Journal of Organometallic Chemistry, 366 (1989) 187–196
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09642

Bis-alkynyl- and hydrido-alkynyl-osmium(II) and ruthenium(II) complexes containing triisopropylphosphine as ligand

H. Werner *, U. Meyer

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

M.A. Esteruelas, E. Sola, and L.A. Oro *

Departamento de Chimica Inorganica, Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza, C.S.I.C. 50009 Zaragoza (Spain)

(Received October 21st, 1988)

Abstract

The five-coordinate bis-alkynyl complexes $M(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Os, Ru) have been prepared by reaction of $HC{\equiv}CPh$ with $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ or $MH(\eta^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Os, Ru). They react with ligands L such as $P(OMe)_3$, PMe_3, CO and $HC{\equiv}CPh$ to give the six-coordinate compounds $M(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2L$. Displacement of the chloride ligand in $MHCl(CO)(PR_3)_2L$ by $C{\equiv}CPh^-$ leads to the hydrido-alkynyl compounds $MH(C{\equiv}CPh)(CO)(PR_3)_2L$. The selective reduction of phenylacetylene to styrene catalysed by the complex $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$, prepared from $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ and $NaBH_4$ in situ, is also described.

Introduction

During the last decade, the chemistry of alkynylmetal compounds has attracted a great deal of attention [1]. Much of this interest has been stimulated by their participation in catalytic important reactions such as acetylene polymerization [2,3] and hydrogen transfer to acetylenes [3].

Schrock and Osborn found that 1-hexyne cannot be reduced to 1-hexene with $RhH(PR_3)_ySx$ complexes as catalysts, and they assumed that formation of the corresponding alkynyl derivative $Rh(C{\equiv}CR)(PR_3)_ySx$ during the hydrogenation reaction might be responsible for the deactivation of the metal catalyst [4]. In general, in addition to the reaction of a hydrido metal compound with an alkyne, alkynyl transition metal complexes can be formed (i) by displacement of a halide ligand by the alkynyl anion [5–8], (ii) by reaction of a terminal acetylene with a 16-electron complex by oxidative addition [9,10], (iii) by deprotonation of a vinyli-

0022-328X/89/$03.50

dene metal compound [11,12], and (iv) by treatment of an *ortho*-metalated phosphine metal complex with a 1-alkyne [13].

We recently described the preparation and reactivity of the five-coordinate complexes $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) [14–18], which were readily obtained from the metal chloride and triisopropylphosphine in methanol. These complexes react with $NaBH_4$ to give initially the compounds $MH(h^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$, which on further treatment with methanol produce $MH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ species [16,17]. As a continuation of our work in this field, we now show that the complexes $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ and $MH(\eta^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) are also good starting materials for the synthesis of new bis-alkynylosmium and -ruthenium complexes. We also describe the preparation of new alkynyl-hydrido compounds of osmium and ruthenium, and the catalytic properties of the complexes $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) in the reduction of phenylacetylene by hydrogen transfer from propan-2-ol.

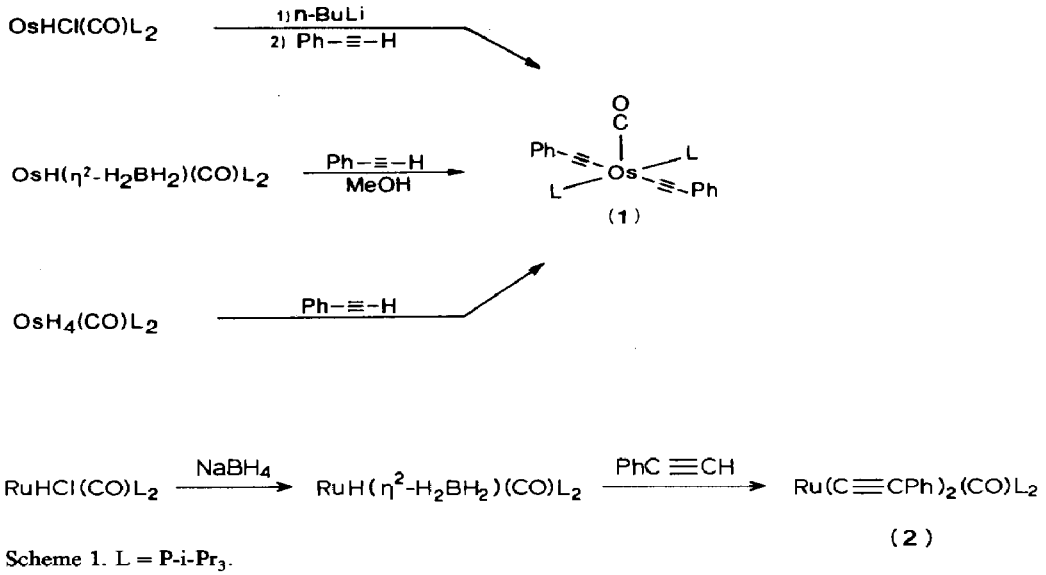
Results and discussion

Bis-alkynyl complexes

Treatment of a suspension of $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ with HC≡CPh in methanol or hexane gives a dark red solid, which according to its elemental analysis and IR and NMR spectra is the five-coordinate bis-alkynyl-osmium(II) complex $Os(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$ (**1**). The yield is almost quantitative. The formation of **1** can be rationalized in terms of the loss of the maximum number of hydrides as H_2, accompanied by binding of the alkynyl anion. Because HC≡CPh is fairly acidic, we suggest that the first step of the reaction may be the protonation of $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ to give a cationic intermediate which reacts rapidly with $C{\equiv}CPh^-$ by liberation of H_2 to give **1**. In this context it is noteworthy that a variety of polyhydrides of tungsten, rhenium, osmium, and iridium react with HBF_4 in MeCN to form H_2 and solvento complexes [19]. Crabtree and Lavin have also investigated the protonation of $IrH_5(PCy_3)_2$ with HBF_4, which leads to the cationic dihydrogen complex $[IrH_2(h^2\text{-}H_2)_2(PCy_3)_2]^+$ [20]; in acetonitrile the nitrogen donor ligand displaces two molecules of H_2 to give $[IrH_2(MeCN)_2(PCy_3)_2]^+$.

The compound $OsH(h^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ is also a good starting material for the synthesis of **1** (see Scheme 1). The addition of HC≡CPh to a suspension of the tetrahydroborate complex in methanol under reflux conditions produces the bis-alkynyl compound in 90% yield. **1** can also be directly obtained by reaction of HC≡CPh with the colourless solution formed by addition of n-BuLi to a suspension of the hydridochloro complex $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ in hexane; in this case, the yield is 72%. As the IR spectrum of **1** shows only one C≡C stretching frequency, at 2060 cm^{-1} (in benzene), we assume that the two alkynyl ligands are symmetrically coordinated, and thus the structure shown in Scheme 1 is tentatively assigned. We note that the five-coordinate chlorovinylosmium complex $Os(CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ also has a square pyramidal configuration, as shown by X-ray analysis [15].

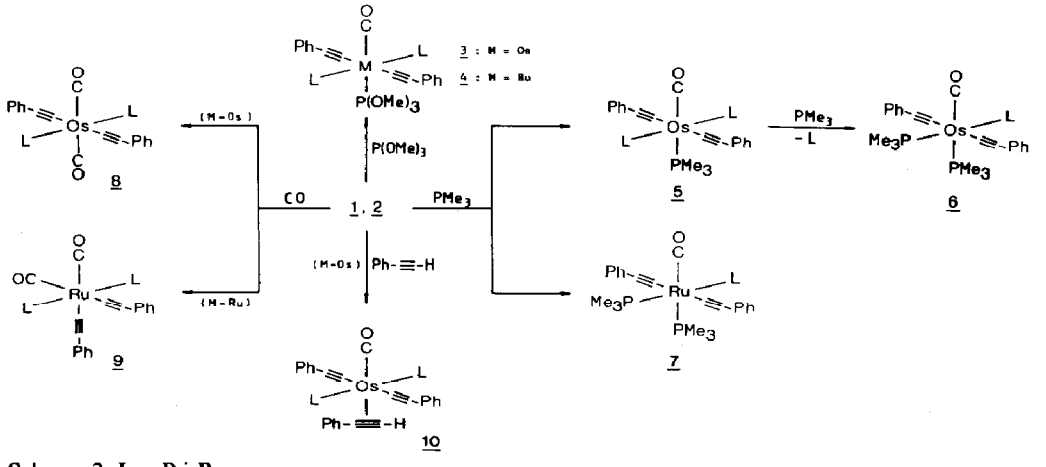
We recently reported that the reaction of $RuHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ with HC≡CPh in the presence of a stoichiometric amount of KOH in methanol gives a mixture of $Ru(CH{=}CHPh)(C{\equiv}CPh)(CO)(P\text{-}i\text{-}Pr_3)_2$ and $Ru(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$ (**2**) [15]. However, the reaction of $RuH(h^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ with HC≡CPh produces



Scheme 1. L = P-i-Pr_3.

only the bis-alkynyl complex **2** in 78% yield. Compounds, **1** and **2**, are dark red solids, and are moderately stable in air and soluble in most organic solvents.

The coordination number six for osmium and ruthenium can be achieved by addition of ligands such as $P(OMe)_3$, PMe_3 or CO to the metal centres of **1** and **2**, respectively. As is shown in Scheme 2, there is a marked difference in reactivity between **1** and **2** towards PMe_3 and CO. Whereas the osmium compound reacts with PMe_3 in hexane at room temperature to give $Os(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2(PMe_3)$ (**5**), the ruthenium analogue on treatment with trimethylphosphine gives $Ru(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)(PMe_3)_2$ (**7**). The corresponding osmium complex **6** can be obtained by addition of PMe_3 to a suspension of **5** in hexane at room temperature. Bubbling of CO through a suspension of **1** in hexane gives the *trans*-dicarbonyl complex **8**, whereas **2** reacts with CO to give the *cis* derivative **9**.



Scheme 2. L = P-i-Pr_3.

Table 1

$^{31}P\{^1H\}$ NMR and IR data for complexes **1–10** at 25 °C (^{31}P: in C_6D_6, δ in ppm, standard 85% H_3PO_4 ext.; IR in C_6H_6, ν in cm^{-1})

Complex	^{31}P [a]					IR	
	δ(P-i-Pr$_3$)	δ(L)	L	J(PL)	J(LL)	ν(C≡C)	ν(CO)
1	37.13(s)					2060	1905
2	51.46(s)					2060	1925
3	−7.11(d)	84.88(t)	[P(OMe)$_3$]	34		2080	1940
4	35.05(d)	132.22(t)	[P(OMe)$_3$]	30		2090	1940
5	14.23(d)	−65.07(t)	[PMe$_3$]	28		2090	1920
6	1.53(dd)	−53.10(dd)	[PMe$_3$]	112	29	2070	1930
		−61.39(dd)		29	29		
7	40.15(dd)	−8.72(dd)	[PMe$_3$]	251	42	2070	1940
		−23.22(dd)		34	42		
8	6.90(s)					2090	1950
9	45.42(s)					2095	1972
							1955
10	[b]					2090	1900
						1930	

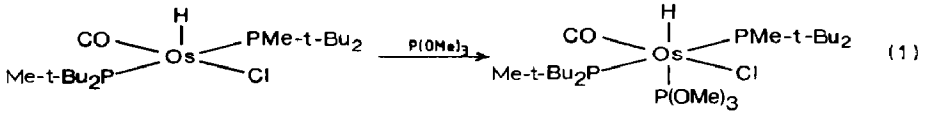
[a] Abbreviations used: s, singlet; t, triplet, dd, doublet of doublets. [b] Two lines (AB pattern) at −1.71 and −2.04 ppm.

There is also a marked difference in reactivity between **1** and **2** towards phenylacetylene. Whereas the osmium complex **1** reacts with HC≡CPh in benzene at room temperature to give the yellow six-coordinate compound **10** in 74% yield, the ruthenium complex **2** is completely inert under such conditions. In previous studies, σ-alkynylmetal species were suggested to be the active intermediates in the catalytic linear oligomerization of acetylenes, and for these reactions, alkyne insertion into a σ-alkynyl–metal bond has been assumed as the crucial mechanistic step [2,3]. For **10**, however, no subsequent insertion of the coordinated HC≡CPh ligand into the Os–C≡CPh bond was observed. The reaction between **1** and HC≡CPh is completely reversible in methanol under reflux.

The ^{31}P NMR and IR spectra of the complexes **3–10** are listed in Table 1 and are in good agreement with the structures proposed.

Hydridoalkynyl complexes

Recently, we have reported that the coordinatively unsaturated complex RuHCl(CO)(P-i-Pr$_3$)$_2$ reacts with CO or P(OMe)$_3$ to form the corresponding six-coordinate compounds RuHCl(CO)(P-i-Pr$_3$)$_2$L (**11**, L = P(OMe)$_3$; **12**, L = CO) [14]. Similarly, addition of a stoichiometric amount of P(OMe)$_3$ to a suspension of OsHCl(CO)(PMe-t-Bu$_2$)$_2$ in hexane gives the octahedral complex **13** (see eq. 1).



(1)

(**13**)

On treatment of **11–13** with LiC≡CPh in benzene, the hydridoalkynyl complexes **14–16** are formed. Although a satisfactory C, H analysis has not been obtained for

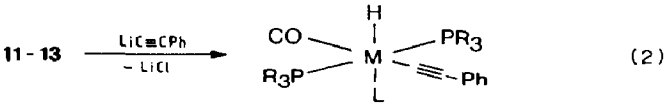
Table 2

^1H, ^{31}P NMR and IR data for the complexes **13–16** (^1H NMR: 60 MHz, 25°C; in C_6D_6, δ in ppm, standard TMS int., J and N in Hz; ^{31}P NMR: 90 MHz, 25°C; in C_6D_6, δ in ppm, standard 85% H_3PO_4 ext.; IR in C_6H_6, ν in cm^{-1})

Complex	^1H		^{31}P	IR
13 [a]	1.40, 1.45	(vt, N 12; $PC(CH_3)_3$)	24.01 (d, J(PP) 18; PMe-t-Bu_2)	2080 (w, ν(OsH))
	1.80	(vt, N 6; PCH_3)	96.36 (t, J(PP)18; $P(OMe)_3$)	1900 (s, ν(CO))
	3.46	(d, J(PH) 10; $P(OCH_3)_3$)		
	−3.80	(dt, J(PH) 20, 80; Os–H)		
14	1.45, 1.50	(dvt, J(HH) 6, N 13; $PCH(CH_3)_2$)	56.67 (d, J(PP) 20; P-i-Pr_3)	2078 (w, ν(C≡C))
	2.75	(m; $PCH(CH_3)_2$)	141.74 (t, J(PP) 20; $P(OMe)_3$)	1950 (w, ν(Ru–H))
	3.62	(d, J(PH) 11; $P(OCH_3)_3$)		1920 (s, ν(CO))
	−8.20	(dt, J(PH) 24, 158; Ru–H)		
15	1.33	(dvt, J(HH) 8, N 14; $PCH(CH_3)_2$)	61.56 (s; P-i-Pr_3)	2090 (w, ν(C≡C))
	2.56	(m; $PCH(CH_3)_2$)		2000, 1940 (s, ν(CO))
	−6.50	(t, J(PH) 20; Ru–H)		1900 (w, ν(RuH))
16 [a]	1.33, 1.38	(vt, N 13; $PC(CH_3)_3$)	21.04 (d, J(PP) 20; PMe-t-Bu_2)	2060 (w, ν(C≡C))
	1.60	(vt, N 8; PCH_3)	95.28 (t, J(PP) 20; $P(OMe)_3$)	1950 (w, ν(OsH))
	3.66	(d, J(PH) 10; $P(OCH_3)_3$)		1920 (s, ν(CO))
	−8.20	(dt, J(PH) 20, 80; Os–H)		

[a] IR in CH_2Cl_2.

the osmium compound **16**, the IR and NMR spectra strongly support the structure suggested in eq. 2. In the IR spectrum of **16** in CH_2Cl_2, there are three absorptions, at 2060, 1950, and 1920 cm^{-1} which correspond to the C≡C, the Os–H and the C≡O stretching frequencies. The ^1H NMR spectrum shows a high-field signal at δ −8.20 as a doublet of triplets with P–H coupling constants of ca. 80 and 20 Hz. Furthermore, the ^{31}P NMR spectrum has a doublet at δ 21.04 (for PMe-t-Bu_2), and a triplet at δ 95.28 (for $P(OMe)_3$) with a P–P coupling constant of ca. 20 Hz. The IR and NMR spectroscopic data of the octahedral complexes **13–16** are summarized in Table 2.



(2)

(14 - 16)

	M	PR_3	L
14	Ru	P-i-Pr_3	$P(OMe)_3$
15	Ru	P-i-Pr_3	CO
16	Os	PMe-t-Bu_2	$P(OMe)_3$

We originally expected that the compounds **14–16** would be suitable starting materials for the preparation of isomeric vinylidene derivatives M(=C=CHPh)$(CO)(PR_3)_2L$. There are various reports in the literature that terminal acetylenes

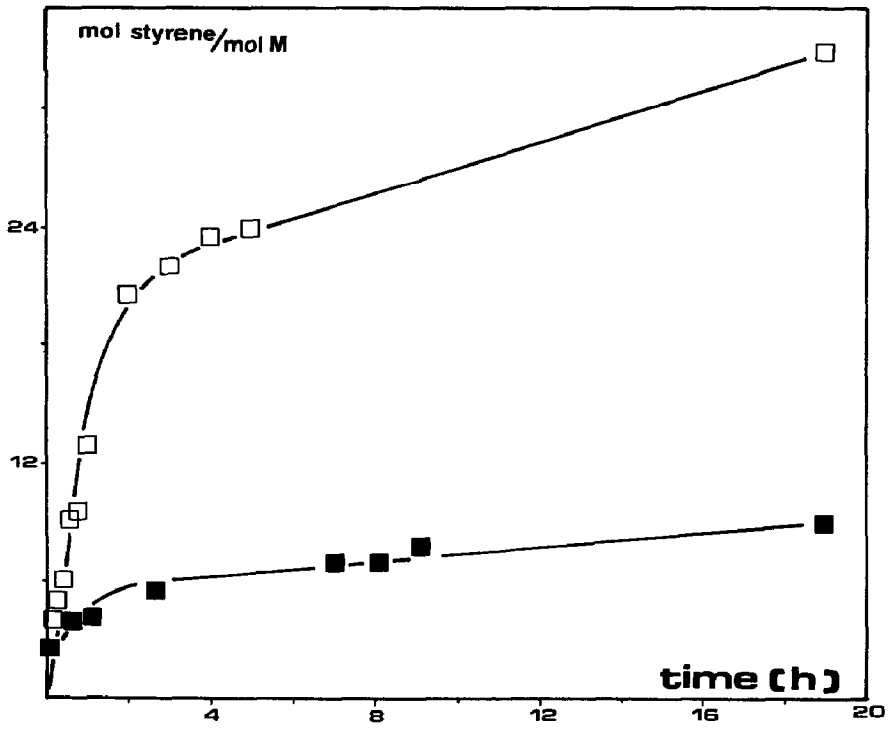


Fig. 1. Hydrogen transfer from propan-2-ol to phenylacetylene catalyzed by $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ in the presence of $NaBH_4$ as cocatalyst □ M = Os; ■ M = Ru.

undergo a 1,2-shift in reactions with unsaturated metal centers to give the corresponding vinylidene complexes; these reactions probably proceed via $L_nM(h^2\text{-}RC{\equiv}CH)$ intermediates [11]. Recently, it has been shown that the conversion $L_nM(h^2\text{-}RC{\equiv}CH) \rightarrow L_nM(=C{=}CHR)$ can proceed in two steps via a hydridoalkynyl complex $L_nMH(C{\equiv}CR)$ formed by intramolecular oxidative addition of the coordinated alkyne to the metal [10]. In contrast, compounds **14–16** are surprisingly stable and no isomerization to the vinylidene (or alkyne) isomers is observed even at higher temperatures. After solutions of **14–16** in benzene are kept at 70 °C for one week, the hydridoalkynyl complexes can be recovered unchanged.

The reduction of phenylacetylene

We have previously reported that the complexes $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) in the presence of $NaBH_4$ catalyze the hydrogen transfer from propan-2-ol to phenylacetylene [17]. A detailed study of the reactions shows that these proceed in stepwise fashion (Fig. 1). Initially, the solution which contains $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$, formed by addition of $NaBH_4$ to $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ in propan-2-ol under reflux [16,17], rapidly reduces phenylacetylene (11.7 mol styrene (mol $M)^{-1}$ h^{-1}. The reaction rate falls, progressively, however, as the colourless solution of $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ turns dark red, and approaches a value of 0.7 mol styrene (mol $M)^{-1}$ h^{-1}. This points to a modification of the active species, and is consistent with the observation that the colourless tetrahydride $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ reacts with HC≡CPh to give the dark red complex $Os(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$ (**1**). The ruthenium compound $RuHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ shows similar behaviour.

The only products of the hydrogen transfer reaction were styrene and acetone. No oligomerization of phenylacetylene was observed, a result which may be related to the stability of the σ-alkynylmetal bonds in **10** towards insertion of phenylacetylene.

The catalytic studies described here show the osmium complex to be more active than its ruthenium analogue. This observation is in contrast to the results of hydrogen transfer reactions from propan-2-ol to saturated and α,β-unsaturated ketones catalyzed by the complexes $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) in the presence of $NaBH_4$ [17,21]. We are at present trying to find out whether there is also a similar relation in the direct reduction of unsaturated substrates with H_2, catalyzed by $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$.

Experimental

All reactions were carried out under N_2 in dried, N_2-saturated solvents. NMR spectra were recorded on a Varian EM 360, a Bruker Cryospec WM 400 (^1H), and a Bruker WM 90 FT (^{31}P), IR spectra on a Perkin–Elmer 457, and mass spectra on a Varian MAT-CH 7 spectrometer. The GLC analyses were performed with a Perkin–Elmer 3920B chromatograph connected to a Perkin–Elmer M-2 integrator.

The starting materials $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) [14], $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$, $MH(h^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) and $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ [16] were prepared by published methods. $RuCl_3 \cdot aq$ and $OsCl_3 \cdot aq$ were commercial products.

Preparation of $Os(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$ (1)

This complex was prepared by three different routes:

(a) Addition of HC≡CPh (0.25 ml) to a suspension of 205.0 mg (0.40 mmol) of $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ in 5 ml of methanol led to precipitation of a dark red solid, which was filtered off, washed with methanol, and dried in vacuum. Yield 290 mg (97%).

(b) 72.6 μl (0.66 mmol) HC≡CPh was added to a suspension of 122.3 mg (0.22 mmol) of $OsH(h^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ in 5 ml of methanol. The mixture was refluxed for 10 min. The resulting suspension was cooled to room temperature and the solid filtered off, washed with methanol, and dried in vacuum. Yield 147 mg (90%).

(c) A suspension of 400.0 mg (0.69 mmol) of $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ in 20 ml of hexane was treated with 3.2 mmol of n-BuLi in 2 ml of hexane. The precipitate (LiCl) was removed by filtration and the colourless filtrate was concentrated in vacuo to ca. 5 ml. Addition of 0.25 ml of HC≡CPh gave a dark red precipitate, which was filtered off, washed with hexane, and dried in vacuum. Yield 370 mg (72%). Anal. Found: C, 57.19; H, 7.42; mol-wt. 687 (osmometric in benzene), 742 (MS). $C_{35}H_{52}OP_2Os$ calcd.: C, 56.74; H, 7.07%; mol-wt. 742. ^1H NMR (C_6D_6): δ 1.42(dvt), J(HH) 6, N 14 Hz, $PCH(CH_3)_2$; 3.25(m), $PCH(CH_3)_2$.

Preparation of $Ru(C{\equiv}CPh)_2(CO)(P\text{-}i\text{-}Pr_3)_2$ (2)

The procedure described for **1** (route b), but starting from 100.0 mg (0.22 mmol) $RuH(h^2\text{-}H_2BH_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ and 72.6 μl (0.66 mmol) HC≡CPh, gave a dark red microcrystalline solid. Yield 115 mg (78%). Anal. Found: C, 63.89; H, 7.95; mol-wt.

652 (MS). $C_{35}H_{52}OP_2Ru$ calc.: C, 64.49; H, 8.04%; mol-wt. 654. ^1H NMR (C_6D_6): δ 1.40(dvt), J(HH) 7, N 14 Hz, PCH(CH_3)$_2$; 3.05(m), PCH(CH$_3$)$_2$.

Preparation of Os(C≡CPh)$_2$(CO)(P-i-Pr$_3$)$_2$[P(OMe)$_3$] (3)

A suspension of 100.0 mg (0.13 mmol) of **1** in 10 ml of hexane containing 45.9 μl (0.39 mmol) P(OMe)$_3$ was kept at room temperature for 30 min. The white precipitate was filtered off, washed with hexane, and dried in vacuum. Yield 89 mg (76%). Anal. Found: C, 52.45; H, 6.94. $C_{38}H_{61}O_4P_3Os$ calcd.: C, 52.76; H, 7.11%. ^1H NMR (C_6D_6): δ 1.64(dvt), J(HH) 6, N 13 Hz, PCH(CH_3)$_2$; 2.85(m), PCH(CH$_3$)$_2$: 3.60(d), J(PH) 6 Hz, P(OCH_3)$_3$.

Preparation of Ru(C≡CPh)$_2$(CO)(P-i-Pr$_3$)$_2$[P(OMe)$_3$] (4)

The procedure described for **3**, but starting from 100.0 mg (0.15 mmol) of **2** and 53.0 μl (0.45 mmol) of P(OMe)$_3$, gave a white microcrystalline solid. Yield 84 mg (71%). Anal. Found: C, 58.54; H, 7.83. $C_{38}H_{61}O_4P_3Ru$ calcd.: C, 58.83; H, 7.92%. MS (70 eV): m/e 450 ($M^+ - 2C{\equiv}CPh - P(OMe)_3$). ^1H NMR (C_6D_6): δ 1.58 (dvt), J(HH) 6, N 12 Hz, PCH(CH_3)$_2$; 2.93(m), PCH(CH$_3$)$_2$; 3.42(d), J(PH) 10 Hz, P(OCH_3)$_3$.

Preparation of Os(C≡CPh)$_2$(CO)(P-i-Pr$_3$)$_2$(PMe$_3$) (5)

The procedure described for **3**, but starting from 100.0 mg (0.13 mmol) of **1** and 34.2 μl (0.45 mmol) of PMe$_3$, gave a pink microcrystalline solid. Yield 97 mg (88%). Anal. Found: C, 55.63; H, 7.86. $C_{38}H_{61}OP_3Os$ calcd.: C, 55.86; H, 7.53%. MS (70 eV): m/e 742 ($M^+ - PMe_3$), 658 ($M^+ -$ P-i-Pr$_3$). ^1H NMR (C_6D_6): δ 1.59(dvt), J(HH) 6, N 13 Hz, PCH(CH_3)$_2$; 2.68(m) PCH(CH$_3$)$_2$; 1.71(d), J(PH) 8 Hz, P(CH_3)$_3$.

Preparation Os(C≡CPh)$_2$(CO)(P-i-Pr$_3$)(PMe$_3$)$_2$ (6)

A solution of 127.6 mg (0.16 mmol) of **5** and 0.5 ml of PMe$_3$ in 5 ml of benzene was kept for 1 h at room temperature. Slow addition of methanol then led to formation of a white solid, which was filtered off, washed with methanol, and dried in vacuum. Yield 64 mg (56%). Anal. Found: C, 51.60; H, 6.72; mol-wt. 734 (MS). $C_{32}H_{49}OP_3Os$ calcd.: C, 52.44; H, 6.73%; mol-wt. 734.

Preparation of Ru(C≡CPh)$_2$(CO)(P-i-Pr$_3$)(PMe$_3$)$_2$ (7)

The procedure described for **3**, but starting from 100.3 mg (0.15 mmol) of **2** and 34.2 μl (0.45 mmol) of PMe$_3$, gave a white microcrystalline solid. Yield 92 mg (82 %). The crystals contained a mole of hexane per mole of **7**. Anal. Found: C, 62.44; H, 8.77. $C_{38}H_{63}OP_3Ru$ calcd.: C, 62.53; H, 8.70%.

Preparation of all-trans-Os(C≡CPh)$_2$(CO)$_2$(P-i-Pr$_3$)$_2$ (8)

Bubbling of carbon monoxide through a suspension of 100.5 mg (0.13 mmol) of **1** in 20 ml of hexane produced a colourless solution, which was concentrated in vacuo to ca. 10 ml, then kept at $-28\,^\circ$C. After 2 days white crystals had formed, and these were filtered off and dried in vacuum. Yield 87 mg (85%). Anal. Found: C, 56.06; H, 6.64; mol-wt. 770 (MS). $C_{36}H_{52}O_2P_2Os$ calcd.: C, 56.23; H, 6.81%; mol-wt. 770. ^1H-NMR (C_6D_6): δ 1.42(dvt), J(HH) 7, N 14 Hz, PCH(CH_3)$_2$; 2.78(m), PCH(CH$_3$)$_2$.

Preparation of cis,cis,trans-Ru(C≡CPh)$_2$(CO)$_2$(P-i-Pr$_3$)$_2$ (9)

The procedure described for **8**, but starting from 100.2 mg (0.15 mmol) of **2** gave a white microcrystalline solid. Yield 66 mg (63%). Anal. Found: C, 63.56; H, 7.64. $C_{36}H_{52}O_2P_2Ru$ calcd.: C, 63.61; H, 7.71%. MS (70 eV): *m/e* 652 ($M^+ - CO$). ^1H NMR (C_6D_6): δ 1.50(dvt), *J*(HH) 7, *N* 14 Hz, PCH(CH_3)$_2$; 2.71(m), PC*H*(CH_3)$_2$.

Preparation of Os(C≡CPh)$_2$(CO)(P-i-Pr$_3$)$_2$(h^2-CH≡CPh) (10)

A solution of 100.0 mg (0.13 mmol) of **1** in 20 ml of benzene was treated with 0.1 ml of HC≡CPh. The resulting solution was evaporated to dryness and the residue stirred with 25 ml of methanol for 1 h. The yellow solid was filtered off, washed with hexane, and dried in vacuum. Yield 84 mg (74%). Anal. Found: C, 60.74; H, 6.68. $C_{43}H_{58}OP_2Os$ calcd.: C, 61.26; H, 6.93%. MS (70 eV): *m/e* 742 ($M^+ -$ HC≡CPh).

Preparation of OsHCl(CO)(PMe-t-Bu$_2$)$_2$[P(OMe)$_3$] (13)

To suspension of 180.4 mg (0.32 mmol) of OsHCl(CO)(PMe-t-Bu$_2$)$_2$ in 50 ml of hexane was treated with 75.7 μl (0.64 mmol) of P(OMe)$_3$. The mixture was stirred for 30 min at room temperature, then the solution was filtered and 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 153 mg (68%). Anal. Found: C, 37.84; H, 7.36; mol-wt. 701 (MS). $C_{22}H_{52}ClO_4P_3Os$ calcd.: C, 37.79; H, 7.49; mol-wt. 701.

Preparation of RuH(C≡CPh)(CO)(P-i-Pr$_3$)$_2$[P(OMe)$_3$] (14)

A solution of 247.6 mg (1.41 mmol) of **11** in 25 ml of benzene was treated with 131.5 mg (1.21 mmol) LiC≡CPh. After 30 min the mixture was heated under reflux with stirring for 24 h. The resulting red solution was evaporated to dryness, the residue was treated with 50 ml of hexane, and the suspension was filtered. The cream filtrate was concentrated in vacuo to ca. 10 ml and kept at −28°C. After 2 days cream crystals of **14** had been formed, and there were filtered off and dried in vacuum. Yield 88 mg (32%). Anal. Found: C, 53.37; H, 8.35. $C_{30}H_{57}O_4P_3Ru$ calcd.: C, 53.32; H, 8.50. MS (70 eV): *m/e* 552 ($M^+ - P(OMe)_3 - H$), 451 ($M^+ -$ C≡CPh $- P(OMe)_3$).

Preparation of RuH(C≡CPh)(CO)$_2$(P-i-Pr$_3$)$_2$ (15)

The procedure described for **14**, but starting from 203.0 mg (0.39 mmol) of **12** and 124.6 mg (1.17 mmol) of LiC≡CPh, gave an orange microcrystalline solid. Yield 108 mg (47%). Anal. Found: C, 57.80; H, 8.34. $C_{28}H_{48}O_2P_2Ru$ calcd.: C, 58.01; H, 8.34%. MS (70 eV): *m/e* 479 ($M^+ -$ C≡CPh), 451 ($M^+ -$ C≡CPh − CO), 420 ($M^+ -$ P-i-Pr$_3$).

Preparation of OsH(C≡CPh)(CO)(PMe-t-Bu$_2$)$_2$[P(OMe)$_3$] (16)

The procedure described for **14**, but starting from 140.4 mg (0.20 mmol) of **13** and 61.5 mg (0.57 mmol) of LiC≡CPh, gave a cream microcrystalline solid. Yield 42 mg (55%). The compound was characterized by IR and NMR spectroscopy.

Catalytic studies

The hydrogen transfer reactions were carried out under nitrogen in refluxing propan-2-ol with magnetic stirring. The equipment consisted of a 50 ml round

bottomed flask fitted with a reflux condenser and provided with a serum cap. The procedure was as follows: To a solution of 0.02 mmol of $MHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (M = Ru, Os) in 2 ml of propan-2-ol was added 3.78 mg (0.1 mmol) of $NaBH_4$ in 2 ml of propan-2-ol. The solution was heated for 1 h under reflux and 2 mmol of substrate (HC≡CPh) in 4 ml of propan-2-ol was injected. Reactions were monitored by GLC using FFAP on Chromosorb 6 HP 80/100 mesh (3.6 m × 1/8 in) at 100 °C.

Acknowledgements

We thank the German-Spanish Joint Programme (Accion Integrada) for making these studies possible. Support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and Degussa AG is gratefully acknowledged.

References

1 R. Nast, Coord. Chem. Rev., 47 (1982) 89; and ref. cited therein.
2 S. Otsuka and A. Nakamura, Adv. Organomet. Chem., 14 (1976) 245.
3 (a) A. Dobson, D.S. Moore, S.D. Robinson, M.B. Hursthouse and L. New, J. Organomet. Chem., 117 (1979) C8; (b) A. Dobson, D.S. Moore, S.D. Robinson, M.B. Hursthouse and L. New, Polyhedron, 4 (1985) 119.
4 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 98 (1976) 2143.
5 D.R. Fahey, Organomet. Chem. Rev., 7 (1972) 245.
6 D.L. Reger and C.A. Swift, Organometallics, 3 (1984) 876.
7 G.A. Carriedo, V. Riera, D. Miguel, A.M. Manotti Lanfredi and A. Tiripicchio, J. Organomet. Chem., 272 (1984) C17.
8 R. Weinand and H. Werner, J. Chem. Soc., Chem. Commun., (1985) 1145.
9 J.D. Atwood, Coord. Chem. Rev., 83 (1988) 93.
10 F.J. Garcia Alonso, A. Höhn, J. Wolf, H. Otto and H. Werner, Angew. Chem., 97 (1985) 401; Angew. Chem. Int. Ed. Engl., 24 (1985) 406.
11 M.I. Bruce and A.G. Swincer, Adv. Organomet. Chem., 22 (1983) 59, and ref. cited therein.
12 C. Bitcon and M.W. Whiteley, J. Organomet. Chem., 336 (1987) 385.
13 J. Gotzig, R. Werner and H. Werner, J. Organomet. Chem., 290 (1985) 99.
14 M.A. Esteruelas and H. Werner, J. Organomet. Chem., 303 (1986) 221.
15 H. Werner, M.A. Esteruelas and H. Otto, Organometallics, 5 (1986) 2295.
16 H. Werner, M.A. Esteruelas, U. Meyer and B. Wrackmeyer, Chem. Ber., 120 (1987) 11.
17 M.A. Esteruelas, E. Sola, L.A. Oro, H. Werner and U. Meyer, J. Mol. Catal., 45 (1988) 1.
18 M.A. Esteruelas, E. Sola, L.A. Oro, U. Meyer and H. Werner, Angew. Chem., 100 (1988) 1621; Angew. Chem. Int. Ed. Engl., 27 (1988) 1563.
19 R.H. Crabtree, G.G. Hlatky, C.P. Parnell, B.E. Segmüller and R.J. Uriarte, Inorg. Chem., 23 (1984) 354.
20 R.H. Crabtree and M. Lavin, J. Chem. Soc., Chem. Commun., (1985) 1661.
21 M.A. Esteruelas, E. Sola, L.A. Oro, H. Werner and U. Meyer, J. Mol. Catal., in press.