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## Synthesis, Reactivity, Molecular Structure, and Catalytic Activity of the Novel Dichlorodihydroosmium(IV) Complexes $\text{OsH}_2\text{Cl}_2(\text{PR}_3)_2$ ( $\text{PR}_3 = \text{P-}i\text{-Pr}_3$ , $\text{PMe-}t\text{-Bu}_2$ )

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The six-coordinate diamagnetic osmium(IV) complexes  $\text{OsH}_2\text{Cl}_2(\text{PR}_3)_2$  [ $\text{PR}_3 = \text{P-}i\text{-Pr}_3$  (2),  $\text{PMe-}t\text{-Bu}_2$  (3)] are prepared from  $\text{OsCl}_3 \cdot x\text{H}_2\text{O}$  and  $\text{PR}_3$  in boiling 2-propanol in ca. 80% yield. Treatment of 3 with CO leads to reductive elimination of  $\text{H}_2$  and formation of *all,trans*- $\text{OsCl}_2(\text{CO})_2(\text{PMe-}t\text{-Bu}_2)_2$  (4). Likewise, 3 reacts with excess  $\text{PMe}_3$  to give *cis*- $\text{OsCl}_2(\text{PMe}_3)_4$  (5). The crystal and molecular structure of 2 has been determined. Crystal data for 2: monoclinic,  $P2_1/c$ ,  $a = 12.2791$  (6) Å,  $b = 8.5700$  (3) Å,  $c = 23.5061$  (9) Å,  $\beta = 103.526$  (4)°,  $Z = 4$ ,  $R = 0.022$ ,  $R_w = 0.024$  based on 3705 observed unique reflections. The coordination polyhedron around the six-coordinate osmium atom is described as a somewhat distorted variant of the  $D_{4d}$  square antiprism with two vacant coordination sites in alternate positions at one square base of this polyhedron. The reaction of 4 with  $\text{LiAlH}_4$  in THF leads to the formation of *all,trans*- $\text{OsH}_2(\text{CO})_2(\text{PMe-}t\text{-Bu}_2)_2$  (6), whereas treatment of 2 and 3 with  $\text{NaBH}_4$  in methanol/benzene affords the hexahydrido complexes  $\text{OsH}_6(\text{PR}_3)_2$  in ca. 60% yield. These hexahydrides are probably catalyst precursors for hydrogen transfer from 2-propanol to ketones such as cyclohexanone, methylcyclohexanones, and acetophenone catalyzed by 2 and 3 in presence of  $\text{NaBH}_4$ . Compound 2 catalyzes the hydrogenation of olefins and dienes such as 1,5- and 1,3- $\text{C}_8\text{H}_{12}$  at considerable initial rates. Benzylideneacetone and benzylideneacetophenone are also reduced with 2 as catalyst to the saturated ketones with high selectivity.

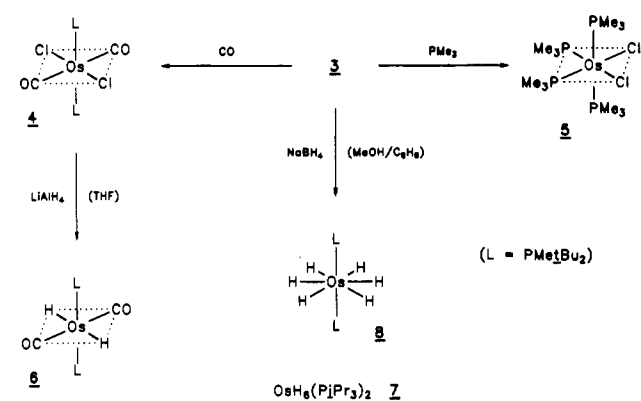
### Introduction

Homogeneous reduction of unsaturated organic compounds by platinum group metal complexes has played a key role in the fundamental understanding of catalytic reactions. The fact that 5d metals form stronger bonds than their 3d and 4d congeners with the ligands typically involved in catalytic transformations, has led to the general assumption that reactions conforming catalytic cycles are too slow for third-row transition-metal complexes and thus of no practical use in catalysis. As a consequence, a number of second-row metal compounds with excellent catalytic properties have been discovered and, in addition, various iridium and osmium complexes synthesized which could serve as stable models of reactive intermediates proposed in catalytic transformations with 4d metal species.<sup>1</sup> Representative examples of second-row metal catalysts are a variety of neutral chloro and hydrido phosphine ruthenium and rhodium complexes, such as  $\text{RuCl}_2(\text{PPh}_3)_3$ ,  $\text{RuHCl}(\text{PPh}_3)_3$ ,<sup>2</sup>  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_n$  ( $n = 2, 3$ ),<sup>3</sup>  $\text{RuH}_2(\eta^2\text{-H}_2)(\text{PPh}_3)_3$ ,<sup>4</sup>  $\text{RhCl}(\text{PPh}_3)_3$ ,<sup>5</sup> or  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ .<sup>6</sup> Furthermore, cationic diolefin rhodium complexes are also active and proved to be particularly selective catalysts.<sup>7</sup>

Besides these rhodium derivatives, it was shown more recently that some cationic iridium compounds behave similarly provided that appropriate ancillary ligands are linked to the metal.<sup>8</sup> As an example, Oro et al. reported that cationic (cyclooctadiene)-iridium complexes containing both P and N donor ligands, e.g.,  $\text{P}(\text{C}_6\text{H}_{11})_3$  and  $\text{PhCN}$ , are more active than their rhodium counterparts and able to reduce tetrasubstituted prochiral olefins.<sup>9</sup> Therefore, the once generalized view that third-row transition-metal compounds are unimportant in catalysis has had to be revised at least for iridium as the metal center.

A similar situation could be anticipated for osmium if the ligands and the reaction conditions would be appropriately selected. Following earlier reports,<sup>10</sup> Sanchez-Delgado et al. have observed that the complex  $\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$  does catalyze not only the isomerization of allylic alcohols but also the hydrogenation of acyclic and cyclic olefins, of dienes, alkynes,  $\alpha,\beta$ -unsaturated aldehydes, ketones, etc.<sup>11</sup> We have found<sup>12</sup> that a related hydridoosmium compound  $\text{OsHCl}(\text{CO})(\text{P-}i\text{-Pr}_3)_2$  (1) which in contrast to  $\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$  is coordinatively unsaturated, behaves similarly, and in presence of KOH or  $\text{NaBH}_4$  serves as a catalyst for hydrogen transfer from 2-propanol to cyclohexanone, acetophenone,<sup>13</sup> benzylideneacetone, benzylideneacetophenone,<sup>14</sup> and phenylacetylene.<sup>15</sup> Under hydrogen, complex 1 also catalyzes the reduction of cyclohexene, 1,3- and 1,4-cyclohexadiene, styrene, and diphenyl- and phenylacetylene.<sup>16,17</sup> In a detailed mechanistic

### Scheme I



investigation, evidence has been presented that in the hydrogenation of  $\text{PhC}\equiv\text{CH}$  the formation of styryl derivatives is the step

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that determines the selectivity for the hydrogenation to the alkene.<sup>17</sup>

As a continuation of our work in this field, we describe in the present article the synthesis of 16-electron six-coordinate osmium(IV) complexes  $\text{OsH}_2\text{Cl}_2(\text{PR}_3)_2$  (**2**, **3**), the X-ray crystal structure of **2**, the conversion of **2** and **3** into the hexahydrides  $\text{OsH}_6(\text{PR}_3)_2$  (**7**, **8**), and the first results of catalytic studies with the new dichlorodihydroosmium(IV) complexes.

## Results

The transformations observed in this work are summarized in Scheme 1. The new osmium(IV) complex **2** was definitely characterized by a X-ray structural study whose results are presented in Figure 1 and Tables I, V, and VI. Finally, an investigation of the catalytic activity of complexes **2** and **3** was undertaken, the results of which are collected in Figures 2-4 and Tables II-IV. These findings will be introduced at appropriate places in the sections that follow.

## Discussion

**Synthesis and Substitution Reactions of  $\text{OsH}_2\text{Cl}_2(\text{PR}_3)_2$  (**2**, **3**).** The five-coordinate hydroosmium(II) compound **1** was prepared by the reaction of  $\text{OsCl}_3 \cdot x\text{H}_2\text{O}$  with triisopropylphosphine in  $\text{CH}_3\text{OH}$  under reflux. We assumed that during the reaction methanol was dehydrogenated by the metal trichloride to give formaldehyde, which is the source of the CO ligand.<sup>12</sup> There is precedent for this process insofar as both Moers<sup>18</sup> and Shaw<sup>19</sup> have previously shown that  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{K}_2\text{OsCl}_6$  react with bulky phosphines such as  $\text{P}(\text{C}_6\text{H}_{11})_3$ ,  $\text{PMe-}t\text{-Bu}_2$ , and  $\text{PEt-}t\text{-Bu}_2$  in 2-methoxyethanol to form complexes  $\text{MHCl}(\text{CO})(\text{PR}_3)_2$ . Later, we have found that the reaction between  $\text{OsCl}_3 \cdot x\text{H}_2\text{O}$  and  $\text{PMe-}t\text{-Bu}_2$  in 2-methoxyethanol affords  $\text{OsHCl}(\text{CO})(\text{PMe-}t\text{-Bu}_2)_2$ .<sup>20</sup>

Provided the assumption that the CO ligand of the hydrido carbonyl compounds  $\text{MHCl}(\text{CO})(\text{PR}_3)_2$  is generated from formaldehyde is correct, the same reaction in 2-propanol instead of 2-methoxyethanol should lead to complexes without a carbonyl ligand. In fact,  $\text{OsCl}_3 \cdot x\text{H}_2\text{O}$  reacts with  $\text{P-}i\text{-Pr}_3$  and  $\text{PMe-}t\text{-Bu}_2$  in boiling 2-propanol to give the dihydridodichloro complexes **2** and **3** in ca. 80% yield. They have been isolated as brown-yellow (**2**) and deep red (**3**) crystalline solids that are moderately air-stable and easily soluble in solvents such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and THF. We note that Chatt and co-workers<sup>21</sup> have already prepared dihydridodichloroosmium(IV) compounds such as  $\text{OsH}_2\text{Cl}_2(\text{PEt}_2\text{Ph})_3$ , which, however, are coordinatively saturated and considered to be derivatives of the well-known tetrahydrides  $\text{OsH}_4(\text{PR}_3)_3$ .

Although **2** and **3** are six-coordinate osmium(IV) compounds, they are diamagnetic, as can be seen from the sharp lines in the NMR spectra. The most characteristic features of the  $^1\text{H}$  NMR spectra are (1) the triplet in the high-field region corresponding to the hydride ligands, and (2) the lack of virtual coupling for the signals of the  $t\text{-Bu}$  and  $i\text{-Pr}$  methyl protons, which points to

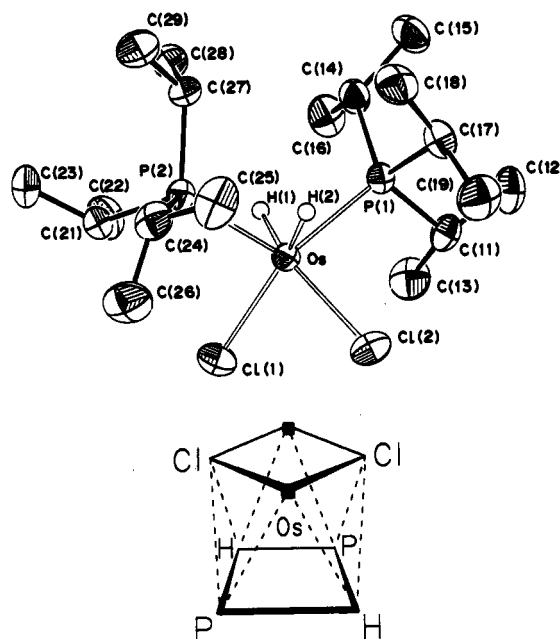


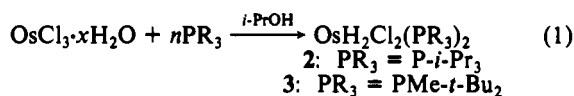
Figure 1. Top: (a) Crystal structure of complex **2**. Hydride ligands were drawn on calculated positions (see text). Bottom: (b) Sketch of the coordination sphere of complex **2** (■ symbolizes open coordination sites).

Table I. Selected Bond Distances (Å) and Angles (deg) for Complex **2**

Os-P(1)	2.304 (3)	Os-P(2)	2.289 (3)
Os-Cl(1)	2.372 (2)	Os-Cl(2)	2.383 (2)
Os-H(1) <sup>a</sup>	1.663	Os-H(2) <sup>a</sup>	1.663
P(1)-Os-P(2)	112.15 (5)	P(2)-Os-H(2)	81.1
P(1)-Os-Cl(1)	145.59 (9)	Cl(1)-Os-Cl(2)	83.43 (5)
P(1)-Os-Cl(2)	91.79 (6)	Cl(1)-Os-H(1)	76.3
P(1)-Os-H(1)	79.5	Cl(1)-Os-H(2)	133.0
P(1)-Os-H(2)	77.1	Cl(2)-Os-H(1)	126.5
P(2)-Os-Cl(1)	91.66 (6)	Cl(2)-Os-H(2)	74.7
P(2)-Os-Cl(2)	141.06 (9)	H(1)-Os-H(2)	148.9
P(2)-Os-H(1)	89.1		

<sup>a</sup>Hydride ligands are placed in calculated positions according to the electrostatic potential calculations (see ref 24).

a cis arrangement of the two phosphine units. The  $^{31}\text{P}$  NMR spectra of both **2** and **3** show only one singlet, which under off-resonance conditions due to P-H coupling is split into a triplet.



The reactivity of compound **3** toward 2-electron donor ligands has been briefly investigated. Treatment of **3** with carbon monoxide leads to reductive elimination of  $\text{H}_2$  and formation of the 18-electron complex  $\text{OsCl}_2(\text{CO})_2(\text{PMe-}t\text{-Bu}_2)_2$  (**4**) (Scheme I). The six-coordinate dihydride thus behaves similarly to the Chatt compound  $\text{OsH}_2\text{Cl}_2(\text{PEt}_2\text{Ph})_3$ , which under comparable conditions reacts with CO to give  $\text{OsCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_3$ .<sup>21</sup> Owing to the IR and NMR spectroscopic data of **4**, there is no doubt that the complex possesses an all,trans configuration, similar to that found in  $\text{OsCl}_2(\text{CO})_2(\text{PR}_3)_2$  ( $\text{PR}_3 = \text{PMe}_2\text{Ph}$ ,  $\text{PEt}_3$ )<sup>22a</sup> and  $\text{OsCl}_2(\text{PMe}_3)_2[\text{P}(\text{OMe})_3]_2$ .<sup>22b</sup> Complex **4** does not isomerize on heating in benzene for several hours at 80 °C.

Elimination of  $\text{H}_2$  from **3** also occurs on reaction with excess  $\text{PMe}_3$ , leading by concomitant phosphine ligand displacement to *cis*- $\text{OsCl}_2(\text{PMe}_3)_4$  (**5**). This compound was originally prepared from  $\text{OsH}(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)_3$  and  $\text{HCl}$ <sup>23</sup> and has been

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characterized by comparison of the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra with those of an authentic sample.

**Molecular Structure of 2.** The crystal structure of **2** is made up of discrete molecules separated by normal van der Waals forces. The molecular structure illustrating the numbering system used is shown in Figure 1a, and selected bond lengths and angles are given in Table I.

Any attempt to describe the metal coordination sphere obviously requires positioning of the two hydrides. Unfortunately, even the careful X-ray analysis did not reveal clearly the location of these ligands. The two highest peaks in the residual electronic density map, calculated after all atoms (including the non-hydride hydrogen atoms) were put into the model, were reasonably assignable to the hydrides, but as is common for hydridometal complexes, they showed too short Os–H distances (mean value 1.43 Å). A refinement of these peaks using the X-ray data did not improve the Os–H separations. As a check on the validity of these positions, an electrostatic potential energy calculation<sup>24</sup> was carried out, based on the whole molecule without the hydrides and with the value of the Os–H bond distance (1.66 (1) Å) determined by neutron diffraction for the related osmium(IV) complex  $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$ .<sup>25</sup> Only two minima were obtained, located in close proximity to the residual peaks mentioned above. With this agreement in mind, we tried to introduce the calculated positions for the two hydrides in the description of the molecular structure of **2**.

We first note that no easy selection of an idealized six-apex polyhedron can be made from the data in Table I to describe the metal environment. However, it is possible to define the coordination sphere around osmium as derived from a distorted square antiprism of ideal  $D_{4d}$  symmetry with two vacant coordination sites. One of the two square planes is made up by the two phosphorus atoms and the two hydrides, which occupy alternate positions (Figure 1b). The chloro ligands are located in the second plane, which ideally should be rotated by  $45^\circ$  from the first one, also occupying trans apices.

The different types of ligands present in **2** and the existence of two vacant coordination sites reduce the actual symmetry of the molecule to a nearly  $C_2$  point group. The 2-fold axis maintained in the molecule passes through the metal and the midpoint of the P(1)–P(2) [or Cl(1)–Cl(2) or H(1)–H(2)] segment. (As is evident from Figure 1, this 2-fold axis is not maintained if the phosphine isopropyl groups are rotated.)

The distortion of the idealized polyhedron can be discussed in several ways. The observed dihedral angle between the planes defined by Cl(1)–Os–Cl(2) and H(1)–Os–H(2) is  $48(1)^\circ$  and thus differs slightly from the theoretical value of  $45^\circ$ . The dihedral angle between the P(1)–Os–P(2) and H(1)–Os–H(2) planes is  $87(1)^\circ$ . Furthermore, the deviations of P(1), H(1), P(2), and H(2) from the least-squares plane passing through these atoms are 0.448 (1), –0.391 (1), 0.396 (1) and –0.454 (1) Å. The thus indicated distortion from the idealized square antiprism probably arises from the different steric requirements and bond distances of the ligands coordinated to the metal center.

However, no steric arguments can be used to justify the unusual arrangement of the ligands around the osmium, as is inferred from the small angle between the two phosphines ( $112.15(5)^\circ$ ) (the most space-requiring ligands in the complex) or the two chlorides ( $83.43(5)^\circ$ ) and the large angle between the two hydrides ( $149^\circ$ ). As steric influences should be minimized if an octahedral coordination would be adopted, we assume that electronic effects are responsible for the unusual arrangement.

The Os–P distances in **2** (2.304 (3) and 2.289 (3) Å) are similar to those found in the complexes  $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$  and  $\text{OsH}_4(\text{PEt}_2\text{Ph})_3$  (mean value 2.297 (3) Å) where the phosphine ligands occupy pseudo-cis positions to the hydrides.<sup>25</sup> They are, however, significantly shorter than calculated on the basis of Pauling's

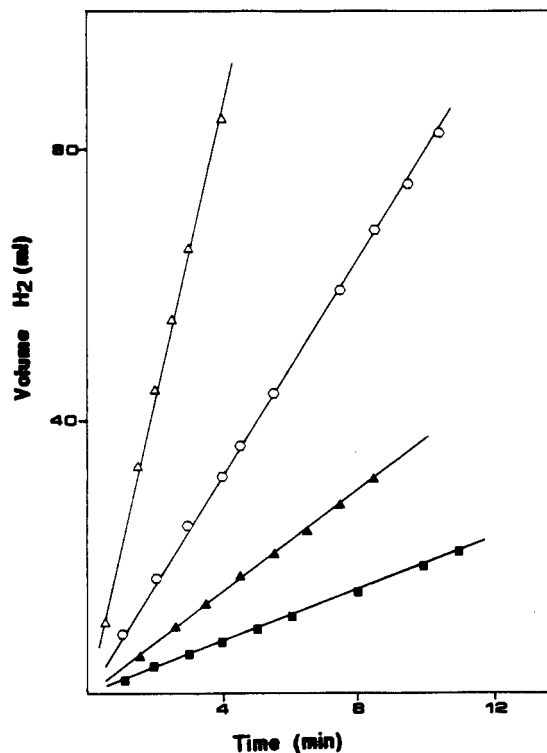


Figure 2.  $\text{H}_2$  gas uptake plots for the hydrogenation of olefins catalyzed by **2** in 2-propanol at  $60^\circ\text{C}$  (1 atm of  $\text{H}_2$ ;  $2.5 \times 10^{-3}$  M **2**, 0.25 M olefin): ( $\Delta$ ) cyclooctene; ( $\circ$ ) styrene; ( $\blacktriangle$ ) cyclohexene; ( $\blacksquare$ ) methylstyrene.

covalent radii (2.43 Å)<sup>26</sup> or compared with the Os–P distances in  $\text{OsCl}_4(\text{PMe}_2\text{Ph})_2$  (2.448 (3) Å).<sup>27</sup> The Os–Cl bond lengths in **2**, on the other hand, are ca. 0.06 Å longer than those of  $\text{OsCl}_4(\text{PMe}_2\text{Ph})_2$ ,<sup>27</sup> which might be a consequence of the different geometry.

**New Osmium(II) and Osmium(VI) Hydrido Complexes.** Whereas the chloro hydrido compound  $\text{OsHCl}(\text{CO})(\text{PMe}-i\text{-Bu})_2$  reacts with  $\text{LiAlH}_4$  in ether followed by subsequent treatment with methanol to give the tetrahydride  $\text{OsH}_4(\text{CO})(\text{PMe}-i\text{-Bu})_2$ ,<sup>28</sup> the reaction of **4** with  $\text{LiAlH}_4$  in THF leads to the formation of the dihydrido complex  $\text{OsH}_2(\text{CO})_2(\text{PMe}-i\text{-Bu})_2$  (**6**). There is good evidence from the IR and NMR spectroscopic data, that during the ligand substitution process the stereochemistry on osmium (all,trans) remains unchanged. Interestingly, in the analogous triisopropylphosphine complex  $\text{OsH}_2(\text{CO})_2(\text{P}-i\text{-Pr})_3$  which is obtained from  $\text{OsH}(\eta^2\text{-H}_2\text{BH}_2)(\text{CO})(\text{P}-i\text{-Pr})_2$  in boiling methanol,<sup>20</sup> the two hydrides are not in the trans but in the cis position.

Reaction of the dichloro dihydrido compounds **2** and **3** with  $\text{NaBH}_4$  in methanol/benzene at room temperature gives the new hexahydrides **7** and **8** (Scheme I) in ca. 60% yield. Other derivatives of general composition  $\text{OsH}_6(\text{PR}_3)_2$  are already known and have been prepared from different osmium(III) and osmium(VI) precursors on treatment with  $\text{LiAlH}_4$ .<sup>29,30</sup>

On the basis of  $T_1$  measurements, Crabtree and co-workers have shown<sup>31</sup> that in contrast to  $\text{RuH}_6(\text{PCy}_3)_2$ ,<sup>32</sup> the corresponding osmium complexes are most probably "classical" hydrides. We assume that this is true also for **7** and **8**. Besides the signals of the phosphine protons, the  $^1\text{H}$  NMR spectra of **7** and **8** show only

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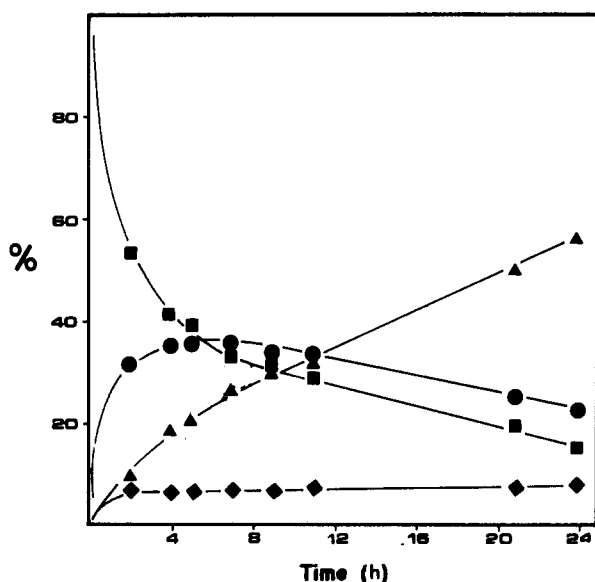
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**Table IV.** Hydrogen Transfer Reactions from 2-Propanol to Ketones Catalyzed by Complexes **2** and **3** in the Presence of NaBH<sub>4</sub>

ketone	time, min	<b>2</b>		<b>3</b>	
		mol of SH <sub>2</sub> / mol of [M]	cis SH <sub>2</sub> / trans SH <sub>2</sub>	mol of SH <sub>2</sub> / mol of [M]	cis SH <sub>2</sub> / trans SH <sub>2</sub>
cyclohexanone	5			29	
	15	98		65	
	45	93		92	
2-methylcyclohexanone	5	12		8	
	15	20		12	
	45	37		22	
3-methylcyclohexanone	5	39	1.78	38	2.17
	15	82	1.73	65	2.25
	45			86	2.30
4-methylcyclohexanone	5	34	0.54	33	0.53
	15	65	0.23	55	0.49
	45	90	0.15	88	0.52
acetophenone	5	10		5	
	15	24		15	
	45	47		23	

Reaction conditions: [M] =  $2.5 \times 10^{-3}$  M; [ketone]/[M] = 100; [NaBH<sub>4</sub>]/[M] = 5; solvent, 2-propanol (8 mL); T = 83 °C, p = 1 atm. Activation was performed at 83 °C over 1 h.



**Figure 4.** Isomerization of cycloocta-1,5-diene catalyzed by **2** in the presence of NaBH<sub>4</sub> (2-propanol; T = 83 °C; 1 atm of Ar;  $2.5 \times 10^{-3}$  M **2**;  $1.25 \times 10^{-3}$  M NaBH<sub>4</sub>; 0.25 M 1,5-C<sub>8</sub>H<sub>12</sub>): (■) 1,5-C<sub>8</sub>H<sub>12</sub>; (▲) 1,3-C<sub>8</sub>H<sub>12</sub>; (●) 1,4-C<sub>8</sub>H<sub>12</sub>; (◆) C<sub>8</sub>H<sub>14</sub>.

shown in Figure 4 provide good evidence that the reaction of 1,5-C<sub>8</sub>H<sub>12</sub> to 1,4-C<sub>8</sub>H<sub>12</sub> occurs more rapidly but that 1,3-C<sub>8</sub>H<sub>12</sub> is the thermodynamically preferred product.

In summary, complex **2** catalyzes the hydrogenation of olefins and diolefins as well as the selective reduction of benzylideneacetone and benzylideneacetophenone. In presence of NaBH<sub>4</sub>, complex **2** also catalyzes the hydrogen transfer from 2-propanol to  $\alpha,\beta$ -unsaturated and saturated ketones and the isomerization of cycloocta-1,5-diene. There is now accumulating evidence<sup>11,13-17,34</sup> that from the metals in the iron triad not only ruthenium but also osmium forms a variety of complexes that behave as good catalysts for the reduction of unsaturated organic substrates.

### Experimental Section

All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under nitrogen prior to use. Styrene, methylstyrene, cyclohexene, cyclooctene, and cycloocta-1,3- and -1,5-diene were purified by passage through an alumina column. Cyclohexanone, methylcyclohexanones, benzylideneacetone, and benzylideneacetophenone (Merck, 98%) were used without further purification.

**Physical Measurements.** NMR spectra were recorded on Varian EM 360 L (<sup>1</sup>H) and Bruker WH 90 FT (<sup>31</sup>P) instruments. Chemical shifts are expressed in ppm upfield from SiMe<sub>4</sub> (<sup>1</sup>H) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Coupling constants *J* and *N* [*N* = *J*(PH) + *J*'(PH)] are given in hertz.

Infrared spectra were measured with a Perkin-Elmer 783 spectrophotometer in CH<sub>2</sub>Cl<sub>2</sub> solutions between NaCl plates. Mass spectra were recorded with a Varian MAT CH7 instrument (70eV). The analyses of the products of the catalytic reactions were carried out with a Perkin-Elmer 3920B gas chromatograph using a FFAP on Chromosorb 6HP 80/100 mesh (3.6 m × 1.8 in.) column. The chromatograph was connected to a Perkin-Elmer M2 calculation integrator.

**Preparation of OsH<sub>2</sub>Cl<sub>2</sub>(P-*i*-Pr)<sub>2</sub> (**2**).** A suspension of OsCl<sub>3</sub>·xH<sub>2</sub>O (54% Os) (500 mg; 1.42 mmol) in 15 mL of 2-propanol was treated with P-*i*-Pr<sub>3</sub> (1.5 mL; 7.5 mmol) and heated for 24 h under reflux. After the mixture was cooled to room temperature, a brown-yellow precipitate was formed, which was filtered off, repeatedly washed with methanol and ether, and dried in vacuo: yield 660 mg (78%); mp 132 °C dec. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\bar{\nu}$ (OsH) 2240, 2235 cm<sup>-1</sup>. <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  2.29 (m, 6 H, PCHCH<sub>3</sub>), 1.32 (dd, *J*(HH) = 7.0, *J*(PH) = 10.0 Hz, 36 H, PCHCH<sub>3</sub>), -16.34 (t, *J*(PH) = 35.0 Hz, 2 H, OsH<sub>2</sub>). <sup>31</sup>P NMR (90 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  44.52 (s; t in off-resonance). Anal. Calcd for C<sub>18</sub>H<sub>44</sub>Cl<sub>2</sub>OsP<sub>2</sub>: C, 37.04; H, 7.60; M<sub>r</sub>, 583.6. Found: C, 36.68; H, 7.72; M<sub>r</sub>, 585 (MS).

**Preparation of OsH<sub>2</sub>Cl<sub>2</sub>(PMe-*t*-Bu)<sub>2</sub> (**3**).** This complex was prepared analogously as described for **2**, starting with OsCl<sub>3</sub>·xH<sub>2</sub>O (500 mg; 1.42 mmol) and PMe-*t*-Bu<sub>2</sub> (1.5 mL; 7.5 mmol): dark red crystals; yield 680 mg (80%); mp 134 °C dec. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\bar{\nu}$ (OsH) 2250 cm<sup>-1</sup>. <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  1.79 (d, *J*(PH) = 9.8 Hz, 6 H, PCH<sub>3</sub>), 1.35 (d, *J*(PH) = 13.8 Hz, 36 H, PCCH<sub>3</sub>), -15.01 (t, *J*(PH) = 35.0 Hz, 2 H, OsH<sub>2</sub>). <sup>31</sup>P NMR (90 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  40.11 (s; t in off-resonance). Anal. Calcd for C<sub>18</sub>H<sub>44</sub>Cl<sub>2</sub>OsP<sub>2</sub>: C, 37.04; H, 7.60; M<sub>r</sub>, 583.6. Found: C, 36.66; H, 7.68; M<sub>r</sub>, 585 (MS).

**Preparation of OsCl<sub>2</sub>(CO)<sub>2</sub>(PMe-*t*-Bu)<sub>2</sub> (**4**).** Carbon monoxide was passed through a solution of **3** (62 mg; 0.11 mmol) in 5 mL of benzene for 10 min at room temperature. The resulting yellow solution was concentrated in vacuo to ca. 0.5 mL. After slow addition of 5 mL of hexane a yellow precipitate was formed, which was filtered off, washed with small quantities of hexane, and dried in vacuo: yield 45 mg (94%); mp 122 °C dec. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\bar{\nu}$ (CO) 1959 cm<sup>-1</sup>. <sup>1</sup>H NMR (60 MHz, C<sub>6</sub>H<sub>6</sub>, 25 °C):  $\delta$  1.83 (vt, *N* = 6.8 Hz, 6 H, PCH<sub>3</sub>), 1.58 (vt, *N* = 12.6 Hz, 36 H, PCCH<sub>3</sub>). <sup>31</sup>P NMR (90 MHz, C<sub>6</sub>H<sub>6</sub>, 25 °C):  $\delta$  3.71 (s). Anal. Calcd for C<sub>20</sub>H<sub>42</sub>Cl<sub>2</sub>O<sub>2</sub>OsP<sub>2</sub>: C, 37.67; H, 6.64; M<sub>r</sub>, 637.6. Found: C, 37.76; H, 6.59; M<sub>r</sub>, 639 (MS).

**Reaction of **3** with PMe<sub>3</sub>: Alternative Preparation of cis-OsCl<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (**5**).** A solution of **3** (60 mg; 0.10 mmol) in 5 mL of benzene was treated with PMe<sub>3</sub> (38  $\mu$ L; 0.40 mmol) and stirred for 10 min at room temperature. The virtually colorless solution was concentrated in vacuo to ca. 0.3 mL, and the residue was then treated with 5 mL of hexane. A white microcrystalline precipitate was formed, which was filtered off, repeatedly washed with hexane, and dried in vacuo: yield 48 mg (85%). **5** was characterized by comparison of the <sup>1</sup>H and <sup>31</sup>P NMR spectra with those of an authentic sample.<sup>23</sup>

**Preparation of OsH<sub>2</sub>(CO)<sub>2</sub>(PMe-*t*-Bu)<sub>2</sub> (**6**).** A suspension of **4** (88 mg; 0.14 mmol) in 10 mL of THF was treated with an excess of LiAlH<sub>4</sub> (ca. 150 mg) and stirred for 30 min at room temperature. After the solvent was removed in vacuo, the solid residue was extracted twice with 5 mL of hexane. The hexane solution was filtered, and the filtrate was concentrated in vacuo until a white precipitate separated. The mixture was stored at -78 °C overnight; the white microcrystalline solid was filtered off, washed with small quantities of hexane (-20 °C) and dried

Table V. Crystallographic Data

formula	$C_{18}H_{44}Cl_2OsP_2$	space group	$P2_1/c$
MW	583.60	$T, K$	293
$a, \text{\AA}$	12.2791 (6)	$\lambda, \text{\AA}$	0.710 69
$b, \text{\AA}$	8.5700 (3)	$\rho, \text{g cm}^{-3}$	1.612
$c, \text{\AA}$	23.5061 (9)	$\mu, \text{cm}^{-1}$	56.65
$\beta, \text{deg}$	103.526 (4)	transm coeff	0.33–0.46
$V, \text{\AA}^3$	2405.0 (2)	$R$	0.022
$Z$	4	$R_w$	0.024

in vacuo: yield 50 mg (63%); mp 120 °C dec. IR ( $CH_2Cl_2$ ):  $\bar{\nu}(\text{CO})$  1880;  $\bar{\nu}(\text{OsH})$  1820  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (60 MHz,  $C_6H_6$ , 25 °C):  $\delta$  1.76 (vt,  $N = 5.7$  Hz, 6 H,  $PCH_3$ ), 1.56 (vt,  $N = 13.0$  Hz, 36 H,  $PCCH_3$ ),  $-8.07$  (t,  $J(\text{PH}) = 20.0$  Hz, 2 H,  $OsH_2$ ).  $^{31}\text{P NMR}$  (90 MHz,  $C_6H_6$ , 25 °C):  $\delta$  34.80 (s; t in off-resonance). Anal. Calcd for  $C_{20}H_{44}O_2OsP_2$ : C, 42.24; H, 7.80. Found: C, 42.21; H, 7.43.

**Preparation of  $OsH_6(\text{P-}i\text{-Pr}_3)_2$  (7).** A solution of **2** (115 mg; 0.20 mmol) in 10 mL of benzene was first treated with  $NaBH_4$  (76 mg, 2.0 mmol) and then dropwise with 1 mL of methanol. After the reaction mixture was stirred for 10 min at room temperature, the solution was filtered. The filtrate was concentrated to ca. 0.5 mL in vacuo, and 10 mL of methanol was added. The solution was again concentrated until a white precipitate separated and then stored at  $-78$  °C for 2 h. The white microcrystalline solid was filtered off, washed with small quantities of methanol, and dried in vacuo: yield 62 mg (60%); mp 43 °C dec. IR ( $CH_2Cl_2$ ):  $\bar{\nu}(\text{OsH})$  1980, 1910  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (60 MHz,  $C_6H_6$ , 25 °C):  $\delta$  1.80 (m, 6 H,  $PCH_2CH_3$ ), 1.23 (dvt,  $N = 13.0$ ,  $J(\text{HH}) = 7.0$  Hz, 36 H,  $PCHCH_3$ ),  $-10.13$  (t,  $J(\text{PH}) = 10.0$  Hz, 6 H,  $OsH_6$ ).  $^{31}\text{P NMR}$  (90 MHz,  $C_6D_6$ , 25 °C):  $\delta$  56.78 (s; sept in off-resonance). Anal. Calcd for  $C_{18}H_{48}OsP_2$ : C, 41.84; H, 9.36. Found: C, 41.73; H, 9.62.

**Preparation of  $OsH_6(\text{PMe-}t\text{-Bu}_2)_2$  (8).** This complex was prepared analogously as described for **7**, starting with **3** (110 mg; 0.19 mmol) and  $NaBH_4$  (80 mg; 2.1 mmol): white crystals; yield 58 mg (59%); mp 59 °C dec. IR ( $CH_2Cl_2$ ):  $\bar{\nu}(\text{OsH})$  1985, 1920  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (60 MHz,  $C_6D_6$ , 25 °C):  $\delta$  1.85 (vt,  $N = 6.0$  Hz, 6 H,  $PCH_3$ ), 1.24 (vt,  $N = 13.0$  Hz, 36 H,  $PCCH_3$ ),  $-9.51$  (t,  $J(\text{PH}) = 10.0$  Hz, 6 H,  $OsH_6$ ).  $^{31}\text{P NMR}$  (90 MHz,  $C_6D_6$ , 25 °C):  $\delta$  46.77 (s; sept in off-resonance). Anal. Calcd for  $C_{18}H_{48}OsP_2$ : C, 41.84; H, 9.36;  $M_r$ , 516.7. Found: C, 41.39; H, 9.56;  $M_r$ , 519 (MS).

**Hydrogenation Reactions.** A degassed solution of the catalyst in 2-propanol, 1,2-dichloroethane, or toluene (4 mL) was syringed through a silicone septum into a 25-mL flask attached to a gas buret (Afora 516256), which was in turn connected to a Schlenk manifold. The system was evacuated and refilled with hydrogen three times, and the flask was then immersed in a constant-temperature bath. The substrate, dissolved in deaerated 2-propanol, 1,2-dichloroethane, or toluene (4 mL) was subsequently introduced through the septum, and the mixture was vigorously shaken during the run. For the experiments involving pre-treatment, the catalyst solution was shaken under hydrogen for 30 min at the reaction temperature prior to introduction of the substrate.

**Hydrogen Transfer Reactions.** These reactions were carried out under argon in refluxing 2-propanol with magnetic stirring. The equipment consisted of a 25-mL round-bottomed flask, fitted with a condenser and provided with a serum cap. In a typical procedure, a solution of **2** (0.02 mmol) in 4 mL of 2-propanol was refluxed for 1 h, and then 2 mmol of the substrate in 4 mL of 2-propanol was injected.

With  $NaBH_4$  as cocatalyst, the procedure was as follows: To a solution of **2** (0.02 mmol) in 2 mL of 2-propanol was added  $NaBH_4$  (3.8 mg, 0.1 mmol) in 2 mL of 2-propanol. The resulting solution was refluxed for 1 h, and then 2 mmol of the substrate in 4 mL of 2-propanol was injected.

**X-ray Data Collection, Solution, and Refinement of the Structure of **2**.** Single crystals were obtained from a  $CH_2Cl_2/OEt_2$  solution at room temperature. A prismatic block of dimensions  $0.48 \times 0.14 \times 0.08$  mm was used for intensity data collection; further details are given in Table V. A Siemens AED diffractometer was used ( $\omega/2\theta$  scan mode), graphite monochromated  $Mo K\alpha$  radiation,  $\theta$  range  $1.5$ – $25^\circ$  ( $0 \leq h \leq 15$ ,  $0 \leq k \leq 10$ ,  $-28 \leq l \leq 28$ ). A total of 4782 reflections were measured; from 4080 unique reflections 3705 with  $F \geq 5\sigma(F)$  were considered observed

Table VI. Final Atomic Coordinates ( $\times 10^4$ ) and Thermal Parameters ( $\text{\AA}^2 \times 10^4$ ) for the Non-Hydrogen Atoms of Complex **2**

atom	$x/a$	$y/b$	$z/c$	$U(\text{equi})^a$
Os	2280 (1)	1345 (1)	1403 (1)	284 (1)
Cl(1)	3141 (1)	-1056 (1)	1261 (1)	603 (5)
Cl(2)	874 (1)	-306 (1)	1626 (1)	531 (4)
P(1)	2024 (1)	3178 (1)	2077 (1)	294 (3)
P(2)	2807 (1)	2455 (1)	623 (1)	311 (3)
C(11)	2073 (3)	2099 (5)	2768 (2)	373 (14)
C(12)	2008 (4)	3112 (6)	3294 (2)	561 (18)
C(13)	3038 (4)	938 (6)	2929 (2)	565 (18)
C(14)	3063 (3)	4791 (5)	2226 (2)	390 (15)
C(15)	2768 (4)	6239 (5)	2556 (2)	535 (20)
C(16)	4243 (4)	4235 (6)	2523 (2)	523 (16)
C(17)	662 (3)	4219 (5)	1952 (2)	417 (15)
C(18)	502 (4)	5313 (6)	1421 (2)	536 (18)
C(19)	-338 (4)	3145 (7)	1896 (2)	636 (21)
C(21)	4089 (4)	1604 (5)	457 (2)	384 (14)
C(22)	5128 (4)	1605 (6)	963 (2)	549 (18)
C(23)	4370 (4)	2258 (6)	-97 (2)	562 (19)
C(24)	1734 (4)	2001 (6)	-61 (2)	445 (15)
C(25)	572 (4)	2588 (7)	-36 (2)	621 (20)
C(26)	1698 (5)	279 (6)	-223 (2)	650 (21)
C(27)	2954 (4)	4622 (5)	622 (2)	387 (13)
C(28)	4110 (4)	5143 (5)	962 (2)	491 (18)
C(29)	2648 (4)	5451 (6)	29 (2)	594 (20)

$$^a U(\text{equi}) = \frac{1}{3} [U(1,1) + U(2,2) + U(3,3)].$$

and used in the refinement. Three standard reflections were measured approximately every hour as a check on crystal and instrument stability; no deviation was observed. An empirical absorption correction using  $\psi$  scans of 12 reflections was applied.

The osmium atom was found on a Patterson map, and all other atoms were found in subsequent Fourier calculations. Hydrogen atoms, except the hydride ligands, were found in successive difference Fourier maps and were refined riding on their carbon atoms with two common thermal parameters (one for the terminal methyls and the other for the CH groups bonded to the phosphorus atoms). All non-hydrogen atoms were anisotropically refined. Full-matrix least-squares refinements were carried out by using the SHELX program.<sup>35</sup> The final weighting scheme used was  $w = k/[\sigma^2(F) + gF^2]$  with  $k = 0.0312$  and  $g = 0.0002$ . The atomic scattering factors, with anomalous dispersion corrections for Os, Cl, and P, were taken from ref 36. Maximum shift/esd was 0.001. The two largest peaks in the last difference map (0.70 and 0.63  $e/\text{\AA}^3$ ) were located close to the positions obtained for the hydride ligands by using electrostatic potential energy calculations.<sup>24</sup> The next peak (0.43  $e/\text{\AA}^3$ ) was close to the osmium metal. Atomic and thermal parameters are summarized in Table VI.

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**Supplementary Material Available:** Listings of crystal data, bond lengths and bond angles, atomic positional parameters, anisotropic thermal parameters, least-squares planes, and interatomic contacts between 2.20 and 3.40  $\text{\AA}$  (17 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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