g (1.2 mmol) of chloropentafluorophenylbis(triethylphosphine)palladium(II) in 20 ml of toluene was added 0.25 g (1.2 mmol) of $AgClO_4$ and the mixture stirred for 45 min at room temperature. After filtering off the AgCl a CO stream at 0°C was passed through the yellow filtrate for 20 min. The resulting white complex IV was isolated by filtration (73.7% yield).

### $[CO(C_6F_5)Pd(PPhEt_2)_2]ClO_4$ (V)

To a solution of 0.5 g (0.8 mmol) of chloropentafluorophenylbis(phenyldiethylphosphine)palladium(II) in 20 ml of toluene was added 0.17 g (0.8 mmol) of $AgClO_4$ and the mixture stirred for 30 min at room temperature. After separating the AgCl, CO gas at 0°C was passed through the yellow filtrate for 25 min. The white complex V was filtered off (76.2% yield).

### $[CO(C_6F_5)Pd(phen)]ClO_4$ (VI)

To a solution of 0.41 g (0.8 mmol) of chloropentafluorophenyl-1,10-phenanthrolinepalladium(II) in 40 ml of acetone was added 0.18 g (0.8 mmol) of $AgClO_4$ and the mixture stirred for 1 h at room temperature. After separating the precipitated AgCl the filtrate was partially evaporated and a few ml of benzene were added to crystallize the yellow ionic perchlorate, which was filtered off and vacuum-dried. A CO stream at 0°C was passed through a suspension of the crystals in 15 ml of chloroform for 30 min. The resulting white complex VI was separated by filtration (83% yield).

*$[CO(C_6F_5)Pd(tmen)]ClO_4$ (VII)*

To a solution of 0.33 g (0.7 mmol) of chloropentafluorophenyl-*N,N,N′,N′*-tetramethylethylenediaminepalladium(II) in 20 ml of acetone was added 0.16 g (0.7 mmol) of $AgClO_4$. After filtering off the AgCl, the yellow filtrate was partially evaporated and a few ml of benzene were added to crystallize a product, which was filtered off and vacuum-dried. A CO stream was passed through a suspension of the crystals in 10 ml of toluene for 3 h at 0°C. The resulting complex VII was filtered off and dried with diethylether (90% yield).

*$[CO(C_6F_5)Pd(AsPh_3)_2]ClO_4$ (VIII)*

To a solution of 0.8 g (0.9 mmol) of chloropentafluorophenylbis(triphenylarsine)palladium(II) in 20 ml of toluene was added 0.18 g (0.9 mmol) of $AgClO_4$ and the mixture stirred for 45 min at room temperature. The AgCl was removed and the filtrate was set aside for 2 h at —30°C. A CO stream was passed for 15 min at —22°C when a voluminous white precipitate was formed which was filtered off at —30°C. When the white compound was allowed to warm to room temperature the CO was quickly released and the covalent perchlorato complex was obtained.

*Reversibility test*

Complex IV was vacuum-dried for 3 h and quantitative release of the CO was confirmed by observation of the IR spectrum. CO gas was bubbled through a solution of the resulting complex in 20 ml of toluene for 1/2 h at 0°C. The white precipitate obtained was identified by IR spectroscopy as complex IV. On storing this product for 16 h at 50°C, release of the CO is once more observed; carbonylation can then be repeated.

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