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# $\gamma$-Radiation Produced Supported Metal Complex Catalysts. Part VI*. The Preparation of *trans*-[RhCl(CO)$L_2$] where L = Unsaturated Tertiary Phosphine and the Exposure of Rhodium(I) Complexes to $\gamma$-Radiation

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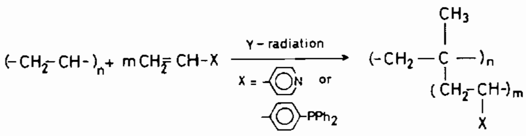
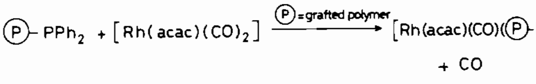
## Introduction

In previous parts of this series we have described ways in which polymer supported metal complex catalysts can be prepared using $\gamma$-radiation grafting [2–4]. Previously we have taken an unsaturated ligand, $\gamma$-radiation grafted it onto polypropylene as in reaction [2, 3], and then treated the resulting functionalised polymer with a metal complex as in reaction 1 [2, 4]. Clearly not all the functional groups introduced into the polymer react with the metal complex, and with a complex such as [Rh(acac)$(CO)_2$] there is a possibility of either one or two carbon monoxide ligands being displaced. As a consequence the resulting catalyst contains a number of species in addition to the ideal metal complex, [Rh(acac)(CO)(Ⓟ-$PPh_2$)] in the case of reaction 2.



(1)



(2)

An alternative route for preparing supported metal complex catalysts would be to synthesise the metal complex complete with olefinic side chain and then graft this on to the polymer support. In this way the nature of the supported catalyst should be clearly defined. This paper reports the synthesis and characterisation of a series of *trans*-[RhCl(CO)$L_2$] complexes in which L is an unsaturated phosphine. The results clearly show that the olefinic functional groups are not coordinated to the rhodium(I) and are therefore for $\gamma$-radiation grafting. The paper also examines the effect of $\gamma$-radiation on these complexes since $\gamma$-radiation grafting to a polymer would only bc possible if $\gamma$-radiation does not effect reaction or decomposition of the rhodium(I) complexes.

TABLE I. Analytical Data for *trans*-[RhCl(CO)$L_2$].

| L | Yield (%) | Microanalysis[a] | | | |
|---|---|---|---|---|---|
| | | C | H | P | Cl |
| $Ph_2PCH{=}CH_2$ | 82 | 59.0(58.95) | 4.4(4.4) | 10.6(10.5) | 6.2(6.0) |
| $Ph_2PCH_2CH{=}CH_2$ | 77 | 60.35(60.2) | 4.85(4.9) | 10.1(10.0) | 6.0(5.7) |
| $Ph_2P(CH_2)_2CH{=}CH_2$ | 81 | 61.0(61.3) | 5.2(5.3) | 9.8(9.6) | 5.6(5.5) |
| $Ph_2P(CH_2)_3CH{=}CH_2$ | 81 | 62.5(62.3) | 5.65(5.7) | 9.3(9.2) | 5.5(5.25) |
| $Ph_2PCH_2C(CH_3){=}CH_2$ | 81 | 61.1(61.3) | 5.4(5.3) | 9.6(9.6) | 5.7(5.5) |
| $Ph_2P(p\text{-}C_6H_4CH{=}CH_2)$ | 52 | 65.95(66.3) | 4.5(4.6) | 8.2(8.3) | 4.9(4.8) |
| $Ph_2P(p\text{-}C_6H_4CH_2CH{=}CH_2)$ | 90 | 66.7(67.0) | 4.9(5.0) | 8.3(8.0) | 4.75(5.0) |
| $Ph_2P(p\text{-}C_6H_4(CH_2)_2CH{=}CH_2)$ | 66 | 67.4(67.7) | 5.4(5.3) | 7.5(7.75) | 4.6(4.4) |
| $Ph_2P(p\text{-}C_6H_4CH_2C(CH_3){=}CH_2)$ | 49 | 67.8(67.6) | 5.5(5.3) | 8.0(7.75) | 4.4(4.4) |
| $Ph_2P(p\text{-}C_6H_4CH{=}CHCH_3)$ | 63 | 67.0(67.0) | 5.0(5.1) | 8.0(7.9) | 4.6(4.4) |

[a]Found (calculated).

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*Part V, reference 1.

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TABLE II. Spectroscopic Data for *trans*-[RhCl(CO)L$_2$].

| L | Infrared (cm$^{-1}$)[a] | | | $^1$H nmr[b] | | | Other | $^{31}$P nmr[c] | |
|---|---|---|---|---|---|---|---|---|---|
| | $\nu_{CO}$ | $\nu_{C=C}$ | $\nu_{Rh-Cl}$ | δ(Ar–H) | δ(–CH=C<) | δ(>C=CH$_2$) | | δ(ppm) | $^1J_{Rh-P}$ (Hz) |
| $Ph_2PCH{=}CH_2$ | 1950 | 1600 | 305 | 7.9–7.3[d] | 7.2–6.7[e] | 6.4–5.3[f] | – | 23.7[g] | 124.5 |
| $Ph_2PCH_2CH{=}CH_2$ | 1960 | 1635 | 310 | 8.0–7.0[d] | 6.5–5.9[e] | 5.1–4.8[f] | 3.7–3.4 (s, 2H, –CH$_2$–) | 25.8[g] | 123.5 |
| $Ph_2P(CH_2)_2CH{=}CH_2$ | 1955 | 1640 | 310 | 7.9–7.3[d] | 6.1–5.6[e] | 5.1–4.9[f] | 2.8–2.2 (m, 4H, (–CH$_2$–)$_2$) | 25.8[g] | 123.5 |
| $Ph_2P(CH_2)_3CH{=}CH_2$ | 1967 | 1642 | 312 | 7.9–7.3[d] | 6.0–5.5[e] | 5.1–4.8[f] | 2.7–1.5 (m, 6H, (–CH$_2$–)$_3$) | 25.8[g] | 122.1 |
| $Ph_2PCH_2C(CH_3){=}CH_2$ | 1970 | 1645 | 310 | 7.8–7.2[d] | – | 4.9–4.7[f] | 3.6–3.4 (m, 2J, –CH$_2$–)<br>1.9 (s, 3H, –CH$_3$) | 23.2[g] | 125.1 |
| $Ph_2P(p\text{-}C_6H_4CH{=}CH_2)$ | 1965 | 1630 | 312 | 8.0–6.9[h] | 6.6–6.2[e] | 5.6–4.9[f] | – | 39.9[g] | 126.5 |
| $Ph_2P(p\text{-}C_6H_4CH_2CH{=}CH_2)$ | 1965 | 1642 | 312 | 7.9–7.1[h] | 6.2–5.6[e] | 5.2–4.9[f] | 3.5–3.3 (brd, 2H, –CH$_2$–) | 29.7[g] | 126.5 |
| $Ph_2P(p\text{-}C_6H_4(CH_2)_2CH{=}CH_2)$ | 1970 | 1640 | 310 | 8.0–7.1[h] | 6.1–5.6[e] | 5.2–4.9[f] | 2.9–2.2 (m, 4H, (–CH–$_2$)$_2$ | 29.6[g] | 126.5 |
| $Ph_2P(p\text{-}C_6H_4CH_2C(CH_3){=}CH_2)$ | 1965 | 1645 | 315 | 7.9–7.1[h] | – | 4.8–4.6[i] | 3.3 (s, 2H, –CH$_2$–)<br>1.65 (s, 3H, –CH$_3$) | 28.5[g] | 126.5 |
| $Ph_2P(p\text{-}C_6H_4CH{=}CHCH_3)$ | 1965 | 1650 | 315 | 7.9–7.2[h] | 6.9–6.75[e] | – | 1.9 (brd, 3H, –CH$_3$) | 28.4[g] | 125.8 |

[a] Recorded as nujol mulls. [b] In CDCl$_3$ solution; δ in ppm relative to TMS = 0. [c] In CHCl$_3$ solution; δ in ppm relative to 85% $H_3PO_4$. [d] Multiplet, integrating as 10 protons. [e] Multiplet, integrating as 1 proton. [f] Multiplet, integrating as 2 protons. [g] Doublet. [h] Multiplet, integrating as 14 protons. [i] Broad multiplet, integrating as 2 protons.

## Experimental

*Trans*-[RhCl(CO)L$_2$], where L = unsaturated tertiary phosphine, were prepared from [RhCl(CO)$_2$]$_2$ and the unsaturated tertiary phosphine as described in the literature [5, 6]. Analytical, infrared, $^1$H and $^{31}$P nmr data are given in Tables I and II. The unsaturated phosphines and [Rh(acac)(CO)(p-CH$_2$=CHC$_6$H$_4$PPh$_2$)] were prepared as described previously [3, 4].

A saturated solution of [Rh(acac)(CO)(*p*-CH$_2$=CHC$_6$H$_4$PPh$_2$)] in C$_6$D$_6$ was γ-irradiated as described previously [2] at a dose rate of 200 krad h$^{-1}$. Samples were withdrawn after 3, 4.8 and 22.5 hours and their nmr spectra compared with those of an unirradiated sample. No difference was detectable between the irradiated and unirradiated samples. In addition no change occurred in the CO absorption region of the infrared spectrum indicating that no reaction had occurred. The same result was obtained when a 2.3 *M* solution of [RhH(CO)(PPh$_3$)$_3$] was irradiated for 43 hours at a dose rate of 300 krad h$^{-1}$ and when *trans*-[RhCl(CO)(Ph$_2$PCH=CH$_2$)$_2$] was irradiated in benzene solution to a total dose of 30 Mrad.

Microanalyses were performed by Elemental Microanalysis Ltd of Beaworthy in Devon. Infrared spectra were recorded on a Perkin Elmer model 577 spectrometer. $^1$H nmr spectra were recorded at 90 MHz on a Perkin Elmer R32 spectrometer, shifts being recorded relative to tetramethylsilane at δ = 0 ppm. $^{31}$P nmr spectra were recorded at 36.4 MHz on a Bruker WH 90 spectrometer; chemical shifts were measured relative to external 85% phosphoric acid using the convention that more positive shifts represent deshielding.

## Results and Discussion

The present complexes, prepared by reaction 3, are formulated as *trans*-square planar complexes

$$[RhCl(CO)_2]_2 + 4Ph_2P \sim\, =$$

$$= \rightarrow 2\,trans\text{-}[RhCl(CO)(Ph_2P \sim =)_2] + 2CO \quad (3)$$

in which the olefinic functional group is not coordinated. This suggestion is based on:

1. The observation of only one $^{31}$P chemical shift which is inconsistent with a *cis*-isomer.

2. $\nu_{CO}$ in the range 1950–1970 cm$^{-1}$ as observed for *trans*-[RhCl(CO)(PPh$_3$)$_2$] ($\nu_{CO}$ = 1965 cm$^{-1}$), as compared to the 1978 cm$^{-1}$ observed in *cis*-[RhCl(CO)(PPh$_3$)$_2$] [7].

3. $\nu_{C=C}$ lies between 1630 and 1650 cm$^{-1}$ for all the unsaturated phosphines except vinyldiphenylphosphine indicating a free double-bond. The $^1$H

nmr data are also indicative of uncoordinated double-bonds.

Although the photochemical behaviour of transition metal complexes has been studied extensively [8], there has been only a limited interest in the action of $\gamma$-radiation on metal complexes [9]. Accordingly it was difficult to predict whether $\gamma$-radiation, in the type of dose needed to effect grafting [2, 4], would result in decomposition or hompolymerisation of the rhodium(I) complexes *trans*-[RhCl(CO)(Ph$_2$P$\sim$=)]. In the event neither these complexes nor [Rh(acac)(CO)(*p*-CH$_2$=CHC$_6$H$_4$-PPh$_2$)] nor [RhH(CO)(PPh$_3$)$_3$] underwent any reaction at all on exposure to quite large doses of $\gamma$-radiation.

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## References

1 F. R. Hartley, S. G. Murray and P. N. Nicholson, *J. Organometal. Chem., 231,* 369 (1982).
2 F. R. Hartley, D. J. A. McCaffrey, S. G. Murray and P. N. Nicholson, *J. Organometal. Chem., 206,* 347 (1981).
3 F. R. Hartley, S. G. Murray and P. N. Nicholson, *J. Polymer Sci., Polym. Chem. Ed.,* in press.
4 F. R. Hartley, S. G. Murray and P. N. Nicholson, *J. Mol. Cat.,* in press.
5 J. A. McCleverty and G. Wilkinson, *Inorg. Synth., 8,* 214 (1966).
6 L. D. Rollman, *Inorg. Chim. Acta, 6,* 137 (1972).
7 J. Blum, E. Oppenheimer and E. D. Bergmann, *J. Am. Chem. Soc., 89,* 2338 (1967).
8 G. L. Geoffroy and M. S. Wrighton, 'Organometallic Photochemistry', Academic Press, 1979.
9 R. Blackburn and A. Kabi, *Radiation Res. Rev., 2,* 103 (1969).