Multihydride Complexes of Rhenium, Osmium or Iridium containing Monodentate Ditertiary Phosphine Ligands: Selective Hydrogen–Deuterium Exchanges of the Rhenium Multihydrides

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Treatment of $[ReH_7(PPh_3)_2]$ with $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2PC(=CH_2)PPh_2$ (vdpp) gave $[ReH_7(PPh_3)_2(L\text{–}L\text{-}P)]$ (L–L = the diphosphine), accompanied by much $[Re_2H_8(PPh_3)_4]$. However, treatment of $[ReH_7\{P(C_6H_{11})_3\}_2]$ with dppm, vdpp, $Ph_2PCH_2CH_2PPh_2$ (dppe), or *cis*-$Ph_2PCH{=}CHPPh_2$ (dppen) gave good yields of the monodentate diphosphine complexes of type $[ReH_5\{P(C_6H_{11})_3\}_2(L\text{–}L\text{-}P)]$ without formation of a dirhenium complex of type $[Re_2H_8\{P(C_6H_{11})_3\}_4]$, or chelating diphosphine complexes. The complexes $[ReOCl_3(PPr^i_3)_2]$ and $[ReOCl_3(PBu_2^tMe)_2]$ were prepared and characterised. These were reduced by $NaBH_4$ in the presence of the phase-transfer catalyst $N(CH_2CH_2OCH_2CH_2OMe)_3$ to give heptahydrides of type $[ReH_7(PR_3)_2]$. Treatment of $[ReOCl_3(AsPh_3)_2]$ with $Bu^t_2P(CH_2)_5PBu^t_2$ probably gave $[\{ReOCl_3[Bu^t_2P(CH_2)_5PBu^t_2]\}_x]$ which with $NaBH_4$ gave $[Re_xH_{7x}\{Bu^t_2P(CH_2)_5PBu^t_2\}_x]$ obtained only in an impure form; x is probably 1 or 2. The complex $[IrH_5\{P(C_6H_{11})_3\}_2]$ with dppm or dppe gave non-fluxional complexes of the type *trans*- *mer*-$[IrH_3\{P(C_6H_{11})_3\}_2(L\text{–}L\text{-}P)]$ (L–L = monodentate dppm or dppe). Substantially pure $[OsH_6\{P(C_6H_{11})_3\}_2]$ was prepared by reducing $[OsO_2Cl_2\{P(C_6H_{11})_3\}_2]$ with $LiAlH_4$. This hexahydride, with dppm, gave $[OsH_4\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ accompanied by $[OsH_4\{P(C_6H_{11})_3\}(dppm\text{-}PP)]$ as the minor product. Highly selective C–H/C–D exchange was shown to occur between C_6D_6 and some of the less sterically hindered sites of the co-ordinated diphosphines when compounds of type $[ReH_5\{P(C_6H_{11})_3\}_2(L\text{–}L)]$ were heated in C_6D_6 *e.g.* with L–L = dppm the product was $[ReH_5\{P(C_6H_{11})_3\}_2\{(C_6H_2D_3)_2PCH_2P(C_6H_2D_3)_2\}]$ in which the *meta*- and *para*-hydrogens were replaced by deuterium but the *ortho*-hydrogens were not replaced to a significant extent. Some of the cyclohexyl hydrogens were replaced by deuterium but the CH_2 and ReH_5 hydrogens were shown to have undergone little exchange with deuterium. Similar results were obtained when $[ReH_5\{P(C_6H_{11})_3\}_2(vdpp\text{-}P)]$ was heated in C_6D_6 solution. Proton and ^{31}P n.m.r. data are given.

There is currently much interest in transition-metal multihydrides, particularly those containing tertiary phosphine ligands. The majority of these multihydrides are of type $[MH_x(PR_3)_y]$ (x = 3—7, R = alkyl or aryl) and the most stable and most studied are those of third-transition-series metals such as W, Re, Os, or Ir. The great majority are mononuclear, *e.g.* $[TaH_5(dmpe)_2]$[1] (dmpe = $Me_2PCH_2CH_2PMe_2$), $[WH_6(PMe_2Ph)_3]$,[2] $[ReH_7(PPh_3)_2]$,[3,4] $[ReH_5(PPh_3)_3]$,[3,4] $[OsH_6(PMe_2Ph)_2]$,[5] and $[IrH_5(PEt_2Ph)_2]$,[6] although deep red dirhenium octahydrides such as $[(Ph_3P)_2H_2Re(\mu\text{-}H)_4ReH_2(PPh_3)_2]$ are well established.[4]

One reason for the interest in multihydrides is their ability to activate C–H bonds in hydrocarbons both aromatic[4,7] and aliphatic, even methane.[8] Another reason is the relationship between multihydrides and η^2-dihydrogen complexes. It has been suggested that many multihydrides are in fact highly fluxional mixed hydride/η^2-dihydrogen complexes.[9] Most of the evidence for this comes from the observation of a very short T_1 relaxation time for the 'hydride' hydrogens, but more recently this has been shown to be not a reliable criterion and the significance of short T_1 has still to be resolved.[10] We have shown that $[ReH_7\{P(C_6H_{11})_3\}_2]$ is protonated to give a highly fluxional mixed η^2-H_2/hydride complex, of type $[Re(H_2)_xH_{8-2x}\{P(C_6H_{11})_3\}_2]^+$[11] ($x$ is probably 1 or 2).

We thought it would be of interest to devise methods of synthesizing heterobimetallic complexes in which at least one of the metal centres is a multihydride. We have in mind to synthesize heterobimetallic systems in which the two metals are bridged in a flexible manner by one or more diphosphine ligands. We have used this approach successfully with a range of metals and ligands such as carbonyl, isonitrile, alkyl, aryl, acetylide, *etc.*[12,13] and in order to extend it to multihydrides we set out to try to synthesize systems of the type $MH_x(P\text{–}P)L_n$ where L = a ligand such as a tertiary phosphine, MH_x = a multihydride moiety, and P-P is a monodentate diphosphine. We hoped subsequently to be able to complex the free end of the diphosphine to a second metal. This paper is concerned with the synthesis and characterization of complexes of the type $MH_x(P\text{–}P)L_n$ where M = Re, Os, or Ir.

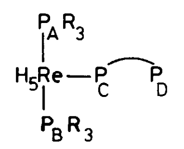
Results and Discussion

A well established reaction of multihydrides of type MH_xL_n, (M = Re, Os, or Ir, L = tertiary phosphine) is the displacement of H_2 on treatment with another ligand L (a tertiary phosphine, *etc.*).Examples of such reactions are (1)[4] and

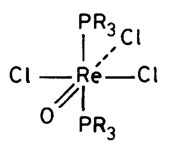
$$[ReH_7(PPh_3)_2] + PEt_2Ph \longrightarrow [ReH_5(PPh_3)_2(PEt_2Ph)] + H_2 \quad (1)$$

$$[IrH_5(PEt_2Ph)_2] + PPh_3 \longrightarrow [IrH_3(PEt_2Ph)_2(PPh_3)] + H_2 \quad (2)$$

(2)[14]. We had hoped to effect such reactions with diphosphines acting as monodentate ligands. We therefore heated $[ReH_7(PPh_3)_2]$ with $Ph_2PCH_2PPh_2$ (dppm) in benzene and found some conversion into the deep red $[(Ph_3P)_2H_2Re(\mu\text{-}H)_4ReH_2(PPh_3)_2]$ but additionally, some of the required

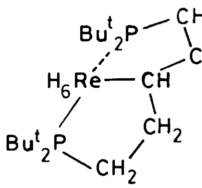


	R	P P
(1a)	Ph	$Ph_2PCH_2PPh_2$
(1b)	C_6H_{11}	$Ph_2PCH_2PPh_2$
(1c)	C_6H_{11}	$CH_2{=}C(PPh_2)_2$
(1d)	C_6H_{11}	$Ph_2PCH_2CH_2PPh_2$
(1e)	C_6H_{11}	*cis*-$Ph_2PCH{=}CHPPh_2$
(1f)	Pr^i	$Ph_2PCH_2PPh_2$



(2a) $PR_3 = PBu^t_2Me$

(2b) $PR_3 = PPr^i_3$



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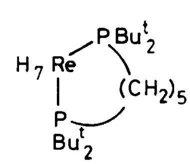

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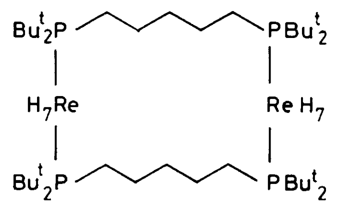

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Table 1. Analytical data[a] (%)

Complex	C	H	Cl
(1a)$\cdot 0.75C_6H_6$[b]	67.95 (67.9)	5.25(5.35)	
(1b)$\cdot 0.5C_6H_6$[c]	65.5(65.4)	8.3(8.4)	
(1c)$\cdot 0.5C_6H_6$[d]	65.4(65.4)	8.2(8.1)	
(1d)	64.35(64.15)	8.25(8.25)	
(1e)	64.6(64.8)	8.25(8.2)	
(2a)	34.35(34.35)	6.7(6.7)	17.2(16.9)
(2b)	33.95 (34.35)	6.7(6.7)	17.25(16.9)
(6a)	64.2(64.2)	7.75(8.0)	
(6b)	64.35(64.6)	8.1(8.1)	

[a] Calculated values in parentheses. [b] ν(Re-H) 1 895m, br cm^{-1} (Nujol) [c] ν(Re-H) 1 890w, br cm^{-1} (Nujol). [d] ν(Re-H) 1 903w, br and 1 954w, br cm^{-1} (Nujol).

$[ReH_5(PPh_3)_2(dppm\text{-}P)]$ **(1a)** was obtained as yellow crystals. However, the yields of **(1a)** varied from 49 to 10%, the main reason for the low yields being the formation of the dirhenium complex $[(Ph_3P)_2H_2Re(\mu\text{-}H)_4ReH_2(PPh_3)_2]$. The required complex $[ReH_5(PPh_3)_2\ (dppm\text{-}P)]$ gave satisfactory elemental analysis for C and H (Table 1), and a broad band due to ν(Re–H) in the i.r. spectrum (Table 1). In the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum the resonance due to P_D (at −23.4 p.p.m.) was readily assigned, being similar in shift to free dppm. Hence the resonance at δ 21.0 p.p.m. with $J(P_CP_D)$ = 74 Hz was assigned to P_C and that at 35.2 p.p.m. to P_A/P_B. In the ^1H n.m.r. pattern the hydride resonance at δ − 4.81 was a 1:3:3:1 quartet with $J(P_CH) \sim J(P_{A/B}H)$ = 18 Hz, *i.e.* the molecule is fluxional.

Many other rhenium heptahydrides of type $[ReH_7(PR_3)_2]$ give the deep red dirhenium complexes $[(R_3P)_2H_2Re(\mu\text{-}H)_4ReH_2(PR_3)_2]$. However, Caulton and co-workers[15] showed that $[ReH_7\{P(C_6H_{11})_3\}_2]$ did not give a dirhenium octahydride of this type, probably because the large cone angle of $P(C_6H_{11})_3$ (179°) prevented the close approach of two rhenium centres. We therefore heated $[ReH_7\{P(C_6H_{11})_3\}_2]$ with dppm in benzene and found that the required product $[ReH_5\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ **(1b)** was formed and isolated in good (74%) yield. This complex was characterized by C and H analysis, i.r. and n.m.r. spectroscopy (Tables 1 and 2). In the preparation we found no evidence for the formation of a bridged complex of type $[\{(H_{11}C_6)_3P\}_2H_5Re(\mu\text{-}dppm)ReH_5\{P(C_6H_{11})_3\}_2]$. We similarly made and characterized $[ReH_5\{P(C_6H_{11})_3\}_2(vdpp\text{-}P)]$ **(1c)** [vdpp = vinylidenebis(diphenylphosphine), $(Ph_2P)_2C{=}CH_2$]. In the synthesis of the dppm and vdpp complexes, **(1b)** and **(1c)**, we found no evidence of another product in which the dppm or the vdpp was chelated to the rhenium. Encouraged by this, we also heated $[ReH_7\{P(C_6H_{11})_3\}_2]$ with $Ph_2PCH_2CH_2PPh_2$ (dppe), a diphosphine which has a very strong tendency to chelate and for which monodentate complexes are very rare, and were pleased and somewhat surprised to obtain the hoped for complex $[ReH_5\{P(C_6H_{11})_3\}_2(dppe\text{-}P)]$ **(1d)** in 89% yield. Similarly $[ReH_5\{P(C_6H_{11})_3\}_2(\textit{cis}\text{-}dppen\text{-}P)]$ was obtained from *cis*-$Ph_2PCH{=}CHPPh_2$. These two rhenium pentahydrides were characterized (Tables 1 and 2).

During the course of this work we developed an improved synthesis of $[ReH_7\{P(C_6H_{11})_3\}_2]$ using phase-transfer catalysis. It was originally prepared by the reduction of $[ReOCl_3\{P(C_6H_{11})_3\}_2]$ with $NaBH_4$ in ethanol over a period of 20 h, in a reported yield of 70%. However, in our hands the yields varied from 30 to 48% and the reaction usually took 48 h. We reasoned that the insolubility of $[ReOCl_3\{P(C_6H_{11})_3\}_2]$ in ethanol contributed to the yield and that a better solvent would be benzene, in which $[ReOCl_3\{P(C_6H_{11})_3\}_2]$ is sparingly soluble. When $[ReOCl_3\{P(C_6H_{11})_3\}_2]$ and $NaBH_4$ were stirred vigorously in the presence of the phase-transfer catalyst $N(CH_2CH_2OCH_2CH_2OMe)_3$ for 2 h, pure $[ReH_7\{P(C_6H_{11})_3\}_2]$ was readily obtained in consistently good yields (65—68%).

We have also attempted to make rhenium heptahydrides with other bulky phosphine ligands. Treatment of $[ReOCl_3(PPh_3)_2]$ with PBu^t_2Me gave *trans*-$[ReOCl_3(PBu^t_2Me)_2]$ **(2a)**, and with PPr^i_3 *trans*-$[ReOCl_3(PPr^i_3)_2]$ **(2b)** was formed. Characterizing data are given in Tables 1 and 3. When *trans*-$[ReOCl_3(PBu^t_2Me)_2]$ was reduced by $NaBH_4$ in benzene using the phase-transfer method (above) the product was obtained as an amber-coloured oil and could not be purified. The major part of the product was the hoped for heptahydride $[ReH_7(PBu^t_2Me)_2]$, present to the extent of *ca.* 75% [$^{31}P\text{-}\{^1H\}$ and other n.m.r. evidence]; characterizing data are given in Table 4. It was further characterized by a $^{31}P\text{-}\{^1H(\text{selective})\}$ n.m.r. spectrum (at 40.5 MHz) in which only the alkyl protons were decoupled. This gave an octet ^{31}P resonance with relative areas 1.2:6.7:20.6:35.0:35.0:21.4:7.3:1.2 compared with theoretical intensity ratios of 1:7:21:35:35:21:7:1. Caulton and co-workers[15] only observed six lines with a similar experiment on $[ReH_7\{P(C_6H_{11})_3\}_2]$ and ours appears to be the first observation of all eight lines in the $^{31}P\text{-}\{^1H(\text{selective})\}$ n.m.r. spectrum of a rhenium heptahydride. The impurity was present

Table 2. ^{31}P-{^{1}H},[a] ^{1}H-{^{31}P},[b] and selected ^{1}H[b] n.m.r. data

Complex	δ(P_A)	δ(P_C)	δ(P_D)	$^{2}J(P_AP_C)$	$^{2}J(P_CP_D)$	δ(H)	^{2}J(PH)	δ(CH_2 or CH=)	^{2}J(PH) or ^{3}J(PH)	Solvent
(1a)	35.2	21.0	−23.4			−4.81	18.1	3.15	7.8, 3.4	C_6D_6
(1b)	42.0	17.8	−20.8	7	37	−6.78	15.4(P_C) 20.2(P_A)	3.49	3.2, 1.7	C_6D_6
(1c)	34.8	45.6	−18.5	<2	66	−7.36	19.2(P_C) 18.8(P_A)	6.06 6.07	6.9, 39.4 6.9, 39.6	C_6D_6
(1d)	40.9	21.4	−12.3	n.r.	34	−6.97[c]	18.8[d]	n.r.	n.r.	C_6D_6
(1e)	41.6	18.0	−30.6	10	5	−6.84	18.3[d]	7.48[e] 6.78	24.8, 28.1 4.0, 31.3	C_6D_6
(1f)	51.0	17.8	−20.3	−7	37	−7.06	20.1(P_A) 15.4(P_C)	3.61	4.9[f]	C_6D_6
(6a)	27.8[g]	3.9	−19.7	15	15	−12.7(H_A) −15.54(H_B)	14.8[d] 22.6(P_A) 122.3(P_C)	2.96	3.4	CD_2Cl_2
(6b)	26.6[h]	7.0	−13.1	15	30	−12.84(H_A) −15.57(H_B)	15.1 23.5(P_A) 117.2(P_C)	2.11	*ca.* 4[i]	CD_2Cl_2
(7)[j]	27.4	−13.7	−19.1	7	22	−10.09	14.7(P_A) 2.9(P_C)	3.23	3.8	$C_6D_5CD_3$

[a] Recorded at 40.3 MHz at 22 °C in CD_2Cl_2, unless stated otherwise. Chemical shifts in p.p.m. relative to 85% H_3PO_4 and coupling constants in Hz. [b] Recorded at 400 MHz at 23 °C, unless stated otherwise. Coupling constants in Hz. [c] Recorded at 100 MHz. [d] Average value. [e] $^{3}J(CH{=}CH)$ = 13.9 Hz. [f] δ($CHCH_3$) *ca.* 1.96, δ($CHCH_3$) 1.29, $^{3}J(CHCH_3)$ 6.9, $^{3}J(PCHCH_3)$ 11.4 Hz, $^{2}J(PCH)$ not resolved. [g] In CD_2Cl_2. [h] In CD_2Cl_2 at −20 °C. [i] The two methylene resonances were almost superimposed, coupling to only one P nucleus was resolved. [j] The minor component with structure (**8**) had the following n.m.r. data: ^{31}P-{^{1}H} at −80 °C in $C_6D_5CD_3$, δ(P_A) 32.6, δ(P_C) −26.4, δ(P_D) −33.2 p.p.m., $^{2}J(P_AP_C)$ 20, $^{2}J(P_AP_D)$ 247, $^{2}J(P_AP_B)$ 40 Hz; at 22 °C, δ(P_A) *ca.* 33, δ(P_C) and δ(P_D) −30.6 p.p.m.; ^{1}H at 22 °C in $C_6D_5CD_3$, δ (H, hydride) −8.69, $^{2}J(P_CH)$ = $^{2}J(P_DH)$ *ca.* 5, $^{2}J(P_AH)$ = 15.3 Hz; δ(CH_2) 5.09, $J(P_CCH_2)$ = $J(P_DCH_2)$ = 9.4 Hz.

Table 3. ^{31}P-{^{1}H}[a] and ^{1}H[b] n.m.r. data for some new rhenium-phosphine complexes

Complex	δ(P)	δ(H)	*J*/Hz
$[ReOCl_3(PBu^t_2Me)_2]$ (**2a**)[c]	−6.8	1.86 [δ(PCH_3)] 1.48 [δ($PCCH_3$)]	7.3 [$^{2}J(PCH_3)$ + $^{4}J(PRePCH_3)$] 12.9 [$^{3}J(PCCH_3)$ + $^{5}J(PRePCCH_3)$]
$[ReOCl_3(PPr^i_3)_2]$ (**2b**)	−14.4	3.17 [δ(PCH)] 1.45 [δ($PCHCH_3$)]	7.3 [$^{3}J(CHCH_3)$] 13.2 [$^{3}J(PCHCH_3)$], $^{2}J(PCH)$ n.r.
$[Re_xO_xCl_{3x}\{Bu^t_2P(CH_2)_5PBu^t_2\}_x]$	*ca.* 45[d]	*ca.* 1.5[e]	n.r.

[a] Recorded at 40.3 MHz and 22 °C in CD_2Cl_2. [b] Recorded at 100 MHz and 22 °C in CD_2Cl_2.[c] In C_6D_6. [d] Very broad resonance (linewidth *ca.* 40 Hz). [e] Very broad resonance (linewidth *ca.* 50 Hz).

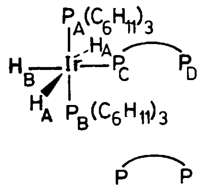
Table 4. Proton and ^{31}P-{^{1}H} n.m.r. data[a] for complexes of the type $[MH_x(PR_3)_2]$ (MH_x = ReH_7 or OsH_6; PR_3 = trialkylphosphine)

Complex	δ(H)	^{2}J(PH)	δ(H)	*N*[b]	δ(P)
$[ReH_7(PBu^t_2Me)_2]$[c]	−6.02	19.0	1.57 (PCH_3) 1.24 ($PCCH_3$)	7.2 12.9	52.7
$[ReH_7(PPr^i_3)_2]$	−6.66	19.1	1.29 (CH_3) 1.93 (CH)[d]	n.r.	60.8
$[Re_xH_{7x}\{Bu^t_2P(CH_2)_5PBu^t_2\}_x]$	−6.33	19.1	1.32 (Bu^t)	12.2	66.8
$[OsH_6\{P(C_6H_{11})_3\}_2]$	−9.44	9.3			45.1

[a] Recorded at 100 (^{1}H) or 40.3 MHz (^{31}P) at 22 °C in C_6D_6, unless stated otherwise; chemical shifts in p.p.m. and coupling constants in Hz. [b] *N* = ^{2}J(PH) + ^{4}J(PH) or ^{3}J(PH) + ^{5}J(PH). [c] Proton n.m.r. spectrum recorded at 400 MHz in deuteriotoluene. [d] $^{3}J(CHCH_3)$ = 6.9 Hz.

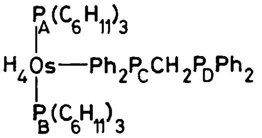
to the extent of about 25%, judging from the intensities of its Bu^t and Me resonances (data as a footnote in Table 4). The characterizing data for $[ReH_7(PPr^i_3)_2]$ are given in Table 4 and suggest that the product was essentially pure since only one resonance (a 1 : 1 doublet) was observed for the Me groups in the ^{1}H-{^{31}P} n.m.r. spectrum. We also attempted to make a rhenium heptahydride containing the pentamethylene diphosphine $Bu^t_2P(CH_2)_5PBu^t_2$. We have shown previously that this diphosphine gives stable 16-atom rings such as *trans,trans*-$[Cl_2Pd\{\mu\text{-}Bu^t_2P(CH_2)_5PBu^t_2\}_2PdCl_2]$[16] and also cyclometallated complexes such as the tetrahydride $[IrH_4\{Bu^t_2PCH_2CH_2CHCHCH_2CH_2PBu^t_2\}]$.[17] The complex $[ReOCl_3(AsPh_3)_2]$, the triphenylarsines of which are easily displaced, was treated with $Bu^t_2P(CH_2)_5PBu^t_2$. This gave a green product which we tentatively formulated as $\{ReOCl_3[Bu^t_2P(CH_2)_5PBu^t_2]\}_x$, in an impure form. Reduction of this with $NaBH_4$ gave what appears to be a rhenium multihydride $[Re_xH_{7x}\{Bu^t_2P(CH_2)_5PBu^t_2\}_x]$ in about 10% yield. The material was not obtained pure but the ^{1}H and ^{31}P n.m.r. data are similar to those of $[ReH_7(PBu^t_2Me)_2]$ (Table 4). A ^{31}P-{^{1}H(selective)} n.m.r. experiment on this material gave a sextet and therefore showed the number of hydride ligands to be odd but the signal:noise ratio was too poor to decide between five or seven hydrides. However, the experiment excludes a hexahydride (**3**) and we suggest that the product is a heptahydride, either mononuclear (**4**) or a 16-atom ring binuclear complex (**5**).

When $[ReH_7(PPr^i_3)_2]$ was heated with dppm at 80 °C in benzene a ^{31}P-{^{1}H} n.m.r. spectrum of the resultant solution suggested that $[ReH_5(PPr^i_3)_2(dppm\text{-}P)]$ (**1f**) was formed (data



(6a) $Ph_2PCH_2PPh_2$

(6b) $Ph_2PCH_2CH_2PPh_2$



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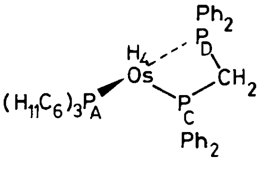


(8)

in Table 2) but we were unable to isolate the product in a pure state. The hydride resonance showed the expected coupling to three P nuclei (P_A,P_B, and P_C) (Table 2). In an experiment in which $[ReH_7(PBu^t{}_2Me)_2]$ was heated with vdpp a complex mixture of products formed (^{31}P-{^1H} n.m.r. evidence), which were not identified.

In view of our success in making several rhenium hydrides containing a dangling (monodentate) diphosphine we attempted to make analogous complexes from iridium and osmium multihydides. The complex $[IrH_5\{P(C_6H_{11})_3\}_2]$ was heated with dppm in benzene for 30 min and gave the hoped for complex *mer*-$[IrH_3\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ **(6a)** in 65% yield. This was fully characterized (Tables 1 and 2) and, as with other trihydrides of the type *mer*-$IrH_3(PR_3)_2L]$, it is not fluxional. We similarly made *mer*-$[IrH_3\{P(C_6H_{11})_3\}_2(dppe\text{-}P)]$ **(6b)** in 75% yield from $[IrH_5\{P(C_6H_{11})_3\}_2]$ and dppe, characterizing data in Tables 1 and 2.

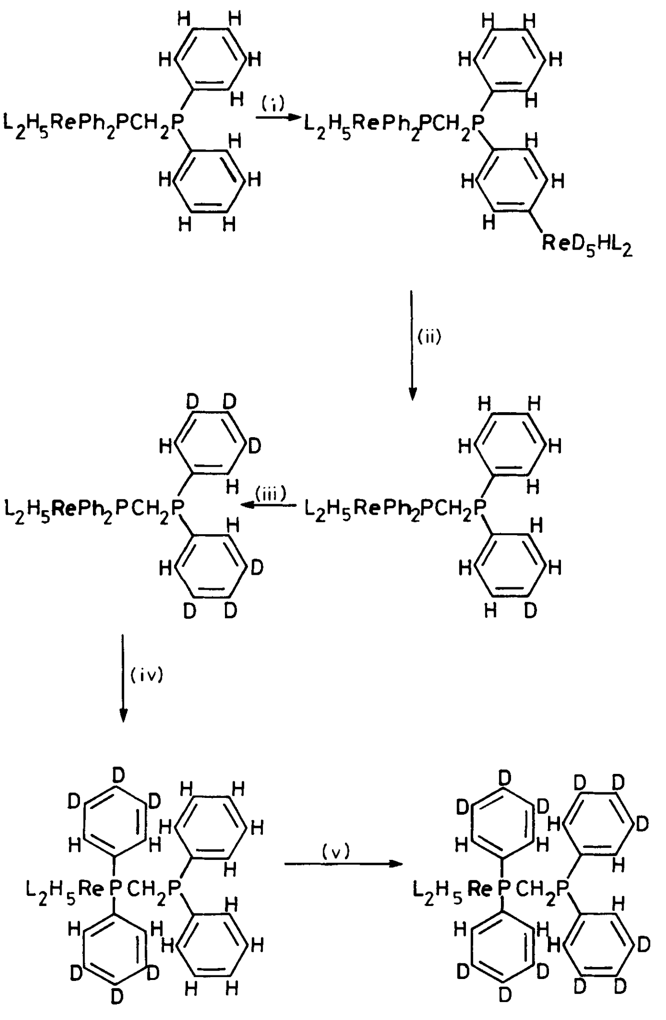
The complex $[OsH_6\{P(C_6H_{11})_3\}_2]$ has not been described previously and we attempted to make it by a method analogous to that used to synthesize $[OsH_6(PPhPr^i{}_2)_2]$.[18] We first synthesized the unstable complex $[OsO_2Cl_2\{P(C_6H_{11})_3\}_2]$ as a brown solid by treating OsO_4 with $P(C_6H_{11})_3$ and HCl (see Experimental section) and then reduced this complex with $LiAlH_4$ in tetrahydrofuran (thf). The product was obtained as air-sensitive white crystals which were not sufficiently pure for elemental analysis but the n.m.r. evidence (Table 2) was in agreement with the structure $[OsH_6\{P(C_6H_{11})_3\}_2]$. Moreover, in a ^{31}P-{^1H(selective)} n.m.r. experiment, in which the cyclohexyl hydrogens were selectively decoupled, the observed peak-height ratios of the heptet of 1.2:5.3:13.2:20:14.7:6.0:1.7 compared well with the theoretical intensity ratios of 1:6:15:20:15:6:1. This appears to be the first report of a heptet structure for the ^{31}P-{^1H(selective)} n.m.r. pattern of an osmium hexahydride.

When we heated $[OsH_6\{P(C_6H_{11})_3\}_2]$ with dppm the n.m.r. evidence indicated that the product was a mixture consisting of *ca.* 80% of the required product $[OsH_4\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ **(7)** and *ca.* 20% of $[OsH_4\{P(C_6H_{11})_3\}(dppm\text{-}PP')]$ **(8)** (data in Table 2). The major component was fluxional with equivalent $P(C_6H_{11})_3$ ligands and a monodentate or dangling dppm ligand. The hydride resonance consisted of a doublet of triplets with coupling of 14.7 Hz to both the $P(C_6H_{11})_3$ groups and a coupling of 2.9 Hz to the complexed phosphorus of the dppm ligand. The minor component was assigned structure **(8)** from the n.m.r. data (Table 2).

C–H/C–D *Activation by Some of the New Rhenium Multihydrides.*—The first demonstration of C–H activation by a multihydride was by Chatt and Coffey[4] who found that on heating $[ReH_7(PEt_2Ph)_2]$ with C_6D_6 at 100 °C the hydridic hydrogens were replaced by deuterium to the extent of over 60% after 5 min. Other C–H/C–D exchanges involving deuteriobenzene have been demonstrated since, including CH ⟶ CD conversions of co-ordinated phosphines, *e.g.*$PPr^i{}_3$,[19] and also of methane.[8] A more detailed study of H/D exchange of rhenium multihydrides has been carried out by Caulton and co-workers who found that on heating $[ReH_7\{P(C_6H_{11})_3\}_2]$ with C_6D_6 the hydridic hydrogens were completely replaced by deuterium at 60 °C and at 80 °C some C–H/C–D exchange occurred on the cyclohexyl groups at C(2) and C(3). Moreover kinetic and other evidence was presented which suggested that the first step in these C–H activation reactions was the conversion of $[ReH_7\{P(C_6H_{11})_3\}_2]$ into $[ReH_5\{P(C_6H_{11})_3\}_2] + H_2$ and that the co-ordinatively unsaturated species $[ReH_5\{P(C_6H_{11})_3\}_2]$ then underwent reversible oxidative addition of C–D from C_6D_6, *etc.*

In some preliminary work, when we were following the conversion of $[ReH_7\{P(C_6H_{11})_3\}_2]$ into compounds of the type **(1)** on treatment with diphosphines, we followed the course of the reactions by ^{31}P and ^1H n.m.r. spectroscopy, using C_6D_6 as solvent and field/frequency lock. When $[ReH_7\{P(C_6H_{11})_3\}_2]$ was heated with vdpp in C_6D_6 the isolated product $[ReD_5\{P(C_6H_{11})_3\}_2(vdpp\text{-}P)]$ was shown by ^1H, ^1H-{^{31}P} (at 400 MHz), and ^2H (at 61.4 MHz) n.m.r. spectroscopy to be extensively but selectively deuteriated. Thus the hydride ligands were completely replaced by deuterium (δ −7.2 p.p.m.) whereas no replacement of the $C{=}CH_2$ hydrogens by deuterium could be detected. Extensive deuteriation of the cyclohexyl groups had taken place and with the aromatic protons of the co-ordinated vdpp ligand virtually all the *meta*- and *para*-hydrogens had been replaced by deuterium but no detectable amount of *ortho*-hydrogen had been replaced. In particular, in the ^1H-{^{31}P} spectrum, there were two strong sharp singlets at δ 8.11 and 7.34 which in the ^1H spectrum became doublets with $^3J(PH)$ = 9.4 and 7.0 Hz, respectively and clearly therefore due to *ortho*-hydrogen. There was also a very sharp singlet at δ 7.20 due to residual $C_6H_{6-x}D_x$ but over the range 6.5—7.18, there was very little absorption in the ^1H n.m.r. spectrum. In this region, for the undeuteriated complex $[ReH_5\{P(C_6H_{11})_3\}_2\{(Ph_2P\text{-}C({=}CH_2)PPh_2\}]$, there were strong, complex resonances presumably due to *meta*- and *para*-hydrogens. In the ^2H n.m.r. spectrum there was a strong peak at δ 7.05 ($w_{\frac{1}{2}} \sim 25$ Hz at 25 °C) but no peak could be detected at δ 8.11.

We also heated $[ReH_5\{P(C_6H_{11})_3\}_2(vdpp\text{-}P)]$ **(1c)** in C_6D_6 at 80 °C and found, after 7 h, that there was extensive deuteriation of the *meta*- and *para*-hydrogens of the phenyl groups but little or no incorporation into the *ortho* position. As before there was no deuterium incorporated into the $C{=}CH_2$ group and, surprisingly, only about 5% incorporation into the hydrides [^2H-{^1H} and ^1H n.m.r. evidence]. The ^{31}P-{^1H} n.m.r. spectrum showed that about 30% of **(1c)** had decomposed and that a major product of decomposition was $[ReD_7\{P(C_6H_{11})_3\}_2]$ (^{31}P, ^1H, and ^2H n.m.r. evidence). Also some minor phosphorus-containing species were produced in this reaction which were not identified. Similarly, when $[ReH_5\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ **(1b)** was heated at 80 °C in C_6D_6 for 7 h, deuteriation again occurred selectively. Before heating the aromatic region showed general overlapping complicated multiplets, although at lowest field in the ^1H-{^{31}P} 400 MHz spectrum there was one doublet (δ 8.3) well separated



Scheme A possible sequence of reactions leading to selective deuteriation in the *meta* and *para* positions of monodentate $Ph_2PCH_2PPh_2$ (dppm) in $[ReH_5L_2(dppm\text{-}P)]$ [L = $P(C_6H_{11})_3$]. We suggest that some $[ReH_5\{P(C_6H_{11})_3\}_2]$ is formed and this undergoes reversible oxidative addition with C_6D_6, giving $[ReD_{5-x}H_x\{P(C_6H_{11})_3\}_2]$ (x = 1—5) which in turn passes on the deuterium to the *meta* and *para* positions of the dppm by oxidative addition/reductive elimination. (i) $[ReD_{5-x}H_xL_2]$ oxidative addition of C–H; (ii) reductive elimination of C–D; (iii) successive oxidative additions/reductive eliminations at the *meta* and *para* positions but not the sterically hindered *ortho* positions; (iv) end-over-end interchange of dppm; (v) successive oxidative additions/reductive eliminations at the *meta* and *para* positions, as in (iii)

from the other resonances and this was clearly due to *ortho*-protons, ^3J(H–H) ~ 8 Hz. After heating, only two singlets could be observed at δ 8.29 and 2.37 and in the ^{1}H n.m.r. pattern these became doublets with ^3J(PH) = 9.8 and 6.9 Hz, respectively. These two singlets were strong and, as with the vdpp complex discussed above, clearly due to the *ortho* aromatic hydrogens on the phenyl rings attached to P_C and P_D, respectively. Little or no deuterium was incorporated into these *ortho* positions but H/D exchange was essentially complete for the *meta* or *para* positions. Little or no deuterium incorporation into the PCH_2P group or into the hydrides [^{1}H, ^{1}H-{^{31}P}, and ^{2}H-{^{1}H}] occurred (n.m.r. evidence). In the experiment about 10% of the starting complex (**1b**) decomposed and some $[ReD_7\{P(C_6H_{11})_3\}_2]$ was detected in the final reaction solution, in addition to other (unidentified) species. Our results on H/D exchange between the complexes (**1b**) and (**1c**) and C_6D_6 are consistent with a process in which an active rhenium hydride species, possibly $[ReH_5\{P(C_6H_{11})_3\}_2]$, exchanges its hydrogens for deuterium by an oxidative addition/reductive elimination process with C_6D_6 and then by a similar oxidative addition/reductive elimination process exchanges D for H in the less sterically hindered positions (*meta* and *para*) of the diphosphine phenyl groups. These processes (simplified) are shown in the Scheme. The phenyl groups attached to the coordinated phosphorus of the dppm or vdpp ligands will be hindered by the very bulky tricyclohexylphosphine groups and we tentatively suggest that the monodentate diphosphine ligands are undergoing 'end over end' exchange by an intramolecular process (see Scheme).

Experimental

General methods and instrumentation were as described in recent publications from this laboratory.[20]

$[ReH_7\{P(C_6H_{11})_3\}_2]$.—This complex was originally prepared by the $NaBH_4$ reduction of $[ReOCl_3\{P(C_6H_{11})_3\}_2]$ in ethanol.[15] We find the phase-transfer method described below gives good yields more reliably.

The complex $[ReOCl_3\{P(C_6H_{11})_3\}_2]$ (4.8 g, 5.5 mmol) was added to a slurry of $NaBH_4$(2.2 g, 58 mmol) in a mixture of dry benzene (200 cm^3), ethanol (2.2 cm^3), and $N(CH_2CH_2OCH_2CH_2OMe)_3$ (0.46 g, 1.4 mmol). The resultant mixture was stirred vigorously with a mechanical stirrer for 2 h, water (50 cm^3) was then added, and stirring was continued for 30 min. The layers were separated without filtration, the benzene layer was washed with water, filtered through Whatman no. 1 filter paper, and evaporated to dryness under reduced pressure. Treatment of the residue with enthanol (20 cm^3) gave the required product as a greyish white crystalline solid. Yield 2.82 g, 68%.

$[ReH_5(PPh_3)_2(dppm\text{-}P)]$ (**1a**).—A solution of $[ReH_7(PPh_3)_2]$ (0.10 g, 0.14 mmol) and dppm (0.065 g, 0.17 mmol) in benzene (5 cm^3) was heated under reflux for 20 min. The resultant orange solution was then cooled to ambient temperature and ethanol (10 cm^3) added. This gave $[Re_2H_8(PPh_3)_2]$ (0.015 g) as red prisms which were filtered off. More (10 cm^3) ethanol was then added giving the required product as white microcrystals. Yield 0.071 g (46%).

$[ReH_5\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ (**1b**).—A solution of $[ReH_7\{P(C_6H_{11})_3\}_2]$ (0.74 g, 0.98 mmol) and dppm (0.41 g, 1.07 mmol) in benzene (25 cm^3) was heated at 80 °C for 3 h. The resultant yellow solution was filtered, methanol (30 cm^3) added, and the mixture was set aside at 4 °C for 16 h to give the required product as yellow crystals. Yield 0.81 g, 74%.

$[ReH_5\{P(C_6H_{11})_3\}_2(vdpp\text{-}P)]$ (**1c**).—This complex was prepared in a similar manner to $[ReH_5\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ by heating $[ReH_7\{P(C_6H_{11})_3\}_2]$ (1.01 g, 1.34 mmol) and vdpp (0.635 g, 1.60 mmol) in benzene (24 cm^3) for 4 h. A red oil precipitated after the addition of methanol. Vigorous scratching of this oil gave the required product as dark yellow microcrystals. Yield 0.87 g, 57%.

$[ReH_5\{P(C_6H_{11})_3\}_2(dppe\text{-}P)]$ (**1d**).—A solution of $[ReH_7\{P(C_6H_{11})_3\}_2]$ (0.500 g, 0.664 mmol) and dppe (0.317 g, 0.798 mmol) in benzene (7 cm^3) was heated at 80 °C for 1 h. The product was isolated by adding methanol to the mixture and then reducing the volume *in vacuo*. The resultant oil was crystallized by vigorous scratching to give the required product as a pale yellow powder. Yield 0.680 g, 89%.

$[ReH_5\{P(C_6H_{11})_3\}_2(cis\text{-dppen-}P)]$ (**1e**).—A solution of $[ReH_7\{P(C_6H_{11})_3\}_2]$ (0.500 g, 0.664 mmol) and *cis*-dppen (0.350 g, 0.884 mmol) was heated in benzene (11 cm^3) at 80 °C for 3 h.

The mixture was then cooled, benzene (14 cm^3) was added, and the yellow liquid was filtered to remove a small quantity of grey solid. Methanol (25 cm^3) was added to the filtrate and the volume of the solution was reduced slowly *in vacuo* to about 10 cm^3. The solid which separated was recrystallized from a mixture of benzene and methanol to give yellow microcrystals of the required product. Yield 0.39 g, 51%.

$[ReOCl_3(PPr^i_3)_2]$ (**2b**).—The phosphine PPr^i_3 (*ca.* 1.06 g, *ca.* 6.8 mmol) was added to a suspension of $[ReOCl_3(PPh_3)_2]$ (1.79 g, 2.04 mmol) in benzene (70 cm^3) and the resultant mixture was stirred for 4 h, after which all the $[ReOCl_3(PPh_3)_2]$ had dissolved. The volume of the solvent was then reduced to 5 cm^3 *in vacuo*, diethyl ether (40 cm^3) was added, and the mixture was set aside at 4 °C for 16 h to give the required product as dark green crystals. Yield 1.06 g, 82%.

$[ReOCl_3(PBu^t_2Me)_2]$ (**2a**).—This was prepared in a similar fashion, except that the reaction was carried out at *ca.* 40 °C for 2 h. Since complex (**2a**) was more soluble than (**2b**), the benzene in this preparation was completely removed *in vacuo* and the residue was washed with diethyl ether (*ca.* 5 cm^3), to give the required product as a dark green, microcrystalline solid in 71% yield.

$[Re_xO_xCl_{3x}\{Bu^t_2P(CH_2)_5PBu^t_2\}_x]$.—A mixture of $Bu^t_2P(CH_2)_5PBu^t_2$ (0.139 g, 0.386 mmol), $[ReOCl_3(AsPh_3)_2]^{21}$ (0.318 g, 0.345 mmol), and benzene (28 cm^3) was stirred under argon for 2 h to give the required product as a pale green powder. Yield 0.20 g.

$[ReH_7(PBu^t_2Me)_2]$.—This complex was prepared similarly to $[ReH_7\{P(C_6H_{11})_3\}_2]$. A solution of $[ReOCl_3(PBu^t_2Me)_2]$ (0.21 g, 0.33 mmol) in benzene (3 cm^3) was added to a mixture of $NaBH_4$ (0.22 g. 5.8 mmol), ethanol (0.10 g, 2.2 mmol), and $N(CH_2CH_2OCH_2CH_2OMe)_3$ (0.25 g, 0.8 mmol) in benzene (4 cm^3). Gas was evolved and the liquid turned brown over a period of 1 min. The mixture was stirred for 10 min, after which water (10 cm^3) was added and stirring was continued until effervescence had finished. The benzene layer was collected without filtration, washed with water (2 × 5 cm^3), filtered, and evaporated to dryness *in vacuo*. The resultant brown oil (0.057 g) could not be crystallized using either polar or non-polar solvents. The ^1H, $^1H-\{^{31}P\}$, and $^{31}P-\{^1H\}$ n.m.r. spectra suggested that the required product was present to the extent of *ca.* 80% in this oil.

The complex $[ReH_7(PPr^i_3)_2]$ was prepared similarly from $[ReOCl_3(PPr^i_3)_2]$ as an oil, in 40% yield. Proton n.m.r. spectroscopy indicated that it was essentially pure.

$[Re_xH_{7x}\{Bu^t_2P(CH_2)_5PBu^t_2\}_x]$.—The complex described above and of probable formulation $[Re_xO_xCl_{3x}\{Bu^t_2P(CH_2)_5PBu^t_2\}_x]$ (0.08 g, 0.12 mmol of Re) was added to a slurry of $NaBH_4$ (0.010 g, 0.26 mmol), ethanol (0.02 g, 0.43 mmol), and dry benzene (10 cm^3) and the resultant mixture was stirred under dinitrogen for 22 h. Water (5 cm^3) was then added and the mixture was stirred for a further 30 min. The benzene layer was collected, filtered, and then evaporated to dryness under reduced pressure. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the resultant brown oil showed that it was a complex mixture, but addition of ethanol to this oil gave, after 3 d, a crystalline white solid which was collected and dried. Proton n.m.r. spectroscopy indicated that the required product was attained with a purity of about 85%. Yield 0.01 g, 13%.

$[OsO_2Cl_2\{P(C_6H_{11})_3\}_2]$.—The analogous $PPhPr^i_2$ compound has been described previously. The adduct $P(C_6H_{11})_3{\cdot}CS_2$ (5.0 g, 14 mmol) was suspended in degassed benzene (1 cm^3) and heated until all the purple colour was discharged. The resultant solution of $P(C_6H_{11})_3$ was added, while still warm, to a solution of OsO_4 (0.738 g, 2.91 mmol) and concentrated HCl (4 cm^3) in ethanol (20 cm^3) and the resultant mixture was stirred for 20 min. The brown precipitate that formed was washed with water, ethanol, and finally, diethyl ether and dried. Yield 2.26 g, 91%.

$[OsH_6\{P(C_6H_{11})_3\}_2]$.—The complex $[OsO_2Cl_2\{P(C_6H_{11})_3\}_2]$ (0.51 g, ~0.6 mmol) was added to a solution of $LiAlH_4$ (0.06 g, 1.6 mmol) in dry, degassed tetrahydrofuran (8 cm^3) and the resultant brown suspension was stirred for 2 h. A second aliquot of $LiAlH_4$ (0.07 g, 1.8 mmol) was added and stirring was continued for a further 2 h. The final clear, colourless solution was hydrolyzed carefully at 0 °C with degassed ethanol (1.5 cm^3) until effervescence had finished. The solvents were then removed *in vacuo*, and degassed water (5 cm^3) and degassed diethyl ether (15 cm^3) were added to the residue. The resultant mixture was stirred rapidly for 5 min, after which the diethyl ether layer was separated, filtered under argon, and evaporated to dryness under reduced pressure. The resultant oily residue was washed with methanol (2 × 1 cm^3) and dried over P_2O_5 *in vacuo* to give a pale brown solid which was stored at −20 °C. The required hexahydride complex accounted for *ca.* 75% of the total intensity in the $^{31}P-\{^1H\}$ n.m.r. spectrum of this solid. Yield 0.16 g.

Purer samples of $[OsH_6\{P(C_6H_{11})_3\}_2]$, which were white, could be obtained by recrystallization of the above solid from ethanol-methanol. However, it could not be obtained pure enough for a satisfactory microanalysis and on crystallization a lot of material was lost.

mer-$[IrH_3\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ (**6a**). A solution of $[IrH_5\{P(C_6H_{11})_3\}_2]^{22}$ (0.046 g, 0.061 mmol) and dppm (0.025 g, 0.065 mmol) in benzene (3 cm^3) was heated at 80 °C for 30 min. The solvent was then removed and the residue was washed with diethyl ether (1 cm^3) and dried *in vacuo* to give the required product as a white powder. Yield 0.045 g, 65%.

The complex *mer*-$[IrH_3\{P(C_6H_{11})_3\}_2(dppe\text{-}P)]$ (**6b**) was prepared similarly as a white powder, in 75% yield, from $[IrH_5\{P(C_6H_{11})_3\}_2]$ and dppe.

$[OsH_4\{P(C_6H_{11})_3\}_2(dppm\text{-}P)]$ (**7**).—A sample of $[OsH_6\{P(C_6H_{11})_3\}_2]$ which was *ca.* 75% pure (0.100 g, *ca.* 0.10 mmol) and dppm (0.050 g, 0.130 mmol) were heated in benzene (4 cm^3) at 80 °C under argon for 1 h. The resultant dark yellow solution was filtered and reduced to 1 cm^3 *in vacuo*, then ethanol (6 cm^3) was added and the mixture was set aside at −20 °C for 6 h. Yield of pale brown-white microcrystals, 0.058 g (*ca.* 46%). The purity of the complex was never better than 90%, even after recrystallization from mixtures of benzene and methanol or cyclohexane and methanol, and satisfactory microanalyses were not obtained.

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