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Syntheses, Spectroscopic Characterizations, and X-ray Structures of New Os(η^2-H_2) Compounds Containing Azole Ligands

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The dihydrido–dichloro complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) reacts with 2,2′-biimidazole (H_2bim) to give the dihydrogen derivative $[OsCl(\eta^2\text{-}H_2)(H_2bim)(P\text{-}i\text{-}Pr_3)_2]Cl$ (**2**). The molecular structure of **2** has been determined by X-ray investigation. **2** crystallizes with a dichloromethane molecule in the triclinic space group $P\bar{1}$ with $a = 12.133(1)$ Å, $b = 16.034(1)$ Å, $c = 18.321(1)$ Å, $\alpha = 105.10(1)°$, $\beta = 90.01(1)°$, $\gamma = 93.87(1)°$, and $Z = 4$. The coordination geometry around the osmium center can be rationalized as a distorted octahedron with the two phosphine ligands disposed mutually *trans*. The remaining coordination sites of the octahedron are occupied by the dihydrogen ligand, the chloride atom, and by two nitrogen atoms of the chelate 2,2′-biimidazole ligand. One of the two acidic NH groups of the 2,2′-biimidazole ligand of **2** can be deprotonated by $NaBH_4$ to give $[OsCl(\eta^2\text{-}H_2)(Hbim)(P\text{-}i\text{-}Pr_3)_2]$ (**3**). Similarly the 2,2′-biimidazole ligand of **2** is deprotonated by dimers of the type $[M(\mu\text{-}OMe)(diolefin)]_2$ to form the heterobimetallic compounds $[(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)ClOs(\mu\text{-}Hbim)RhCl(COD)]$ (COD = 1,5-cyclooctadiene, **4**), $[(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)ClOs(\mu\text{-}Hbim)IrCl(COD)]$ (**5**), and $[(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)ClOs(\mu\text{-}Hbim)IrCl(TFB)]$ (TFB = tetrafluorobenzobarrelene, **6**). The addition of pyrazole to **1** leads to the complex *trans-dichloro*-$[OsCl_2(\eta^2\text{-}H_2)(Hpz)(P\text{-}i\text{-}Pr_3)_2]$ (**7**), which is transformed into its isomer *cis-dichloro*-$[OsCl_2(\eta^2\text{-}H_2)(Hpz)(P\text{-}i\text{-}Pr_3)_2]$ (**8**) by stirring in hexane at 60 °C. The molecular structure of **8** has also been determinated. **8** crystallizes with a pyrazole molecule in the monoclinic space group $C2/c$ (No. 15) with $a = 21.575(3)$ Å, $b = 8.743(1)$ Å, $c = 31.341(9)$ Å, $\beta = 90.98(2)°$, and $Z = 8$. The coordination geometry around the osmium center could be described as based on a distorted octahedron with the two phosphine ligands occuping the apical positions. The equatorial plane is formed by the dihydrogen and the pyrazole ligands mutually *cis*-disposed and the two chloride atoms are also *cis*-disposed.

Introduction

Since the first report by Kubas *et al.* on the coordination of molecular hydrogen to a transition metal,[1] the spectroscopic characterization and some theoretical aspects, on the nature and stability of the $M(\eta^2\text{-}H_2)$ bond of such compounds have been intensively studied.[2] However, the investigation of the roles that this type of compounds can play during some homogeneous catalytic processes has received relatively little attention.[3] This has in part been due to the reported compounds and the ancillary ligands contained by them being very similar. This problem is a result of the scarce number of useful synthetic routes described for the preparation of dihydrogen complexes.

The dihydrogen compounds previously reported have generally been prepared by coordination of molecular hydrogen to an unsaturated metallic fragment or by protonation of saturated hydride complexes.[2e] We have recently observed that the addition of HX molecules to osmium(II) hydrides also leads to dihydrogen complexes. Thus, the silyl–dihydrogen derivative $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P\text{-}i\text{-}Pr_3)_2$[3g] and the alkynyl–hydride–dihydrogen compounds $OsH(C_2R)(\eta^2\text{-}H_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (R = Ph, $SiMe_3$)[3h] were prepared by reaction of $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ and $OsH_2(CO)(P\text{-}i\text{-}Pr_3)_2$ with $HSiEt_3$ and $H{-}C{\equiv}C{-}R$ (R = Ph, $SiMe_3$) respectively.

Two years ago, the synthesis, reactivity and the catalytic activity of the complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) was described.[4] This compound has been found to be a very useful starting material to prepare $Os(\eta^2\text{-}H_2)$ derivatives. We recently reported that **1** reacts with $K[EtOCS_2]$ and $K[CH_3COS]$ in methanol to give the dihydrogen complexes $Os(\eta^2\text{-}S_2COCH_3)Cl(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$, $Os(\eta^2\text{-}S_2COEt)(\eta^1\text{-}SC(S)OEt)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$, $Os(\eta^2\text{-}OSCCH_3)Cl(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$, and $Os(\eta^2\text{-}OSCCH_3)(\eta^1\text{-}SC(O)CH_3)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$, which are the first dihydrogen compounds containing S-donor ligands.[5]

As a continuation of our work in this field, we have now studied the reactivity of **1** toward azole compounds. The reactions carried out lead to new $Os(\eta^2\text{-}H_2)$ complexes containing N-donor ligands.[6] The present paper describes the synthesis and spectroscopic characterization of the new compounds and the molecular structure of two of them.

Results and Discussion

2,2′-Biimidazolate Compounds. Treatment of $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) with 2,2′-biimidazole (H_2bim) in a 2:5 molar ratio, in toluene at 65 °C, gives a yellow solution from which the compound $[OsCl(\eta^2\text{-}H_2)(H_2bim)(P\text{-}i\text{-}Pr_3)_2]Cl$ (**2**, eq1) is separated as a

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[⊕] Abstract published in *Advance ACS Abstracts*, January 1, 1994.

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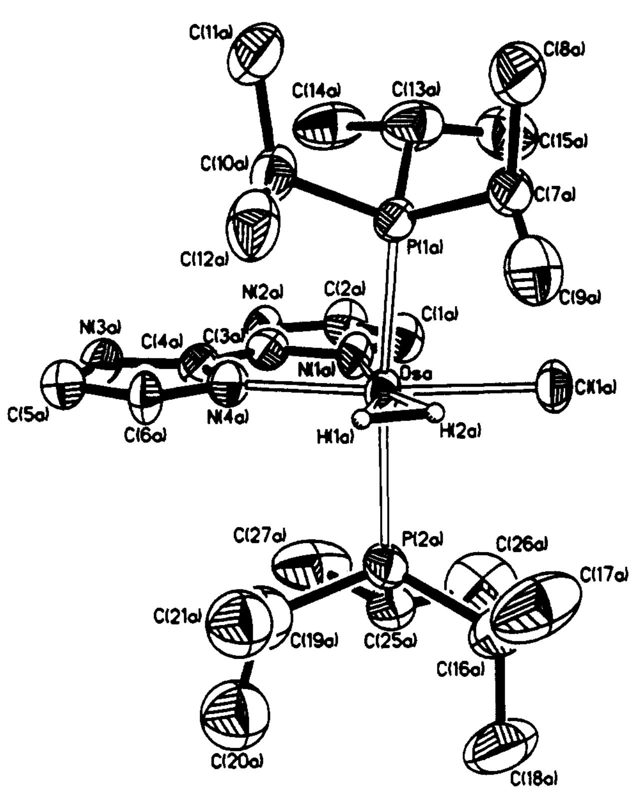
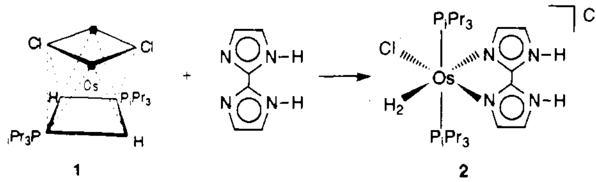


Figure 1. ORTEP diagram of $[OsCl(\eta^2\text{-}H_2)(H_2bim)(P\text{-}i\text{-}Pr_3)_2]^+$ (**2**). Thermal ellipsoids are shown at the 50% level.

yellow solid in 80% yield. **2** was fully characterized by elemental analysis, IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies, and by an X-ray diffraction study.



(1)

The IR spectrum in Nujol shows a very strong ν(N–H) absorption between 3300 and 3000 cm^{-1}. At room temperature, the ^1H NMR spectrum in chloroform-d_1 contains a triplet due to the dihydrogen ligand at –5.7 ppm, with a P–H coupling constant of 9.6 Hz. At temperatures lower than room temperature, a broadening of this signal is observed. The T_1(min) value found at 300 MHz is 22 ms. In agreement with the nonclassical structure, the hydrogen–hydrogen distance calculated from the T_1(min) value, assuming rapid internal motion of the dihydrogen ligand, is 0.95 Å.[7] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at –1.80 ppm, indicating that the two phosphine ligands are equivalent.

A view of the molecular geometry of **2**[8] is shown in Figure 1. Selected bond distances and angles are listed in Table 1. The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands disposed mutually *trans* (P–Os–P= 169.62 (6)°). The osmium coordination sphere is completed by the dihydrogen ligand and the chloride atom mutually *cis* disposed and by the chelate 2,2′-biimidazole ligand bonded through two nitrogen atoms.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $[OsCl(\eta^2\text{-}H_2)(H_2bim)(P\text{-}i\text{-}Pr_3)_2]Cl$ (**2**)[a]

	a	b		a	b
Os–P(1)	2.396(2)	2.389(2)	Os–N(4)	2.110(8)	2.101(7)
Os–P(2)	2.390(2)	2.396(2)	Os–H(1)	1.65(10)	1.54(6)
Os–Cl(1)	2.426(2)	2.426(2)	Os–H(2)	1.66(9)	1.59(6)
Os–N(1)	2.135(6)	2.135(6)	H(1)–H(2)	0.95(16)	1.02(13)
N(1)–C(1)	1.378(10)	1.368(9)	N(4)–C(4)	1.329(11)	1.331(11)
N(1)–C(3)	1.318(13)	1.341(12)	N(4)–C(6)	1.353(10)	1.361(10)
C(1)–C(2)	1.354(14)	1.351(14)	C(4)–N(3)	1.357(13)	1.364(13)
C(2)–N(2)	1.349(13)	1.346(13)	N(3)–C(5)	1.350(12)	1.350(11)
N(2)–C(3)	1.351(12)	1.360(11)	C(5)–C(6)	1.405(15)	1.374(16)
C(3)–C(4)	1.417(11)	1.406(11)			
P(1)–Os–P(2)	169.49(8)	169.74(8)	Cl(1)–Os–N(1)	87.5(2)	87.4(2)
P(1)–Os–Cl(1)	89.28(8)	88.42(8)	Cl(1)–Os–N(4)	163.1(2)	163.5(2)
P(1)–Os–N(1)	95.0(2)	95.8(2)	Cl(1)–Os–H(1)	113(4)	116(3)
P(1)–Os–N(4)	92.0(2)	91.9(2)	Cl(1)–Os–H(2)	80(3)	79(4)
P(1)–Os–H(1)	85(4)	86(3)	N(1)–Os–N(4)	75.6(3)	76.1(3)
P(1)–Os–H(2)	81(3)	83(3)	N(1)–Os–H(1)	160(4)	156(3)
P(2)–Os–Cl(1)	88.39(8)	89.12(8)	N(1)–Os–H(2)	167(3)	166(4)
P(2)–Os–N(1)	95.1(2)	94.0(2)	N(4)–Os–H(1)	84(4)	80(3)
P(2)–Os–N(4)	93.2(2)	93.3(2)	N(4)–Os–H(2)	117(3)	118(4)
P(2)–Os–H(1)	87(4)	87(3)	H(1)–Os–H(2)	33(5)	38(4)
P(2)–Os–H(2)	88(3)	87(3)			

[a] The first set of values (a) corresponds to the bond distances and angles of the molecule shown in Figure 1; the second set of values (b) corresponds to the related parameters observed in the second independent molecule.

The Os–P bond distances are significantly longer (ca. 0.1 Å) than the Os–P lengths found for the two phosphine ligands similarly disposed in the osmium(IV) complexes $OsH_4(PMe_2Ph)_3$ (2.317(2), 2.307(2) Å)[9] and $OsH_4(PEt_2Ph)_3$ (2.294, 2.298 Å).[10] These observed distances are, however, similar to those found in the osmium(II) complexes $Os(C_2CO_2Me)(CH{=}C(H)C(OMe){=}O)(CO)(P\text{-}i\text{-}Pr_3)_2$ (2.400(4), 2.403(4) Å),[3h] $Os((E)\text{-}CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (2.398(2), 2.395(2) Å),[11] $OsH(CH_3)(CO)_2(P\text{-}i\text{-}Pr_3)_2$ (2.384(1), 2.377(1) Å),[12] and $OsHCl_2(\equiv CCH_2Ph)(P\text{-}i\text{-}Pr_3)_2$ (2.429(1), 2.424(1) Å),[13] where the triisopropylphosphine ligands also occupy relative *trans* positions. The Os–Cl bond length, 2.426(1) Å, is also longer than the typical Os–Cl distances in osmium(IV) halides;[14] however, this distance agrees well with the Os–Cl separation observed in the osmium(II) complex $Os((E)\text{-}CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (2.444(3) Å). With regard to this structural data, there is no doubt that **2** is an osmium(II) derivative and, therefore, a dihydrogen compound.

The atoms of the dihydrogen ligand were assigned to residual electron density situated at about 1.6 Å from the metallic center, and then the two hydrogen atoms were refined freely, which resulted in the parameters shown in Table 1. The hydrogen–hydrogen separations for the two molecules of the complex in the asymmetric unit so calculated, 0.95(16) and 1.02(13) Å, agree well with those previously reported for other dihydrogen compounds characterized by X-ray diffraction.[15] In addition, it should

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(7) At the temperature of minumum T_1, $\tau = 0.62/(2\pi\nu)$ and equation for dipolar relaxation simplify to $r_{H-H} = 4.611\ (T_1\ (min)/\nu)^{1/6}$ for rapid rotation (ν (MHz), T_1 (s)). See: Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876.

(8) The structure of **2** has two chemically equivalent, but crystallographically independent, molecules of the complex in the asymmetric unit. Values used in the discusion of the geometry of **2** correspond to the average value of those shown in Table 1.

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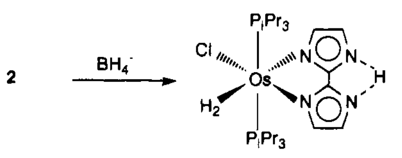
be mentioned that the H–H axis is located within the plane perpendicular to the P–Os–P vector.

The 2,2′-biimidazole group coordinates as a chelate planar ligand. The Os–N(1) distance (*trans* to H$_2$) is slightly longer than the Os–N(4) length (*trans* to Cl), suggesting that the dihydrogen ligand has a higher *trans* influence than the chloride ligand. The N–C distances are clearly in the range expected and deserve no further comments.

One of the two acidic NH groups of the 2,2′-biimidazole ligand of **2** can be easily deprotonated by NaBH$_4$. Treatment of **2** with NaBH$_4$ in toluene at room temperature leads to **3**, which was separated by addition of methanol, as a white solid in 82% yield.

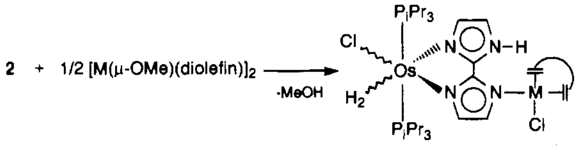


(2)

3

The spectroscopic data of **3** are consistent with the formulation shown in eq 2. The IR spectrum shows a very broad ν(NH) absorption from 3000 to 2300 cm^{-1}, indicating the presence of an NH bond remaining in the coordinated monoanion [Hbim]$^-$.[16] The ^{1}H NMR spectrum in chloroform-d_1 at room temperature has in the high-field region a broad signal at −5.80 ppm due to the dihydrogen ligand. The T_1(min) value of this signal at 300 MHz is 28 ms, which corresponds to an H–H distance of 0.98 Å.[7] The ^{31}P{^{1}H} NMR spectrum contains a singlet at −1.59 ppm, indicating that the two phosphine ligands are equivalent.

The 2,2′-biimidazole ligand of **2** can also be deprotonated by dimers of the type [M(μ-OMe)(diolefin)]$_2$ (M = Rh, Ir; diolefin = 1,5-cyclooctadiene (COD), tetrafluorobenzobarrelene (TFB)). The reaction of **2** with these compounds leads to the heterobinuclear complexes **4**–**6** according to eq 3.



(3)

M = Rh, diolefin = COD (**4**)
M = Ir, diolefin = COD (**5**), TFB (**6**)

These complexes were isolated as yellow solids in 88 (**4**), 85 (**5**), and 78% (**6**) yield. Their IR and NMR spectra are in good agreement with the proposed structures; the IR spectra show strong and narrow ν(N–H) absorptions at about 3305 cm^{-1}. In accordance with a square-planar disposition of ligands around the rhodium and iridium atoms, the ^{1}H NMR spectra of **4** and **5** contain four resonances assignable to the diolefin, two due to the olefinic protons at about 5.0 and 3.0 ppm, and the other two due to the aliphatic protons at about 2.3 and 1.7 ppm. The ^{1}H NMR spectra of **6** shows three diolefinic resonances, one aliphatic resonance at 5.30 ppm, and two olefinic resonances at 3.40 and 2.30 ppm. The high-field regions of the spectra of the three compounds show broad signals between −5.62 and −5.71 ppm, corresponding to the dihydrogen ligands. T_1(min) values found at 300 MHz are between 31 and 35 ms, which correspond to H–H distances of about 1.0 Å (Table 2).[7,17] Interestingly Table 2 shows that T_1(min) values of the dihydrogen ligands of **4**–**6** are higher (ca. 10 ms) than that observed for the dihydrogen ligand of **2**. This suggests that the H–H distances of the dihydrogen ligands of dinuclear complexes **4**–**6** are longer (ca. 0.05 Å) than the H–H distance in **2**.

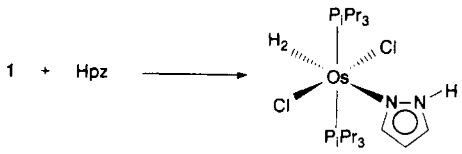
Table 2. Minimum T_1 Value and Distance $r_{\text{H-H}}$ of the Dihydrogen Ligand

complex	ν (MHz)	T (K)	T_1(min) (ms)	$r_{\text{H-H}}$ (Å)[a]
2	300	213	22	0.95
3	300	233	28	0.98
4	300	243	32	1.00
5	300	243	31	1.00
6	300	233	35	1.02
7	300	223	25	0.97
8	300	233	33	1.01

[a] For no rotation, see ref 17.

Pyrazole Compounds. We have previously reported that the reactions of **1** with anionic bidentate nucleophilic ligands such as [EtOCS$_2$]$^-$ and [CH$_3$COS]$^-$ produce the substitution of a chloride anion and the formation of dihydrogen compounds.[5] In this paper, we described above that the reaction of **1** with the neutral bidentate nucleophilic 2,2′-biimidazole ligand also produces the substitution of a chloride group and subsequent formation of the dihydrogen derivative **2**.

The dihydride–dihydrogen transformation involved in these reactions could be a result of the rearrangement of the coordination polyhedron, which changes from square antiprism with two vacant coordination sites in **1** to octahedron in the above mentioned dihydrogen derivatives. This possibility prompted us to investigate the simple addition of pyrazole (Hpz) to **1**. In fact, treatment of a hexane suspension of **1** with pyrazole leads to a white solid in 70% yield, which was characterized as the dihydrogen complex **7** (eq 4) by elemental analysis, IR and ^{1}H and ^{31}P{^{1}H} NMR spectroscopies.

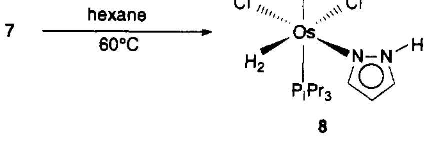


(4)

7

The mutually *trans* disposition of the two chloride ligands of **7** was inferred from the IR spectrum in Nujol, which contains a ν(Os–Cl) absorption at 305 cm^{-1}. The dihydrogen ligand appears in the ^{1}H NMR spectrum at room temperature in benzene-d_6 as a triplet at −6.47 ppm, with a P–H coupling constant of 10 Hz. At 223 K in toluene-d_8 a value of T_1(min) = 25 ms was obtained for this signal, which corresponds to a H–H distance of 0.97 Å.[7] In accordance with the mutually *trans* disposition of the phosphine ligands, a singlet at −1.37 ppm was observed, in the ^{31}P{^{1}H} NMR spectrum.

The complex **7** is transformed into its isomer **8** by stirring in hexane at 60 °C (eq 5). The IR spectrum of **8**, in contrast to the IR spectrum of **7**, contains two ν(Os–Cl) absorptions at 300 and 240 cm^{-1}. In this case, the dihydrogen ligand appears in the ^{1}H NMR spectrum at room temperature in benzene-d_6 as a triplet at −8.16 ppm, with a P–H coupling constant of 11 Hz. The T_1(min) value found at 300 MHz is 33 ms, which corresponds to a H–H distance of 1.01 Å.



(5)

8

The definitive characterization of **8** as a *cis*-dichloro complex came from an X-ray diffraction experiment on a single crystal of **8**. A view of the molecular geometry of this complex is shown in Figure 2. Selected bond distances and angles are listed in Table 3.

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(17) For no rotation, according to the equation $r_{\text{H-H}} = 5.815\,(T_1\,(\text{min})/\nu)^{1/6}$ (ν (MHz), the hydrogen–hydrogen distances of the dihydrogen ligands of the complexes **2**–**8** should be 1.19 (**2**), 1.24 (**3**), 1.27 (**4**), 1.26 (**5**), 1.29 (**6**), 1.22 (**7**), and 1.27 (**8**) Å.[7]

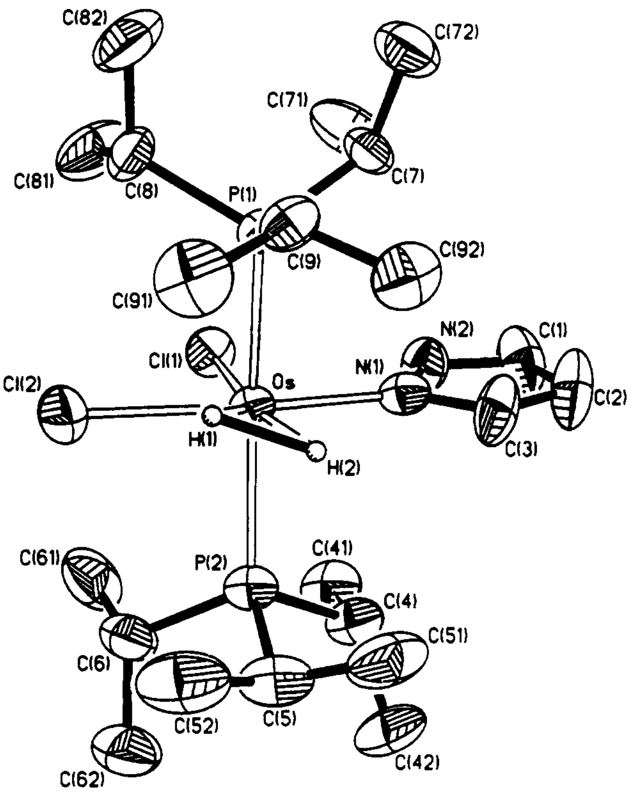

Figure 2. ORTEP diagram of *cis-dichloro*-[$OsCl_2(\eta^2\text{-}H_2)(Hpz)(P\text{-}i\text{-}Pr_3)_2$] (**8**). Thermal ellipsoids are shown at the 50% level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complex *cis-dichloro*-[$OsCl_2(\eta^2\text{-}H_2)(Hpz)(P\text{-}i\text{-}Pr_3)_2$] (**8**)

Os–P(1)	2.390(2)	H(1)–H(2)	1.3(1)
Os–P(2)	2.384(2)	N(1)–N(2)	1.336(9)
Os–Cl(1)	2.496(2)	N(1)–C(3)	1.342(11)
Os–Cl(2)	2.426(2)	N(2)–C(1)	1.335(13)
Os–N(1)	2.103(7)	C(1)–C(2)	1.369(15)
Os–H(1)	1.54(6)	C(2)–C(3)	1.378(14)
Os–H(2)	1.67(8)		
P(1)–Os–P(2)	168.99(8)	H(1)–Os–P(1)	72(2)
P(1)–Os–Cl(1)	95.76(7)	H(1)–Os–P(2)	98(2)
P(1)–Os–Cl(2)	89.96(7)	H(1)–Os–Cl(1)	145(2)
P(1)–Os–N(1)	90.6(2)	H(1)–Os–Cl(2)	61(2)
P(2)–Os–Cl(1)	95.23(7)	H(1)–Os–N(1)	126(2)
P(2)–Os–Cl(2)	89.91(8)	H(1)–Os–H(2)	49(3)
P(2)–Os–N(1)	91.0(2)	H(2)–Os–P(1)	87(3)
Cl(1)–Os–Cl(2)	87.04(7)	H(2)–Os–P(2)	82(3)
Cl(1)–Os–N(1)	85.0(2)	H(2)–Os–Cl(1)	165(3)
Cl(2)–Os–N(1)	172.0(2)	H(2)–Os–Cl(2)	108(3)
		H(2)–Os–N(1)	80(3)

The geometry around the metal center could be ideally described as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying relative *trans*-positions (P(1)–Os–P(2) = 168.99(8)°). The normal plane to the P–Os–P vector contains the dihydrogen and the pyrazole ligands mutually *cis*-disposed, and the two chloride atoms also *cis*-disposed (Cl(1)–Os–Cl(2)) = 87.04(7)°).

The Os–P(1) and Os–P(2) distances are 2.390(2) and 2.384(2) Å, statistically identical to those observed in **2**. So, they can be considered as typical Os–P distances in osmium(II) derivatives containing phosphine ligands disposed mutually *trans*. The Os–Cl(2) distance (Cl *trans* to N), 2.426(2) Å, is the same as that found in **2**, where the chloride atom is also disposed *trans* to the nitrogen atom. However, the Os–Cl(1) bond length (Cl *trans* to H_2), 2.496(2), is significatively longer than the Os–Cl distance in **2** and about 0.17 Å longer than the typical Os–Cl distances in osmium(IV) halides.[14]

The atoms of the dihydrogen ligand were assigned to residual electron density situated at about 1.6 Å from the metallic center, then the two hydrogen atoms were refined freely, which resulted in the parameters shown in Table 3. From the H–H separation obtained, 1.3(1) Å, it is not possible to deduce the nature of the hydrogen–hydrogen interaction. However, on the basis of the Os–P and Os–Cl distances and the spectroscopic properties described above, we assume that **8** is a dihydrogen derivative.

Concluding Remarks. The study of the reactivity of the dihydride–dichloro complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) toward nucleophilic reagents shows that **1** is a very useful starting material to prepare dihydrogen compounds. The reactions of **1** with anionic and neutral bidentate and neutral monodentate nucleophilic ligands lead to $Os(\eta^2\text{-}H_2)$ derivatives. These transformations are a result of the rearrangement of the coordination polyhedron, which changes from square antiprism with two vacant coordination sites in **1** to octahedron in the dihydrogen derivatives.

In addition, it should be mentioned that these reactions are a new route for the synthesis of dihydrogen complexes. So, we can conclude that not only are useful routes to prepare $M(\eta^2\text{-}H_2)$ derivatives the coordination of molecular hydrogen to an unsaturated metallic fragment, the protonation of saturated hydride complex and the addition of HX molecules to unsaturated metal hydride complexes, but also the coordination of nucleophilic ligands to unsaturated dihydrides.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere by using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) was prepared by a published method.[4]

Physical Measurements. NMR spectra were recorded on a Varian 200 XL or on a Varian UNITY 300 spectrophotometer at room temperature. Chemical shifts are expressed in parts per million, upfield from $Si(CH_3)_4$ (^1H), and 85% H_3PO_4 (^{31}P). Coupling constants J and N [$N = J(PH) + J(P'H)$] are given in hertz. Infrared spectra were recorded on a Perkin-Elmer 783 instrument. C and H analyses were carried out on a Perkin-Elmer 240 C microanalyzer. X-ray measurements were recorded on a Siemens-Stoe AED-2 diffractometer. Full-matrix least-squares refinements were carried out by using the SHELTL-PLUS system of computer programs.[18]

Preparation of [$OsCl(\eta^2\text{-}H_2)(H_2bim)(P\text{-}i\text{-}Pr_3)_2$]Cl (2). A suspension of compound **1** (150 mg, 0.26 mmol) in 10 mL of toluene was treated with H_2bim (87 mg, 0.65 mmol). After being stirred for 16 h at 65 °C, the solution was concentrated to dryness and then 12 mL of dichloromethane were added and the solution was filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL; addition of hexane caused the precipitation of a yellow solid. The solvent was decanted, and the solid was washed twice with hexane and then dried in vacuo. Yield: 148 mg (80%). Anal. Calcd for $C_{24}H_{50}Cl_2N_4OsP_2$: C, 40.15; H, 7.03; N, 7.80. Found: C, 40.54; H, 7.33; N, 7.78. IR (Nujol): ν(NH) 3000–3300 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 14.08, 13.87 (each br, each 1H, NH), 7.98, 7.31, 7.08, 6.95 (each br, each 1H, =CH bim), 1.99 (m, 6 H, PC*H*CH$_3$), 1.06 (dvt, N = 12.9 Hz, J(HH) = 6.7 Hz, 18 H, PCHC*H*$_3$), 0.86 (dvt, N = 13.1 Hz, J(HH) = 6.7 Hz, 18 H, PCHC*H*$_3$), −5.70 (t, J(PH) = 9.6 Hz, 2H, $Os(\eta^2\text{-}H_2)$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ −1.80 (s). T_1 (ms, $Os(\eta^2\text{-}H_2)$, 300 MHz, CD_2Cl_2) = 72 (293 K), 38 (253 K), 27 (233 K), 23 (223 K), 22 (213 K), 27 (193 K).

Preparation of [$OsCl(\eta^2\text{-}H_2)(Hbim)(P\text{-}i\text{-}Pr_3)_2$] (3). A suspension of compound **2** (100 mg, 0.14 mmol) in 16 mL of toluene was treated with $NaBH_4$ (106 mg, 2.8 mmol). After the mixture was stirred for 20 min at room temperature, the suspension was filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL; addition of methanol caused the precipitation of a white solid. The solvent was decanted, and the solid was washed twice with methanol and then dried in vacuo. Yield: 78 mg (82%). Anal. Calcd for $C_{24}H_{49}ClN_4OsP_2$: C, 42.31; H, 7.24; N, 8.22. Found: C, 42.71; H, 7.41; N, 7.98. IR (Nujol): ν(NH) 2300–3000 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 15.52 (br, 1H, NH), 7.82, 7.24, 7.13, 6.92 (each br, each 1H, =CH bim), 2.02 (m, 6 H, PC*H*CH$_3$), 1.08 (dvt, N = 12.6, J(HH) = 6.6 Hz, 18 H, PCHC*H*$_3$), 0.85 (dvt, N = 12.5, J(HH) = 6.5 Hz, 18 H, PCHC*H*$_3$), −5.80 (br, 2H, $Os(\eta^2\text{-}H_2)$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ −1.59 (s). T_1 (ms, $Os(\eta^2\text{-}H_2)$, 300 MHz, CD_2Cl_2) = 40 (293 K), 31 (253 K), 28 (233 K), 31 (213 K).

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(18) Sheldrick, G. M. SHELXTL PLUS; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

Table 4. Atomic Coordinates (×10^4; ×10^5 for Os Atoms) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^4; Å^2 × 10^5 for Os Atoms) for the Compound [OsCl(η^2-H$_2$)(H$_2$bim)(P-*i*-Pr$_3$)$_2$]Cl·CH$_2$Cl$_2$ (**2**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]/U_{iso}[b]	atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]/U_{iso}[b]
Os(a)	60430(3)	79240(2)	29811(2)	317(1)	Cl(1b)	448(2)	644(1)	2052(1)	43(1)
H(1a)	6370(87)	7323(72)	2146(57)	84(36)	P(1b)	2474(2)	2074(1)	1806(1)	35(1)
H(2a)	6504(72)	7908(62)	2123(48)	57(27)	P(2b)	−1274(2)	2261(2)	2575(1)	39(1)
Cl(1a)	6146(2)	9460(1)	3052(1)	44(1)	N(1b)	−8(5)	1782(4)	927(3)	33(2)
P(1a)	7988(2)	8033(2)	3250(1)	36(1)	N(2b)	−413(7)	2113(6)	−132(4)	43(3)
P(2a)	4203(2)	7822(2)	2484(1)	43(1)	N(3b)	224(6)	4075(5)	935(4)	42(3)
N(1a)	5573(5)	8257(4)	4138(4)	34(3)	N(4b)	523(5)	3340(4)	1770(4)	33(3)
N(2a)	5073(7)	7887(6)	5166(5)	43(3)	C(1b)	−323(7)	1039(6)	386(5)	38(3)
N(3a)	5383(7)	5960(5)	4066(5)	45(3)	C(2b)	−558(8)	1247(6)	−263(5)	46(4)
N(4a)	5826(6)	6725(4)	3256(4)	36(3)	C(3b)	−76(7)	2435(5)	601(5)	36(3)
C(1a)	5407(7)	8991(6)	4705(5)	44(4)	C(4b)	213(7)	3272(6)	1059(5)	37(3)
C(2a)	5096(7)	8759(6)	5338(5)	48(4)	C(5b)	578(8)	4653(6)	1582(6)	52(4)
C(3a)	5370(7)	7600(6)	4438(5)	38(3)	C(6b)	747(7)	4197(6)	2107(5)	43(4)
C(4a)	5504(7)	6766(6)	3957(5)	38(3)	C(7b)	3202(7)	1467(6)	2377(5)	46(4)
C(5a)	5601(8)	5391(6)	3406(5)	48(4)	C(8b)	4442(9)	1447(9)	2301(7)	91(6)
C(6a)	5897(7)	5881(5)	2893(5)	41(3)	C(9b)	2924(9)	1745(8)	3224(6)	70(5)
C(7a)	8799(7)	8625(6)	2649(5)	46(4)	C(10b)	3203(7)	3166(6)	1907(6)	53(4)
C(8a)	10060(8)	8631(8)	2746(8)	84(6)	C(11b)	4356(9)	3225(8)	1579(7)	80(5)
C(9a)	8481(9)	8393(7)	1817(5)	63(4)	C(12b)	3219(9)	3698(6)	2737(6)	64(4)
C(10a)	8518(8)	6941(6)	3136(6)	52(4)	C(13b)	2914(9)	1505(7)	837(5)	61(4)
C(11a)	9661(9)	6896(7)	3486(7)	77(5)	C(14b)	2538(9)	1911(8)	224(5)	74(5)
C(12a)	8466(9)	6421(6)	2312(6)	63(4)	C(15b)	2609(11)	570(8)	624(6)	87(6)
C(13a)	8517(9)	8619(7)	4212(5)	63(4)	C(16b)	−1466(7)	1679(7)	3333(5)	50(4)
C(14a)	8075(9)	8199(8)	4823(5)	70(5)	C(17b)	−546(9)	1821(9)	3915(6)	85(6)
C(15a)	8367(9)	9582(7)	4422(6)	70(5)	C(18b)	−2569(8)	1777(8)	3740(6)	69(5)
C(16a)	4083(8)	8450(8)	1764(6)	69(5)	C(19b)[b]	−1560(17)	3438(16)	2842(14)	57(7)
C(17a)	4988(11)	8373(11)	1181(7)	106(8)	C(20b)[b]	−2777(18)	3655(19)	2902(16)	90(10)
C(18a)	2956(9)	8334(9)	1352(7)	96(7)	C(21b)[b]	−898(28)	3934(22)	3558(16)	72(12)
C(19a)[b]	3745(17)	6629(18)	2188(15)	75(9)	C(22b)[b]	−1768(18)	3362(13)	3128(12)	61(7)
C(20a)[b]	2487(18)	6419(20)	2105(17)	93(10)	C(23b)[b]	−2072(20)	3907(14)	2589(12)	76(8)
C(21a)[b]	4362(23)	6125(19)	1494(16)	75(9)	C(24b)[b]	−895(25)	3853(21)	3729(17)	76(11)
C(22a)[b]	3580(18)	6724(13)	1870(13)	71(7)	C(25b)	−2485(8)	1764(8)	1961(6)	66(5)
C(23a)[b]	3096(21)	6137(15)	2356(13)	81(8)	C(26b)	−2575(9)	799(7)	1732(6)	68(5)
C(24a)[b]	4365(17)	6307(15)	1240(12)	61(7)	C(27b)	−2580(8)	2140(8)	1251(6)	70(5)
C(25a)	3030(8)	8243(6)	3102(6)	58(4)	Cl(2b)	507(3)	6295(2)	755(1)	70(1)
C(26a)	3102(10)	9211(9)	3348(8)	95(6)	C(30)	2681(10)	4879(8)	4668(7)	80(5)
C(27a)	2928(9)	7837(10)	3787(6)	89(6)	Cl(3)	1947(4)	5530(3)	4210(2)	114(2)
Cl(2a)	5285(3)	3740(2)	4251(1)	66(1)	Cl(4)	1792(3)	4042(3)	4813(2)	115(2)
Os(b)	5534(3)	21679(2)	20780(2)	304(1)	C(31)	7694(10)	5099(8)	360(7)	81(5)
H(1b)	942(71)	2811(51)	2830(35)	44(28)	Cl(5)	6888(4)	4473(3)	841(2)	127(2)
H(2b)	973(75)	2208(64)	2909(30)	75(29)	Cl(6)	6934(4)	5893(3)	166(3)	135(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] These atoms were observed disordered and were refined isotropically.

Table 5. Crystal Data and Data Collection and Refinement for [OsCl(η^2-H$_2$)(H$_2$bim)(P-*i*-Pr$_3$)$_2$]Cl·CH$_2$Cl$_2$ (**2**) and *cis-dichloro*-[OsCl$_2$(η^2-H$_2$)(Hpz)(P-*i*-Pr$_3$)$_2$]·0.5Hpz (**8**)

	$C_{24}H_{50}Cl_2N_4OsP_2 \cdot CH_2Cl_2$ (**2**)	$C_{21}H_{48}Cl_2N_2OsP_2 \cdot 0.5C_3H_4N_2$ (**8**)
space group	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)
temp, K	233	295
a, Å	12.133(1)	21.575(3)
b, Å	16.034(1)	8.743(1)
c, Å	18.321(1)	31.341(9)
α, β, γ, deg	105.10(1), 90.01(1), 93.87(1)	90.0, 90.98(2), 90.0
V, Å^3	3432.8(5)	5911(2)
Z	4	8
ρ(calcd), g cm^{-3}	1.549	1.541
mol wt	800.66	685.72
λ(Mo K$_\alpha$), Å	0.71073	0.71073
μ, mm^{-1}	4.15	4.6
transm or cor factor	0.5077, 0.2387	1.151, 0.856
R, R_w[a]	0.0348, 0.0364	0.0299, 0.0309

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F_o) + g(F_o)^2$; $g = 0.00100$ for **2** and 0.00051 for **8**.

Preparation of [(P-*i*-Pr$_3$)$_2$(η^2-H$_2$)ClOs(μ-Hbim)RhCl(COD)] (4). A solution of compound **2** (100 mg, 0.14 mmol) in 12 mL of dichloromethane was treated with [Rh(μ-OMe)(COD)]$_2$ (34 mg, 0.07 mmol). After being stirred for 90 min at room temperature, the solution was concentrated to ca. 0.1 mL; addition of hexane caused the precipitation of a yellow solid. The solvent was decanted, and the solid was repeatedly washed with hexane and then dried in vacuo. Yield: 114 mg (88%). Anal. Calcd for $C_{32}H_{61}Cl_2N_4OsP_2Rh$: C, 41.42; H, 6.64; N, 6.03. Found: C, 41.38; H, 6.63; N, 5.84. IR (Nujol): ν(NH) 3310 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 12.95 (br, 1H, NH), 8.06, 6.82, 6.79, 6.44 (each br, each 1H, =CH bim), 5.30, 3.65 (each br, each 2H, =CH COD), 2.35 (br, 4H, CH$_2$ COD), 2.1 (m, 6 H, PC*H*CH$_3$), 1.8 (br, 4H, CH$_2$ COD), 1.06 (dvt, *N* = 12.6 Hz, *J*(HH) = 6.5 Hz, 18 H, PCHC*H*$_3$), 0.92 (dvt, *N* = 12.8 Hz, *J*(HH) = 6.7 Hz, 18 H, PCHC*H*$_3$), −5.65 (br, 2H, Os(η^2-H$_2$)). ^{31}P{^{1}H} NMR (80.98 MHz, CDCl$_3$): δ −2.18 (s). T_1 (ms, Os(η^2-H$_2$), 300 MHz, C$_7$D$_8$) = 53 (293 K), 34 (253 K), 32 (243 K), 33 (233 K).

Preparation of [(P-*i*-Pr$_3$)$_2$(η^2-H$_2$)ClOs(μ-Hbim)IrCl(COD)] (5). This complex was prepared analogously to that described for **4**, starting from **2** (100 mg, 0.14 mmol) and [Ir(μ-OMe)(COD)]$_2$ (46.4 mg, 0.07 mmol). A yellow solid was formed. Yield: 121 mg (85%). Anal. Calcd for $C_{32}H_{61}Cl_2IrN_4OsP_2$: C, 37.78; H, 6.06; N, 5.51. Found: C, 38.02; H, 6.72; N, 5.34. IR (Nujol): ν(NH) 3305 cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 11.78 (br, 1H, NH), 7.92, 6.90, 6.54, 6.20 (each br, each 1H, =CH bim), 4.85, 3.25 (each br, each 2H, =CH COD), 2.24 (br, 4H,

CH_2 COD), 1.98 (m, 6 H, PC*H*CH_3), 1.50 (br, 4H, CH_2 COD), 1.04 (dvt, N = 12.6 Hz, J(HH) = 6.4 Hz, 18 H, PCHCH_3), 0.91 (dvt, N = 12.9, J(HH) = 6.5 Hz, 18 H, PCHCH_3), –5.71 (br, 2H, Os(η^2-H_2)). $^{31}P\{^1H\}$ NMR (80.98 MHz, C_6D_6): δ –1.46 (s). T_1 (ms, Os(η^2-H_2), 300 MHz, C_7D_8) = 52 (293 K), 33 (253 K), 31 (243 K), 33 (233 K), 58 (213 K).

Preparation of [(P-*i*-Pr$_3$)$_2$(η^2-H$_2$)ClOs(μ-Hbim)IrCl(TFB)] (6). This complex was prepared analogously to that described for **4**, starting from **2** (100 mg, 0.14 mmol) and [Ir(μ-OMe)(TFB)]$_2$ (63 mg, 0.07 mmol) after being stirred for 30 min. A yellow solid was formed. Yield: 124 mg (78%). Anal. Calcd for $C_{36}H_{55}Cl_2F_4IrN_4OsP_2$: C, 38.09; H, 4.89; N, 4.94. Found: C, 38.09; H, 4.94; N, 5.01. IR (Nujol): ν(NH) 3300 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 12.50 (br, 1H, NH), 8.12, 6.85, 6.65, 6.40 (each br, each 1H, =CH bim), 5.30 (br, 2H, CH TFB), 3.40, 2.30 (each br, each 2H, =CH TFB), 2.05 (m, 6 H, PC*H*CH_3), 1.05 (dvt, N = 12.9 Hz, J(HH) = 6.5 Hz, 18 H, PCHCH_3), 0.94 (dvt, N = 12.9 Hz, J(HH) = 6.4 Hz, 18 H, PCHCH_3), –5.62 (br, 2H, Os(η^2-H_2)). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ –2.18 (s). T_1 (ms, Os(η^2-H_2), 300 MHz, C_7D_8) = 47 (293 K), 37 (253 K), 35 (233 K), 41 (223 K), 67 (213 K).

Preparation of *trans-dichloro*-[OsCl$_2$(η^2-H$_2$)(Hpz)(P-*i*-Pr$_3$)$_2$] (7). A suspension of compound **1** (100 mg, 0.17 mmol) in 22 mL of hexane was treated with pyrazole (23.3 mg, 0.34 mmol). After the mixture was stirred for 15 min at room temperature, the suspension was filtered through Kieselguhr, and the filtrate was concentrated to ca. 6 mL; a white solid was formed. The solvent was decanted, and the solid was washed twice with hexane and then dried in vacuo. Yield: 78 mg (70%). Anal. Calcd for $C_{21}H_{48}Cl_2N_2OsP_2$: C, 38.70; H, 7.44; N, 4.30. Found: C, 38.71; H, 7.77; N, 4.32. IR (Nujol): ν(NH) 3240, ν(Os–Cl) 305 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 13.20 (br, 1H, NH), 9.10, 6.59, 5.96 (each br, each 1H, =CH pz), 2.68 (m, 6 H, PC*H*CH_3), 1.21 (dvt, N = 11.6 Hz, J(HH) = 7.0 Hz, 18 H, PCHCH_3), 1.15 (dvt, N = 10.9 Hz, J(HH) = 7.1 Hz, 18 H, PCHCH_3), –6.47 (t, J(PH) = 10 Hz, 2H, Os(η^2-H_2)). $^{31}P\{^1H\}$ NMR (80.98 MHz, C_6D_6): δ –1.37 (s). T_1 (ms, Os(η^2-H_2), 300 MHz, C_7D_8) = 98 (293 K), 42 (253 K), 33 (243 K), 29 (233 K), 25 (223 K), 30 (213 K).

Preparation of *cis-dichloro*-[OsCl$_2$(η^2-H$_2$)(Hpz)(P-*i*-Pr$_3$)$_2$] (8). A solution of compound **7** (100 mg) in 15 mL of hexane was stirred for 1 h at 60 °C. A yellow solid was formed, and after the mixture was cooled to room temperature, the solvent was decanted. The solid was repeatedly washed with hexane and then dried in vacuo. Yield: 94 mg (94%). Anal. Calcd for $C_{21}H_{48}Cl_2N_2OsP_2$: C, 38.70; H, 7.44; N, 4.30. Found: C, 39.01; H, 8.14; N, 4.23. IR (Nujol): ν(NH) 3200, ν(Os–Cl) 240, 300 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 13.62 (br, 1H, NH), 7.12, 6.22, 5.58 (each br, each 1H, =CH pz), 2.16 (m, 6 H, PC*H*CH_3), 1.24 (dvt, N = 11.5 Hz, J(HH) = 6.9 Hz, 18 H, PCHCH_3), 1.21 (dvt, N = 10.7 Hz, J(HH) = 7.0 Hz, 18 H, PCHCH_3), –8.16 (t, J(PH) = 11 Hz, 2H, Os(η^2-H_2)). $^{31}P\{^1H\}$ NMR (80.98 MHz, C_6D_6): δ –1.24 (s). T_1 (ms, Os(η^2-H_2), 300 MHz, C_7D_8) = 72 (293 K), 35 (243 K), 33 (233 K), 37 (223 K), 46 (213 K).

X-ray Data Collection, Solution, and Refinement of the Structure of [OsCl(η^2-H$_2$)(H$_2$bim)(P-*i*-Pr$_3$)$_2$]Cl·CH$_2$Cl$_2$ (2). Single crystals were obtained by slow diffusion of hexane into a dichloromethane solution of the complex at room temperature. An irregular block was used for intensity data collection; further details are given in Table 5. Cell constants were obtained from the least-squares fit on the setting angles of 68 reflections in the range 20 ≤ 2θ ≤ 42°. Three standard reflections were measured approximately every hour as a check of crystal and instrument stability; no variation was observed. Reflections were also corrected for absorption by a semiempirical (Ψ-Scan) method.[19]

The structure was solved by Patterson and difference Fourier techniques. The asymmetric unit was formed by two crystallographically independent, but chemically analogous, molecules of [OsCl(η^2-H_2)(H_2bim)(P-*i*-Pr_3)$_2$]Cl. Two isopropyl groups of the different phosphine ligands were observed as disordered. The disordered groups were modeled by including a complementary occupance factor assigned on the basis of thermal parameters (0.47 for the C(19), C(20), and C(21) atoms, and 0.53 for the C(21), C(22), and C(23)) and with the internal C–C bond distances restrained to 1.54(1) Å. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms, except those involved in the disorder. Hydrogen atoms of the dihydrogen ligands and the hydrogens linked directly to nitrogen atoms of 2,2′-biimidazole ligands were refined as free isotropic atoms (the Os(b)–H(1b) and Os(b)–H(2b) distances were restrained to 1.66(5) Å in the refinement). All the rest of the hydrogen atoms were located from difference Fourier maps and included in the refinement (some of them in calculated positions: C–H = 0.97 Å) riding on carbon atoms with a common isotropic thermal parameter. Hydrogen atoms bonded to disordered atoms were not included in the refinement. The atomic scattering, with anomalous dispersion corrections for Os, Cl, and P, were taken from ref 20. Atomic and thermal parameters are summarized in Table 4.

Table 6. Atomic Coordinates (×10^4; ×10^5 for Os Atom) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^4; Å^2 × 10^5 for Os Atom) for the Compound *cis-dichloro*-[OsCl$_2$(η^2-H$_2$)(Hpz)(P-*i*-Pr$_3$)$_2$]·0.5Hpz (**8**)

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Os	21597(1)	84570(4)	37841(1)	331(1)
H(1)	2067(26)	8619(68)	3297(18)	22(17)
H(2)	2101(34)	10011(94)	3478(24)	64(24)
Cl(1)	2325(1)	6632(2)	4388(1)	44(1)
Cl(2)	1716(1)	6329(3)	3387(1)	58(1)
P(1)	3138(1)	8005(2)	3460(1)	33(1)
P(2)	1147(1)	9217(3)	3992(1)	41(1)
N(1)	2566(3)	10082(8)	4197(2)	40(3)
N(2)	2765(3)	9756(9)	4593(2)	47(3)
C(1)	3015(5)	10981(13)	4783(3)	68(4)
C(2)	2974(5)	12172(12)	4501(3)	74(4)
C(3)	2691(5)	11571(10)	4141(3)	56(4)
C(4)	1133(4)	10348(11)	4496(3)	52(3)
C(41)	1202(4)	9347(11)	4883(3)	61(4)
C(42)	591(5)	11469(11)	4558(3)	73(4)
C(5)	789(4)	10580(12)	3602(3)	60(4)
C(51)	1175(5)	12030(12)	3556(3)	79(5)
C(52)	661(5)	9855(14)	3170(3)	85(5)
C(6)	551(4)	7665(12)	4008(3)	54(3)
C(61)	719(4)	6325(12)	4293(3)	75(4)
C(62)	–112(4)	8197(12)	4093(4)	81(5)
C(7)	3822(3)	8652(10)	3785(3)	43(3)
C(71)	3935(4)	7688(14)	4174(3)	73(4)
C(72)	4424(4)	8935(12)	3549(3)	66(4)
C(8)	3273(4)	6005(10)	3270(3)	48(3)
C(81)	3218(5)	4828(11)	3606(3)	75(4)
C(82)	3853(5)	5764(12)	3007(3)	76(4)
C(9)	3230(4)	9108(10)	2956(2)	43(3)
C(91)	2765(5)	8635(12)	2611(3)	70(4)
C(92)	3202(4)	10839(10)	3026(3)	60(4)
N(3)	270(6)	4141(16)	2635(4)	138(8)
C(10)	426(6)	5635(15)	2708(4)	83(5)
C(11)	0	6519(24)	2500	117(10)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Data Collection, Solution, and Refinement of the Structure of *cis-dichloro*-[OsCl$_2$(η^2-H$_2$)(Hpz)(P-*i*-Pr$_3$)$_2$]·0.5Hpz (8). Crystals suitable for an X-ray diffraction experiment were obtained along the preparation described for **8** above, from the decanted solvent after cooling at –20 °C. The crystal was checked on a Perkin-Elmer 1730 FTIR. A summary of crystal data is reported in Table 5. Atomic coordinates and U_{eq} values are listed in Table 6. Cell constants were obtained from the least-squares fit on the setting angles of 30 reflections in the range 20 ≤ 2θ ≤ 37°. Three orientation and intensity standards were monitored every 55 min of measuring time; no significant variations were observed. Reflections were also corrected for absorption by an empirical method (Difabs).[21]

The structure was solved by Patterson (Os atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least-squares techniques with initial isotropic thermal parameters. The hydrogens of the dihydrogen ligand were refined as free isotropic atoms. All the rest of hydrogen atoms were partially located from difference Fourier maps and included in the refinement (some of them in calculated positions; C–H = 0.97 Å) riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Os, Cl, and P, were taken from ref 20.

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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, full experimental details of the X-ray studies, bond distances, and bond angles (26 pages). Ordering information is given on any current masthead page.

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