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INFRARED SPECTROSCOPIC EVIDENCE FOR TRICARBONYL-(TRIPHENYLPHOSPHINE)-PLATINUM AND -PALLADIUM

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SUMMARY

IR spectral evidence has been obtained for the reversible formation of $Pt(CO)_3PPh_3$ and $Pd(CO)_3PPh_3$ from the reactions of $Pt_3(CO)_3(PPh_3)_4$ [or $Pt(CO)_2(PPh_3)_2$] and $Pd_3(CO)_3(PPh_3)_3$ respectively with carbon monoxide under pressure. The mononuclear tricarbonyl species decompose in the absence of an adequate carbon monoxide pressure. No evidence has been obtained for the further replacement of triphenylphosphine by carbon monoxide with the formation of $Pt(CO)_4$ or $Pd(CO)_4$.

INTRODUCTION

Although the complexes $M(PPh_3)_4$, $M(CO)(PPh_3)_3$ [M = Pt, Pd], and $Pt(CO)_2(PPh_3)_2$ are well documented[1–5] and the formation of $M(CO)_4$ has been recently inferred from matrix isolation experiments[6,7] there is little evidence for the existence of the monosubstituted tricarbonyl species $M(CO)_3PPh_3$[8]. Since the stability of the known compounds decreases with increasing carbon monoxide content it seems unlikely that $M(CO)_3PPh_3$ would be stable under normal conditions of temperature and pressure.

Two approaches appeared feasible towards obtaining evidence for these tricarbonyl species. Firstly the report of Chatt and Chini[9], illustrating the ready rupture of the trinuclear compound $Pt_3(CO)_3(PPh_3)_4$ by carbon monoxide under ambient conditions (I), suggested that it would be profitable to study this reaction under pressures of carbon monoxide in the absence of excess phosphine [*i.e.* a deficiency of triphenylphosphine for the sole formation of $Pt(CO)_2(PPh_3)_2$]. Secondly, by analogy with the reversible equilibrium (II) established for the corresponding nickel complexes[10], an investigation of the reaction of $Pt(CO)_2(PPh_3)_2$ under high pressures of carbon monoxide may also yield information concerning the formation of $Pt(CO)_3PPh_3$. These reactions, and that of the related compound $Pd_3(CO)_3(PPh_3)_3$ with carbon monoxide, have now been investigated by the following infrared spectral

$$Pt_3(CO)_3(PPh_3)_4 + 2\,PPh_3 + 3\,CO \rightarrow 3\,Pt(CO)_2(PPh_3)_2 \qquad (I)$$

$$Ni(CO)_2(PR_3)_2 + CO \rightleftarrows Ni(CO)_3PR_3 + PR_3 \qquad (II)$$

changes using a high pressure spectrophotometric cell[11] and details are described herein.

RESULTS AND DISCUSSION

Reaction of $Pt_3(CO)_3(PPh_3)_4$ and $Pt(CO)_2(PPh_3)_2$ with carbon monoxide

The reactions of both $Pt_3(CO)_3(PPh_3)_4$ and $Pt(CO)_2(PPh_3)_2$ with carbon monoxide were studied as solutions of the complexes in *p*-xylene, the absorptions due to *p*-xylene in the ν(CO) region being virtually balanced out using a second identical high pressure cell situated in the reference beam of the spectrometer. Reactions of $Pt(CO)_2(PPh_3)_2$ with carbon monoxide were also studied as suspensions in liquid paraffin/heptane mixtures.

Spectral changes in the range 2200–1700 cm^{-1} which are observed when a *p*-xylene solution of $Pt_3(CO)_3(PPh_3)_4$ at 25° is pressurised with carbon monoxide are illustrated in Fig 1. The initial spectrum of $Pt_3(CO)_3(PPh_3)_4$ [Fig. 1(b)], displaying essentially one band at 1799 cm^{-1}, changes rapidly on introduction of carbon monoxide [Fig. 1(c)] and two new absorptions appear at 1996 and 1954 cm^{-1}, consistent with the spectrum of $Pt(CO)_2(PPh_3)_2$ in *p*-xylene. Only partial conversion into $Pt(CO)_2(PPh_3)_2$ occurs, however, the 1799 cm^{-1} peak remaining with significant intensity, and little further spectral change occurs until the pressure is increased to 300–400 atm. Then, on standing at 25° [Fig. 1(d)], a new band appears at 2056 cm^{-1} and the 1996 cm^{-1} absorption increases in relative intensity [compared with the 1954 cm^{-1} peak] as the 1799 cm^{-1} absorption due to $Pt_3(CO)_3(PPh_3)_4$ slowly disappears. Finally, after 5 h total reaction time [Fig. 1(e)] the 1954 cm^{-1} band also decreases in intensity as those at 2056 and 1996 cm^{-1} increase

If at this stage the system is heated, little further change occurs until 140° is reached when the 1954 cm^{-1} band decreases further in intensity Above 160° all the absorptions decrease in intensity presumably with the onset of decomposition. No new

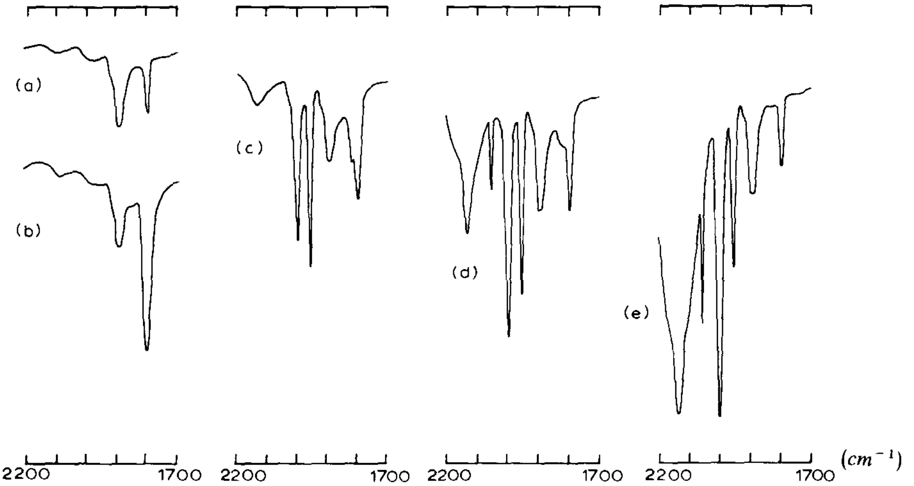

Fig 1 Reaction of $Pt_3(CO)_3(PPh_3)_4$ with carbon monoxide in *p*-xylene at room temperature (a) *p*-xylene, (b) 1 atm N_2, (c) 100 atm CO, $1\frac{1}{2}$ h, (d) 350 atm CO, 2 h, (e) 350 atm CO, 5 h.

TABLE 1

ν(CO) STRETCHING FREQUENCIES (in cm^{-1})

Compound	*Conditions*	*Solvent*	*Frequencies*
$Pt_3(CO)_3(PPh_3)_4 + CO$	350 atm, 25°	*p*-Xylene	2056 ms, 1996 vs, 1954 m
$Pt(CO)_2(PPh_3)_2$		*p*-Xylene	1996 s, 1954 s
$Pd_3(CO)_3(PPh_3)_3 + CO$	550 atm, 25°	*p*-Xylene	2074 ms(sh), 2023 s
$Ni(CO)_3PPh_3$	ref 12	Cetane	2070 m, 1997 s
$Ni(CO)_2(PPh_3)_2$	ref 12	Cetane	2005 s, 1950 s

absorptions are observed during this decomposition

When the pressure of the system corresponding to Fig 1(e) is decreased to atmospheric rapid reformation of $Pt(CO)_2(PPh_3)_2$ and $Pt_3(CO)_3(PPh_3)_4$ occurs as the new species decomposes; the band at 2056 cm^{-1} disappears, that at 1996 cm^{-1} decreases in intensity to parallel the 1954 cm^{-1} peak, and the 1799 cm^{-1} absorption reappears. The final spectrum is very similar to Fig. 1(c)

Comparison of the frequencies and intensities of the bands observed in Fig 1(e) with the spectra of $Pt(CO)_2(PPh_3)_2$, $Ni(CO)_2(PPh_3)_2$[12] and $Ni(CO)_3PPh_3$[12] (Table 1) suggests that the 2056 and 1996 cm^{-1} absorptions are the A_1 and E vibrations respectively expected for the molecule $Pt(CO)_3PPh_3$ with C_{3v} symmetry Support for the fact that these absorptions are not due to a platinum cluster species is provided by a study of the reactions of $Pt(CO)_2(PPh_3)_2$ with carbon monoxide in both *p*-xylene and liquid paraffin/heptane. Using *p*-xylene as solvent some initial reaction occurs at room temperature when an additional weak band at 2056 cm^{-1} is observed almost immediately on pressurising to 300 atm with carbon monoxide. This initial reaction probably arises through slight dissociation of $Pt(CO)_2(PPh_3)_2$ on first dissolving in *p*-xylene resulting in the formation of some $Pt_3(CO)_3(PPh_3)_4$[9], followed by reaction to give $Pt(CO)_3PPh_3$ on application of carbon monoxide pressure. No further spectral changes are noted until the temperature is increased above 140° when the 1954 cm^{-1} band due to $Pt(CO)_2(PPh_3)_2$ decreases in intensity and the 2056 and 1996 cm^{-1} absorptions increase slightly. Above 150° all the bands decrease in overall intensity suggesting that some decomposition is occurring but further transformation of $Pt(CO)_2(PPh_3)_2$ into $Pt(CO)_3PPh_3$ occurs up to 180° at 430 atm pressure No additional absorptions are observed during decomposition above 180°. On cooling to room temperature the starting spectrum of $Pt(CO)_2(PPh_3)_2$ is restored.

Even under the high pressure and temperature conditions employed (430 atm CO, 180°) the extent of conversion of $Pt(CO)_2(PPh_3)_2$ into $Pt(CO)_3PPh_3$ is considerably less than that observed in the reaction of $Pt_3(CO)_3(PPh_3)_4$ with carbon monoxide at room temperature. The reason for this is presumably associated with the differences in triphenylphosphine to platinum ratios in the two compounds A ratio of 4/3 in the trinuclear cluster compounds means that $Pt(CO)_2(PPh_3)_2$ cannot be the sole product of the reaction with carbon monoxide in the absence of excess of ligand.

Similar spectral changes to those occurring in *p*-xylene are noted when liquid paraffin/heptane suspensions of $Pt(CO)_2(PPh_3)_2$ are pressurised with carbon monoxide and heated. A new band at 2056 cm^{-1} is first noted at 510 atm pressure and 140° and at 175° (and 530 atm) the spectrum consists of absorptions at 2056 sh, 2002 s and 1961 mw cm^{-1} Above this temperature decomposition occurs.

Reaction of $Pd_3(CO)_3(PPh_3)_3$ with carbon monoxide

When *p*-xylene solutions of $Pd_3(CO)_3(PPh_3)_3$ are initially pressurised to 100 atm with carbon monoxide, the absorption at 1850 cm^{-1} due to the starting compound shifts to 1880 cm^{-1} and new bands appear at 2074 vw, 2050 vw, 2023 w and 1985 w cm^{-1}. The peaks at 2023 and 1985 probably correspond with the formation of a small amount of $Pd(CO)_2(PPh_3)_2$[8]. On gradually increasing the pressure to 500 atm over $2\frac{1}{2}$ h the 2074 and 2023 cm^{-1} absorptions increase significantly in intensity as that at 1880 cm^{-1} decreases. At 550 atm pressure complete conversion into the new species has occurred, the other bands observed initially at 2050 and 1985 cm^{-1} having disappeared By analogy with the behaviour of the trinuclear platinum cluster towards carbon monoxide and with the spectrum of $Ni(CO)_3PPh_3$ it seems likely that the 2074 and 2023 cm^{-1} absorptions are the A_1 and E vibrations respectively, expected for the molecule $Pd(CO)_3PPh_3$.

This system is considerably more sensitive to temperature than the $Pt(CO)_3$-PPh_3 system and on heating above room temperature, even at 550 atm pressure, the absorption bands decrease in intensity, presumably due to decomposition, without the appearance of any additional absorptions. As with the platinum system, on decreasing the pressure to atmospheric, $Pd(CO)_3PPh_3$ reverts to the trinuclear species, in this case $Pd_3(CO)_3(PPh_3)_3$.

EXPERIMENTAL

Details of the high pressure spectrophotometric cell have been described previously[11]. Infrared spectra were recorded on a Perkin Elmer Model 257 spectrophotometer using X10 scale expansion and calibration with either water vapour or gaseous carbon monoxide.

The complexes $Pt_3(CO)_3(PPh_3)_4$[9], $Pt(CO)_2(PPh_3)_2$[13] and $Pd_3(CO)_3(PPh_3)_3$[4,5] were prepared by published methods.

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