*Journal of Organometallic Chemistry*, 303 (1986) 221–231
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# FIVE- AND SIX-COORDINATE HYDRIDO(CARBONYL)-RUTHENIUM(II) AND -OSMIUM(II) COMPLEXES CONTAINING TRIISOPROPYLPHOSPHINE AS LIGAND

M.A. ESTERUELAS and H. WERNER*

*Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg (F.R.G.)*

(Received September 30th, 1985)

## Summary

The five-coordinate hydrido(carbonyl) complexes $MHCl(CO)(PPr^i_3)_2$ (I, M = Ru; II, M = Os) have been prepared in excellent yields from $MCl_3 \cdot aq$ and $PPr^i_3$ in methanol. They react with ligands L such as $P(OMe)_3$, $PMe_3$, CO, and olefins $CH_2{=}CHR$ (R = H, $CO_2Me$, CN, COMe) to produce the six-coordinate compounds $MHCl(CO)(PPr^i_3)_2L$ (III–VI, VIII–XIII). Displacement of the chloride ligand in I,II by acetate or acetylacetonate also leads to the six-coordinate complexes $MH(\eta^2\text{-}O_2CMe)(CO)(PPr^i_3)_2$ (XVI, XVII) and $MH(\eta^2\text{-acac})(CO)(PPr^i_3)_2$ (XVIII, XIX), respectively. The synthesis of the dichloro complexes *trans*-$OsCl_2[P(OPh)_3]_4$ (XXI) and *trans-mer*-$RuCl_2(PMe_3)_3P(OPh)_3$ (XXII) is also described.

## Introduction

The ruthenium(II) and osmium(II) complexes of trialkylphosphines are generally six-coordinate 18-electron species of the type $MX_2L_4$. Triarylphosphines, on the other hand, often form five-coordinate 16-electron complexes, $MX_2L_3$, which are catalytically active in hydrogenation reactions [1]. Reactive 16-electron species $[ML_4]$ containing ruthenium or osmium in the oxidation state zero are also known. They are formed as intermediates on reduction of the 18-electron complexes $MX_2L_4$ and can react, as was first observed by Chatt and Davidson in 1965 [2], with aromatic hydrocarbons by oxidative addition. We recently showed that this reactivity, however, depends critically on the electronic and steric properties of the ligands L coordinated to the metal. Whereas the homoleptic fragment $[Ru(PMe_3)_4]$ generated by reduction of *trans*-$RuCl_2(PMe_3)_4$ with Na/Hg in benzene undergoes intramolecular C–H activation to give $RuH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$ [3], the corresponding mixed complex *all,trans*-$RuCl_2(PMe_3)_2[P(OMe)_3]_2$ reacts under the same conditions by intermolecular addition of benzene to form $RuH(C_6H_5)(PMe_3)_2[P(OMe)_3]_2$ [4]. We also showed during investigations of the reactivity of

0022-328X/86/$03.50 

areneosmium(0) complexes that even a small change in the coordination sphere of the metal can direct the course of the reaction towards either intra- or intermolecular C–H activation [5].

The need to understand the way in which the properties of L and the presence or absence of other ligands influence the reactivity of the metal prompted us to extend our studies to triisopropylphosphine-ruthenium and -osmium derivatives. It was already known from earlier work in our group that areneruthenium compounds of the type $(ArH)RuH_2(PPr^i_3)$ react under UV irradiation in hydrocarbon solvents to give either $(ArH)RuH(\eta^2\text{-}CH_2CHMePPr^i_2)$ or $(ArH)RuH(R)(PPr^i_3)$ by intra- or intermolecular oxidative addition [6,7]. The present paper describes the synthesis of novel triisopropylphosphine-ruthenium(II) and -osmium(II) complexes, and shows that stable 16-electron as well as 18-electron compounds can be obtained.

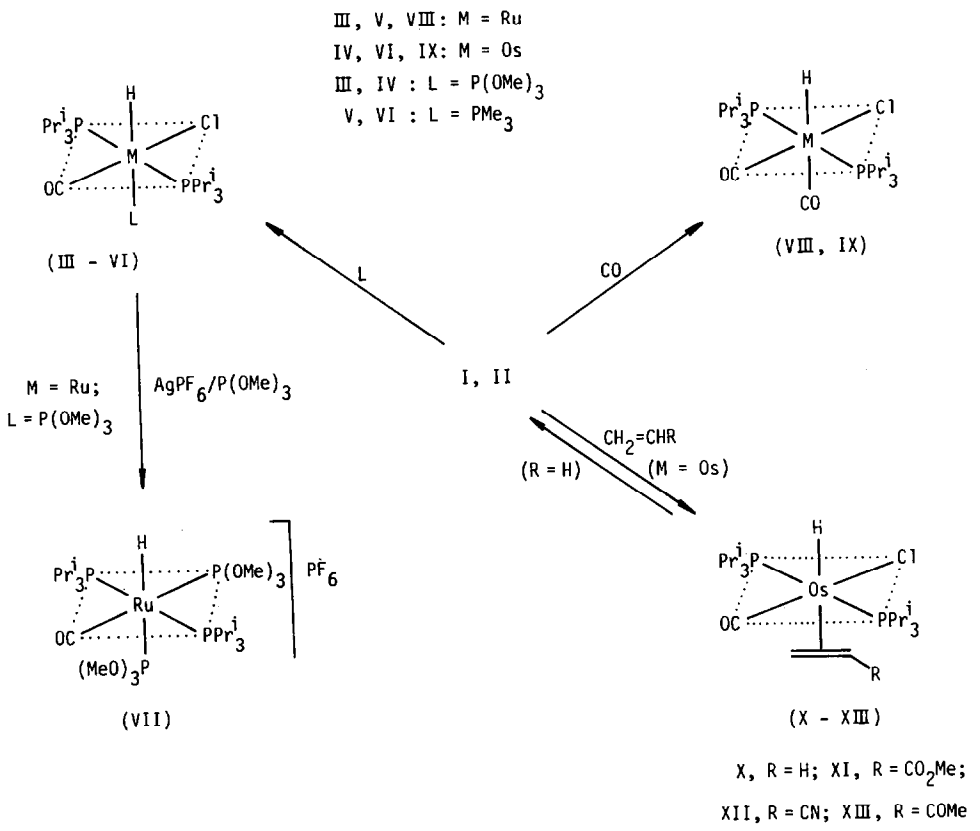
**Results and discussion**

The route which has most frequently been used to prepare phosphine-ruthenium(II) and -osmium(II) derivatives is ligand displacement, using, for example, $RuCl_2(PPh_3)_3$ or $OsCl_2(PPh_3)_3$ as starting materials. These compounds also react with $PMe_3$ to give $RuCl_2(PMe_3)_4$ [3b,8,9] and $OsCl_2(PMe_3)_4$ [10,11], respectively.

$RuCl_2(PPh_3)_3$ and $OsCl_2(PPh_3)_3$ are, however, surprisingly inert towards triisopropylphosphine. Under various conditions used for the synthesis of $MCl_2L_4$ or $MCl_2L_{4-n}L'_n$ [4,12,13] no reaction occurs. An alternative method for the synthesis of $MCl_2(PR_3)_n$ compounds (M = Ru, Os), namely the interaction of $MCl_3 \cdot aq$ with $PR_3$ [14,15], fails for $R = Pr^i$ in hexane or benzene but in methanol gives $RuHCl(CO)(PPr^i_3)_2$ (I) and $OsHCl(CO)(PPr^i_3)_2$ (II) in 70 and 96% yield, respectively. We assume that during the reaction methanol is dehydrogenated by the metal trichlorides to give formaldehyde [16], which is probably the source of the carbonyl ligand. There are precedents for such a process in that Moers [17] and Shaw [18] have shown that $RuCl_3 \cdot aq$ and $K_2OsCl_4$ react with bulky phosphines such as $PCy_3$, $PMeBu^t_2$ and $PEtBu^t_2$ in 2-methoxyethanol to form carbonyl(chloro)hydrido complexes $MHCl(CO)(PR_3)_2$.

$$MCl_3 \cdot aq + n\,PPr^i_3 \xrightarrow{MeOH} \underset{\text{(I, M = Ru; II, M = Os)}}{\text{H, } Pr^i_3P, \text{ M, Cl, OC, } PPr^i_3} \qquad (1)$$

Complex I forms yellow and complex II red, moderately air-stable crystals which are soluble in most organic solvents except saturated hydrocarbons such as pentane and hexane. Although both compounds are coordinatively unsaturated, they are monomeric in benzene and, in terms of their coordination number, resemble the well-known five-coordinate triarylphosphine complexes $MCl_2(PR_3)_3$ [1]. Regarding the structure of I and II proposed in eq. 1 we note that a similar compound of composition $RhHCl_2(PPr^nBu^t_2)_2$ also containing one hydride and two bulky phosphine ligands, has been shown by X-ray structure analysis to be square-pyramidal [19]. It appears that in this case as well as for I and II, dimerisation via Cl bridges, which would provide an 18-electron configuration at the metal, is hindered for steric reasons.




SCHEME 1

The coordination number six for ruthenium and osmium can be achieved, however, by addition of ligands such as $PMe_3$, $P(OMe)_3$ or CO to the metal centers of I and II, respectively (see Scheme 1). Shaw [18] and Moers [17,20] have previously shown that the complexes $RuHCl(CO)(PR_3)_2$ ($PR_3 = PCy_3$, $PMeBu^t_2$, $PEtBu^t_2$) and $OsHCl(CO)(PCy_3)_2$ also react with CO to form the corresponding octahedral dicarbonyl compounds. There is, however, no precedent for the addition of another phosphine or a phosphite ligand to the metal in these five-coordinate carbonyl(hydrido) complexes.

In contrast to the osmium compound VI, the analogous ruthenium derivative V is unstable in solution and, as shown in eq. 2, reacts to produce a mixture of I, XIV and $PPr^i_3$. The reaction, which can be easily monitored by IR or NMR spectroscopy in benzene solution, probably starts by ligand migration to produce XIV and XV, and the latter, owing to steric crowding, dissociates to give I and triisopropylphosphine. The process can be reversed by addition of $PPr^i_3$. The most characteristic change in the spectroscopic data on going from I, II to III–VI and VIII–XIV is the significant downfield shift of the hydride signal in the $^1H$ NMR spectra, which is observed at $-24.20$ and $-31.92$ ppm for I and II, but at about $-4$ to $-7$ ppm for the octahedral complexes (for complete list of data see Table 1). The ruthenium compound III reacts with $AgPF_6$ in the presence of trimethylphosphite to form the

*(Continued on p. 226)*

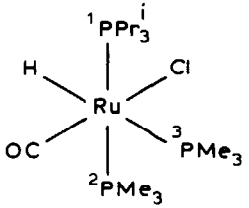
TABLE 1

$^1H$ AND $^{31}P$ NMR DATA FOR COMPLEXES I–VI, VIII–XIV, XVI–XIX IN $C_6D_6$ AT 25°C ($^1H$: $\delta$ in ppm, TMS int.; $^{31}P$: $\delta$ in ppm, 85% $H_3PO_4$ ext.; $J$ and $N$ in Hz)

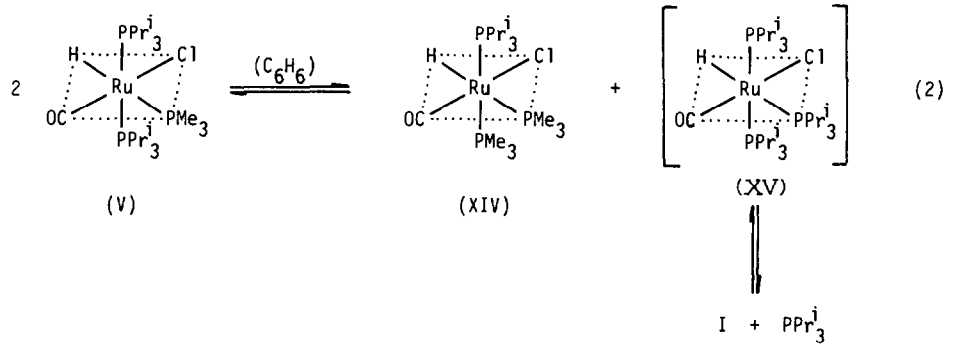
| Complex | $^1H$ | | | | | | | | | $^{31}P$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\delta(PCHCH_3)$ [a] | $J(HH)$ | $N$ | $\delta(PCH)$ | $\delta(L/X)$ | | $\delta(MH)$ | $J(^1PH)$ [b] | $J(^2PH)$ [b] | $\delta(^1P)$ [b] | $\delta(^2P)$ [b] | $J(PP)$ |
| I | 1.38; 1.31 | 7.0 | 13.0 | 2.63(m) | | | −24.20(t) | 20 | | 56.61(s) | | |
| II | 1.27; 1.20 | 6.5 | 14.0 | 2.83(m) | | | −31.92(t) | 14 | | 47.34(s) | | |
| III | 1.47; 1.40 | 7.0 | 13.0 | 2.87(m) | 3.64(d) [c] | $[P(OMe)_3]$ | −6.80(dt) | 25 | 195 | 52.16(d) | 133.12(t) | 24 |
| IV | 1.48; 1.45 | 6.5 | 13.5 | 2.88(m) | 3.63(d) [c] | $[P(OMe)_3]$ | −6.73(dt) | 25 | 152 | 19.77(d) | 102.24(t) | 18 |
| V | 1.39; 1.35 | 6.5 | 11.5 | 2.50(m) | 1.43(d) [d] | $[PMe_3]$ | −7.27(dt) | 25 | 112 | 51.61(d) | −36.22(t) | 16 |
| VI | 1.31; 1.30 | 7.0 | 12.5 | 2.57(m) | 1.50(d) [d] | $[PMe_3]$ | −7.45(dt) | 25 | 87 | 17.87(d) | −56.98(t) | 13 |
| VIII | 1.35 [e] | | | 2.60(m) | | | −5.15(t) | 20 | | 58.57(s) | | |
| IX | 1.35 [f] | | | 2.65(m) | | | −4.70(t) | 20 | | 27.82(s) | | |
| X | 1.38; 1.32 | 7.0 | 13.5 | 2.78(m) | 5.19(br) | $[C_2H_4]$ | −4.48(t) | 27 | | | | |
| XI | 1.25 [g] | | | 2.92(m) | 3.82(br) | $[C_2H_3]$ | −4.42(t) | 29 | | [h] | | |
| | | | | | 3.62(s) | $[CO_2Me]$ | | | | | | |
| XII [i] | 1.32 [g] | | | 2.65(m) | [j] | | −3.81(t) | 28 | | 23.12(s) | | |
| XIII | 1.31 [g] | | | 2.98(m) | 4.10(m) | $[C_2H_3]$ | −4.25(t) | 26 | | 10.33(s) | | |
| | | | | | 2.13(s) | [COMe] | | | | | | |
| XIV | [k] | | | [k] | [k] | | −7.02(ddd) [l] | | | 57.78(dd) | −4.97(dd) [m] | |
| | | | | | | | | | | | −24.67(dd) [n] | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| XVI | 1.32; 1.28 | 6.5 | 13.5 | 2.25(m) | 1.87(s) | [OAc] | −16.42(t) | 20 | 56.33(s) |
| XVII | 1.35; 1.27 | 6.5 | 13.0 | 2.42(m) | 1.88(s) | [OAc] | −20.25(t) | 16 | 37.99(s) |
| XVIII | 1.40; 1.28 | 7.0 | 12.5 | 2.30(m) | 5.28(s) | [CH] | −15.08(t) | 20 | 54.45(s) |
| | | | | | 1.90(s) | [$CH_3$] | | | |
| | | | | | 1.77(s) | [$CH_3$] | | | |
| XIX | 1.31; 1.22 | 7.0 | 12.5 | 2.28(m) | 5.12(s) | [CH] | −17.20(t) | 17.5 | 34.56(s) |
| | | | | | 1.69(s) | [$CH_3$] | | | |
| | | | | | 1.55(s) | [$CH_3$] | | | |

[a] All the signals from the diastereotopic $CH_3$ groups of the $PPr^i_3$ ligands are doublets of virtual triplets, except those for complexes VIII, IX, XI–XIV. [b] $^1P$ corresponds to the $^{31}P$ nucleus of $PPr^i_3$, and $^2P$ to the $^{31}P$ nucleus of $PMe_3$ and $P(OMe)_3$, respectively. [c] $J(PH)$ 10.0 Hz. [d] $J(PH)$ 7.0 Hz. [e] Doublet of doublets, $J(HH)$ 6.0, $J(PH)$ 12.0 Hz. [f] Doublet of doublets, $J(HH)$ 7.0, $J(PH)$ 14.0 Hz. [g] Complex pattern owing to overlap of the signals of the non-equivalent $PCHCH_3$. [h] Two lines (AB pattern) at $\delta$ 10.86 and 10.70 ppm. [i] In $C_6D_6/CH_2Cl_2$. [j] Signal of $C_2H_3$ protons not exactly located. [k] Signal overlaps with corresponding signals of I and $PPr^i_3$. [l] $J(^1PH) = J(^2PH)$ 25 Hz, $J(^3PH)$ 120 Hz; for relation see structure below. [m] Signal corresponding to $^2P$; $J(^1P^2P)$ 272, $J(^1P^3P)$ 21 Hz. [n] Signal corresponding to $^3P$; $J(^1P^3P) = J(^2P^3P)$ 21 Hz.

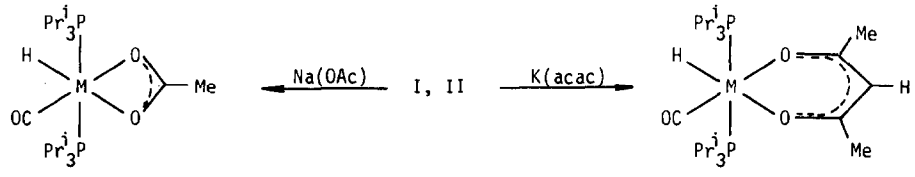


ionic product VII, in which the two phosphine ligands are *trans* and the two phosphite ligands *cis* to each other (Scheme 1).




There is a marked difference in reactivity between I and II towards olefins. Whereas the osmium compound reacts with ethylene, methylacrylate, acrylonitrile and methyl vinyl ketone in hexane at room temperature to give the six-coordinate complexes X–XIII in 70–95% yield, the ruthenium analogue is completely inert under the same conditions. The reaction between II and $C_2H_4$ is completely reversible, and therefore complex X has to be prepared, and preferably stored, under an ethylene atmosphere. As expected, electron-withdrawing substituents such as CN, COMe and $CO_2Me$ stabilize the olefin-to-metal bond. The compounds X–XIII do not react by intramolecular insertion of the olefinic ligand into the Os–H bond to form the corresponding alkyl complexes, probably owing to the *trans* position of these ligands. The olefin(hydrido)osmium complexes seem to be stable even at higher temperatures, because XIII is recovered unchanged after its solution in benzene is kept at 70°C for one day. There is no reaction between II and diolefins such as cyclohexa-1,3-diene or cycloocta-1,5-diene even when the substrates are stirred together in hexane solution for 2 d.

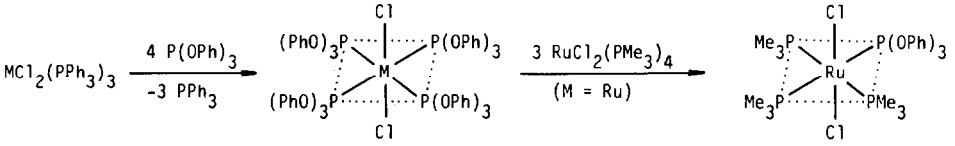
With I and II as starting materials, octahedral six-coordinate complexes can not only be obtained by addition of ligands L (Scheme 1) but also by displacement of chloride by acetate and acetylacetonate anions. The corresponding hydrido(acetate) and hydrido(acetylacetonate) compounds XVI–XIX (see eq. 3), which are air-stable microcrystalline solids, are isolated in good to excellent yields. The IR spectra indicate that the OAc and acac groups are coordinated via both oxygen atoms, i.e., as chelating ligands. The observation of two stretching frequencies at ca. 1525 and 1445 $cm^{-1}$ (for XVI, XVII) and 1585 and 1500 $cm^{-1}$ (for XVIII, XIX) is in accord with this structural proposal [21,22]. The triphenylphosphine complexes MH(acac)-$(CO)(PPh_3)_2$ (M = Ru, Os) analogous to XVIII and XIX have already been prepared by similar routes [23].




(XVI, M = Ru;
XVII, M = Os)

(XVIII, M = Ru;
XIX, M = Os)

Attempts to use the new triisopropylphosphine-ruthenium(II) and -osmium(II) compounds $MHCl(CO)(PPr^i_3)_2L$ (L = CO, $PMe_3$, $P(OMe)_3$) as precursors for the synthesis of corresponding 16-electron species $[M(CO)(PPr^i_3)_2L]$, which might possibly be able to induce C–H activation, have so far been unsuccessful. Similar experiments using the tetrakis(triphenylphosphite) complexes XX and XXI (not included in our previous studies [4]) also failed. The ruthenium compound XX reacts with *trans*-$RuCl_2(PMe_3)_4$ in the molar ratio 1/3 by ligand exchange to form $RuCl_2(PMe_3)_3P(OPh)_3$ (XXII), which is another member of the $MCl_2L_{4-n}L'_n$ series. The osmium complex XXI is completely inert towards $OsCl_2(PMe_3)_4$ under the same conditions.




(XX, M = Ru [12]; XXI, M = Os)

(XXII)

## Experimental

All reactions were carried out under $N_2$ and in dried, $N_2$-saturated solvents. NMR spectra were recorded on a Varian EM 360, a Bruker Cryospec WM 400 ($^1H$) and a Bruker WH-90 FT ($^{31}P$), IR spectra on a Perkin–Elmer 457 and mass spectra on a Varian MAT CH 7. The starting materials $RuCl_2(PPh_3)_3$ [14], $OsCl_2(PPh_3)_3$ [15], *trans*-$RuCl_2(PMe_3)_4$ [8,9] and *trans*-$RuCl_2[P(OPh)_3]_4$ (XX) [12] were prepared by published methods. $RuCl_3 \cdot aq$ and $OsCl_3 \cdot aq$ were commercial products.

*Preparation of $RuHCl(CO)(PPr^i_3)_2$ (I)*

A solution of 2.0 g (7.65 mmol) $RuCl_3 \cdot aq$ in 75 ml methanol was treated with 6 ml (35.0 mmol) $PPr^i_3$ and the mixture was heated for 24 h under reflux. The resulting yellow precipitate was filtered off, washed with methanol and diethyl ether, and dried in vacuo. Yield 2.15 g (70%). IR ($C_6H_6$): $\nu$(CO) 1910 $cm^{-1}$, $\nu$(RuH) not observed. Found: C, 57.79; H, 3.89; mol.-wt. 486 (MS), 462 (osmometric in $C_6H_6$). $C_{19}H_{43}ClOP_2Ru$ calcd.: C, 57.57; H, 4.02%; mol.-wt. 486.02.

*Preparation of $OsHCl(CO)(PPr^i_3)_2$ (II)*

The procedure described for I, but starting with 2.0 g (5.70 mmol) $OsCl_3 \cdot aq$. gave red crystals. Yield 3.1 g (96%). IR ($C_6H_6$): $\nu$(CO) 1886 $cm^{-1}$, $\nu$(OsH) not observed. Found: C, 39.61; H, 7.98; mol-wt. 575 (MS), 526 (osmometric in $C_6H_6$). $C_{19}H_{43}ClOOsP_2$ calcd.: C, 39.68; H, 7.55%; mol.-wt. 575.15.

*Preparation of $RuHCl(CO)(PPr^i_3)_2P(OMe)_3$ (III)*

A suspension of 100 mg (0.21 mmol) I in 50 ml hexane was treated with 49.7 µl (0.32 mmol) $P(OMe)_3$ and the mixture was stirred for 15 min at room temperature then filtered. The colourless filtrate was concentrated in vacuo until a white precipitate separated. The solid was filtered off, washed with cold pentane, and dried in vacuo. Yield 90 mg (72%). IR ($C_6H_6$): $\nu$(CO) 1920, $\nu$(RuH) 1985 $cm^{-1}$. MS (70

eV): *m/e* 486 ($M^+ - P(OMe)_3$), 450 ($M^+ - PPr^i_3$), 124 ($P(OMe)_3^+$). Found: C, 43.44; H, 8.94. $C_{22}H_{52}ClO_4P_3Ru$ calcd.: C, 43.31; H, 8.59%.

*Preparation of $OsHCl(CO)(PPr^i_3)_2P(OMe)_3$ (IV)*

The procedure as described for III, but starting with 175.6 mg (0.31 mmol) II and 75.7 μl (0.64 mmol) $PPr^i_3$, gave a white microcrystalline solid. Yield 146 mg (68%). IR ($C_6H_6$): ν(CO) 1900, ν(OsH) 2045 $cm^{-1}$. Found: C, 37.63; H, 7.64; mol.-wt. 699 (MS). $C_{22}H_{52}ClO_4OsP_3$ calcd.: C, 37.79; H, 7.49%; mol.-wt. 699.22.

*Preparation of $RuHCl(CO)(PPr^i_3)_2PMe_3$ (V)*

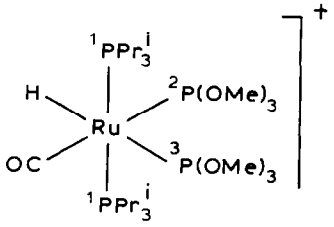
A suspension of 100 mg (0.21 mmol) I in 50 ml hexane was treated with 32 μl (0.42 mmol) $PMe_3$ and the mixture was stirred for 15 min at room temperature then filtered. The yellow filtrate was treated with excess $PPr^i_3$ (ca. 0.5 ml) and concentrated in vacuo until a white precipitate separated. The solid was filtered off, washed with methanol and ether, and dried in vacuo. Yield 72 mg (62%). Found: C, 46.78; H, 9.37. $C_{22}H_{52}ClOP_3Ru$ calcd.: C, 47.01; H, 9.32%.

*Preparation of $OsHCl(CO)(PPr^i_3)_2PMe_3$ (VI)*

The procedure described for III, but starting with 156.6 mg (0.27 mmol) II and 44 μl (0.58 mmol) $PMe_3$, gave a white microcrystalline solid. Yield 138 mg (78%). IR ($C_6H_6$): ν(CO) 1892, ν(OsH) 2080 $cm^{-1}$. Found: C, 41.00; H, 8.68; mol.-wt. 610 (osmometric in $C_6H_6$). $C_{22}H_{52}ClOOsP_3$ calcd.: C, 40.57; H, 8.05%; mol.-wt. 651.22.

*Preparation of $[RuH(CO)(PPr^i_3)_2(P(OMe)_3)_2]PF_6$ (VII)*

A suspension of 433 mg (0.71 mmol) III in 20 ml methanol was treated with 180 mg (0.71 mmol) $AgPF_6$ and 85 μl (0.71 mmol) $P(OMe)_3$ and the mixture was stirred for 30 min. The precipitated AgCl was removed by filtration through Kieselguhr, and the colourless filtrate concentrated in vacuo. Addition of ether gave a colourless precipitate, which was filtered off and recrystallized from acetone/ether. Yield 389 mg (65%). IR ($CH_2Cl_2$): ν(CO) and ν(RuH) 1975 and 1980 $cm^{-1}$. Found: C, 34.90; H, 7.47. $C_{25}H_{61}F_6O_7P_5Ru$ calcd.: C, 35.59; H, 7.29%. $^1$H-NMR (acetone-$d_6$): δ 3.90(d); *J*(PH) 10 Hz, $P(OMe)_3$; 3.80(d), *J*(PH) 10 Hz, $P(OMe)_3$; 2.42(m), PC*H*; 1.37(dvt), *J*(HH) 7 Hz, *N* 13 Hz, $PCHCH_3$; 1.34(dvt), *J*(HH) 7 Hz, *N* 14 Hz, $PCHCH_3$; −9.50(ddt), $J(^1PH)$ 25, $J(^2PH)$ 20, $J(^3PH)$ 120 Hz, RuH. $^{31}$P-NMR (acetone-$d_6$): δ 47.00(dd), $^1$P; 137.45(dt), $^3$P; 132.62(dt), $^2$P; $J(^1P^2P)$ 22, $J(^1P^3P)$ 41, $J(^2P^3P)$ 60 Hz; for relation see structure below.




*Preparation of $RuHCl(CO)_2(PPr^i_3)_2$ (VIII)*

Carbon monoxide was bubbled through a suspension of 100 mg (0.21 mmol) I in 10 ml hexane for 10 min at room temperature. The resulting white precipitate was

filtered off and repeatedly extracted with hexane (ca. 50 ml). The combined initial filtrate and the hexane washings were concentrated in vacuo until a white solid separated. This was filtered off, washed with pentane, and dried in vacuo. Yield 63 mg (60%). IR ($C_6H_6$): $\nu$(CO) 1905, 1970 $cm^{-1}$; $\nu$(RuH) 2030 $cm^{-1}$. Found: C, 46.73; H, 8.43; mol-wt. 514 (MS). $C_{20}H_{43}ClO_2P_2Ru$ calcd.: C, 46.31; H, 8.72%; mol.-wt. 514.03.

*Preparation of $OsHCl(CO)_2(PPr^i_3)_2$ (IX)*

The procedure described for VIII, but starting with 156 mg (0.26 mmol) II gave a white microcrystalline solid. Yield 108 mg (68%). IR ($C_6H_6$): $\nu$(CO) 1920, 1950; $\nu$(OsH) 2020 $cm^{-1}$. Found: C, 40.30; H, 7.77; mol.-wt. 603 (MS). $C_{20}H_{43}ClO_2OsP_2$ calcd.: C, 40.59; H, 7.54%; mol.wt. 603.16.

*Preparation of $OsHCl(CO)(C_2H_4)(PPr^i_3)_2$ (X)*

Ethene was bubbled through a suspension of 212 mg (0.37 mmol) II in 25 ml hexane until the solution became colourless and a white solid separated. This was filtered off, washed with pentane, and dried in an ethene atmosphere. Yield 155 mg (70%). IR ($C_6H_6$): $\nu$(CO) 1900; $\nu$(OsH) 2110 $cm^{-1}$. Found: C, 41.24; H, 7.95. $C_{21}H_{47}ClOOsP_2$ calcd.: C, 41.81; H, 7.69%.

*Preparation of $OsHCl(CO)(CH_2{=}CHCO_2Me)(PPr^i_3)_2$ (XI)*

A suspension of 415.7 mg (0.72 mmol) II in 50 ml hexane was treated with 69 $\mu$l (0.76 mmol) methyl acrylate and the mixture was stirred for 15 min at room temperature then filtered. The colourless filtrate was concentrated in vacuo until a white solid separated. This was filtered off, repeatedly washed with pentane, and dried in vacuo. Yield 344 mg (72%). IR ($C_6H_6$): $\nu$(CO) 1920, 1695; $\nu$(OsH) 2100 $cm^{-1}$. MS (70 eV): *m/e* 576 ($M^+ - CH_2CHCO_2Me$), 86 ($CH_2CHCO_2Me^+$). Found: C, 41.92; H, 8.09. $C_{23}H_{49}ClO_3OsP_2$ calcd.: C, 41.78; H, 7.62%.

*Preparation of $OsHCl(CO)(CH_2{=}CHCN)(PPr^i_3)_2$ (XII)*

A suspension of 407 mg (0.71 mmol) II in 10 ml hexane was treated with 49 $\mu$l (0.74 mmol) acrylonitrile and the mixture was stirred for 15 min at room temperature. The yellow solid formed was filtered off, repeatedly washed with pentane, and dried in vacuo. Yield 422 mg (95%). IR ($C_6H_6$): $\nu$(CO) 1875; $\nu$(CN) 1925; $\nu$(OsH) 2210 $cm^{-1}$. Found: C, 42.38; H, 8.01; N, 2.29. $C_{22}H_{46}ClNOOsP_2$ calcd.: C, 42.06; H, 7.38; N, 2.22%.

*Preparation of $OsHCl(CO)(CH_2{=}CHCOMe)(PPr^i_3)_2$ (XIII)*

The procedure described for XI, but starting with 110 mg (0.19 mmol) II, gave a yellow microcrystalline solid. Yield 94 mg (76%). IR ($C_6H_6$): $\nu$(CO) 1910 $cm^{-1}$; $\nu$(OsH) not observed. Found: C, 42.52; H, 7.76. $C_{23}H_{49}ClO_2OsP_2$ calcd.: C, 42.81; H, 7.65%.

*Preparation of $RuH(\eta^2\text{-}O_2CMe)(CO)(PPr^i_3)_2$ (XVI)*

A suspension of 358.2 mg (0.74 mmol) I in 20 ml methanol was treated with a solution of 60.7 mg (0.74 mmol) sodium acetate in 5 ml methanol. After 1 h stirring at room temperature the solvent was removed and the solid residue extracted with 25 ml benzene. The benzene solution was filtered, and the yellow filtrate concentrated

in vacuo to ca. 0.5 ml. After slow addition of 10 ml methanol a yellow precipitate separated, and this was filtered off, repeatedly washed with methanol, and dried in vacuo. Yield 282 mg (75%). IR ($C_6H_6$): $\nu$(CO) 1895; $\nu$(RuH) 2030, $\nu(CO_2Me)$ 1525, 1445 $cm^{-1}$. Found: C, 49.51; H, 9.33; mol.-wt. 480 (osmometric in $C_6H_6$). $C_{21}H_{46}O_3P_2Ru$ calcd.: C, 49.49; H, 9.10%; mol.-wt. 509.62.

*Preparation of $OsH(\eta^2\text{-}O_2CMe)(CO)(PPr^i_3)_2$ (XVII)*

The procedure described for XVI, but starting with 342.7 mg (0.6 mmol) II and 80 mg (0.9 mmol) sodium acetate gave a white microcrystalline solid. Yield 150 mg (42%). IR ($C_6H_6$): $\nu$(CO) 1875; $\nu$(OsH) 2130; $\nu(CO_2Me)$ 1530, 1445 $cm^{-1}$. Found: C, 41.90; H, 7.76; mol.-wt. 556 (osmometric in $C_6H_6$). $C_{21}H_{46}O_3OsP_2$ calcd.: C, 42.12; H, 7.74%; mol.-wt. 598.75.

*Preparation of $RuH(acac)(CO)(PPr^i_3)_2$ (XVIII)*

A solution of 21.7 mg (0.38 mmol) KOH in 4 ml methanol was treated with 186.7 mg (0.38 mmol) I and then with 39.2 $\mu$l (0.38 mmol) pentane-2,4-dione. After 30 min stirring at room temperature the solvent was removed, and the solid residue extracted with 10 ml benzene. The benzene solution was worked up as described for XVI to give a yellow microcrystalline solid. Yield 169 mg (80%). IR ($C_6H_6$): $\nu$(CO) 1890; $\nu$(RuH) 2040; $\nu$(acac) 1590, 1500 $cm^{-1}$. Found: C, 52.80; H, 9.42; mol.-wt. 532 (osmometric in $C_6H_6$). $C_{24}H_{50}O_3P_2Ru$ calcd.: C, 52.44; H, 9.17%; mol.-wt. 549.68.

*Preparation of $OsH(acac)(CO)(PPr^i_3)_2$ (XIX)*

The procedure described for XVIII, but starting with 290 mg (0.5 mmol) II and stoichiometric amounts of KOH and pentane-2,4-dione, gave a yellow microcrystalline solid. Yield 284 mg (88%). IR ($C_6H_6$): $\nu$(CO) 1870; $\nu$(OsH) 2100; $\nu$(acac) 1580, 1500 $cm^{-1}$. Found: C, 45.26; H, 8.18; mol.-wt. 639 (MS). $C_{24}H_{50}O_3OsP_2$ calcd.: C, 45.12; H, 7.89%; mol.-wt. 638.81.

*Preparation of $trans\text{-}OsCl_2[P(OPh)_3]_4$ (XXI)*

A suspension of 100 mg (0.1 mmol) $OsCl_2(PPh_3)_3$ in 10 ml hexane was treated with an excess (ca. 0.5 ml) $P(OPh)_3$ and the mixture was stirred for 3 h at room temperature. The resulting white precipitate was filtered off, washed with hexane, and dried in vacuo. Yield 84 mg (58%). Found: C, 57.79; H, 3.89; mol.-wt. 1502 (MS). $C_{72}H_{60}Cl_2O_{12}OsP_4$ calcd.: C, 57.57; H, 4.02%; mol.-wt. 1502.27.

*Preparation of $trans,mer\text{-}RuCl_2(PMe_3)_3P(OPh)_3$ (XXII)*

A solution of 141.3 mg (0.1 mmol) XX in 5 ml benzene was treated with a solution of 142.9 mg (0.3 mmol) $RuCl_2(PMe_3)_4$ in 5 ml benzene and the mixture was stirred for 1 h at room temperature. The solution was then concentrated in vacuo to ca. 0.5 ml and hexane (ca. 3 ml) was added. The yellow precipitate formed was filtered off and recrystallized from benzene/hexane. Yield 288 mg (89%). The crystals contain 1/2 mol of $C_6H_6$ per mol of XXII. Found: C, 48.07; H, 6.28. $C_{30}H_{45}Cl_2O_3P_4Ru$ calcd.: C, 48.07; H, 6.05%.

**Acknowledgements**

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and the Spanish Ministry of Education for a

scholarship (to M.A.E.). We also thank Mrs. U. Neumann for the elemental analyses, Mrs. Dr. G. Lange for the mass spectra, Dr. W. Buchner and Mr. C.P. Kneis for NMR spectra, and the DEGUSSA company for gifts of chemicals.

## References

1 (a) M.A. Bennett and T.W. Matheson in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon Press, Oxford, 1982, p. 931; (b) F.M. Jardine, Prog. Inorg. Chem., 31 (1984) 265.
2 J. Chatt and J.M. Davidson, J. Chem. Soc., (1965) 843.
3 (a) H. Werner and R. Werner, J. Organomet. Chem., 209 (1981) C60; (b) J. Gotzig, R. Werner and H. Werner, J. Organomet. Chem., 290 (1985) 99.
4 H. Werner and J. Gotzig, J. Organomet. Chem., 284 (1985) 73.
5 (a) R. Werner and H. Werner, Angew. Chem., 93 (1981) 826; Angew. Chem. Int. Ed. Engl., 20 (1981) 793; (b) H. Werner and K. Zenkert, J. Chem. Soc., Chem. Commun., (1985) 1607.
6 H. Kletzin and H. Werner, Angew. Chem., 95 (1983) 916; Angew. Chem. Int. Ed. Engl., 22 (1983) 873.
7 H. Werner, Angew. Chem., 95 (1983) 932; Angew. Chem. Int. Ed. Engl., 22 (1983) 927.
8 R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Gales, M.B. Hursthouse and K.M. Abdul Malik, J. Chem. Soc., Dalton Trans., (1980) 511.
9 H. Schmidbaur and G. Blaschke, Z. Naturforsch. B, 35 (1980) 584.
10 A.S. Alves, D.S. Moore, R.A. Andersen and G. Wilkinson, Polyhedron, 1 (1982) 83.
11 H. Werner and J. Gotzig, Organometallics, 2 (1983) 547.
12 J.J. Levison and S.D. Robinson, J. Chem. Soc. A, (1970) 639.
13 P.W. Armit and T.A. Stephenson, J. Organomet. Chem., 57 (1973) C80; P.W. Armit, A.S.F. Boyd and T.A. Stephenson, J. Chem. Soc., Dalton Trans., (1975) 1663; W.J. Sime and T.A. Stephenson, J. Organomet. Chem., 161 (1978) 245.
14 T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 28 (1966) 945.
15 P.R. Hoffmann and K.G. Caulton, J. Am. Chem. Soc., 97 (1975) 4221.
16 S. Shinoda, H. Itagaki and Y. Saito, J. Chem. Soc., Chem. Commun., (1985) 860.
17 F.G. Moers, Chem. Commun., (1971) 79; F.G. Moers and J.P. Langhout, Rec. Trav. Chim. Pays. Bas, 91 (1972) 591.
18 D.F. Giel and B.L. Shaw, Inorg. Chim. Acta, 32 (1979) 19.
19 C. Masters, W.S. McDonald, G. Raper and B.L. Shaw, Chem. Commun., (1971) 210.
20 F.G. Moers, R.W.M. Ten Hoedt and J.P. Langhout, J. Inorg. Nucl. Chem., 36 (1974) 2279; J. Organomet. Chem., 65 (1974) 93.
21 L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces and F.H. Cano, J. Organomet. Chem., 258 (1983) 357.
22 D.A. Tocher, R.O. Gould, T.A. Stephenson, M.A. Bennett, J.P. Ennett, T.W. Matheson, L. Sawyer and V.K. Shah, J. Chem. Soc., Dalton Trans., (1983) 1571.
23 M.A.M. Queiros and S.D. Robinson, Inorg. Chem., 17 (1978) 310.