Osmium and Ruthenium Complexes Containing an N-Heterocyclic Carbene Ligand Derived from Benzo[*h*]quinoline

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Benzo[*h*]quinoline (**Hbq**) undergoes 1,2-hydrogen shift from the carbon at the 2-position to the nitrogen in the presence of the complexes $MH_2Cl_2(P^iPr_3)_2$ (M = Os (**1**), Ru (**1a**)). The coordination of the undressed carbon atom of the resulting NH tautomer (**HNbq**) to the metal center of the osmium and ruthenium complexes gives rise to the formation of the osmium-elongated dihydrogen species $OsCl_2\{\kappa$-*C*-[HNbq]$\}(\eta^2$-$H_2)(P^iPr_3)_2$ (**2**; H−H = 1.22 Å) and to the five-coordinate ruthenium derivative $RuCl_2\{\kappa$-*C*-[HNbq]$\}(P^iPr_3)_2$ (**3**), respectively. Under a hydrogen atmosphere, complex **3** is in equilibrium with the dihydrogen $RuCl_2\{\kappa$-*C*-[HNbq]$\}(\eta^2$-$H_2)(P^iPr_3)_2$ (**4**; H−H = 0.91 Å). The X-ray structure of **2** and the ^{1}H NMR spectra of **2**−**4** suggest that a hydrogen bond involving the NH group of the heterocycle and a chloride ligand plays an important role in the stabilization of these complexes. Both **2** and **4** undergo deprotonation to afford species containing the usual metalated benzo[*h*]quinoline group (**bq**). Treatment of **2** with Et_3N gives $OsCl\{\kappa^2$-*N*,*C*-[bq]$\}(\eta^2$-$H_2)(P^iPr_3)_2$ (**5**; H−H = 1.29 Å), whereas the reaction of **4** with the amine leads to $RuCl\{\kappa^2$-*N*,*C*-[bq]$\}(\eta^2$-$H_2)(P^iPr_3)_2$ (**6**; H−H = 1.01 Å). Complexes **5** and **6**, which have been characterized by X-ray diffraction analysis, can be directly obtained by reaction of the corresponding dihydride-dichloro starting materials with benzo[*h*]quinoline in the presence of Et_3N.

Introduction

Transition metal elements have the remarkable ability to modify the chemical properties of organic molecules. Thus, we have recently shown that complexes $MH_2Cl_2(P^iPr_3)_2$ (M = Os, Ru) promote the tautomerization of quinoline and 8-methylquinoline to NH tautomers, which lie about 44 kcal·mol^{-1} above the usual C−H tautomers.[1] These species are stabilized by coordination of the carbon atom at the 2-position of the heterocycle to the metal center and by means of a Cl···H−N interaction between the NH-hydrogen atom and a chloride of the metal fragment. At the same time, Carmona, Poveda and co-workers[2] reported the stabilization of related NH tautomers of α-pyridines by coordination to iridium. A few months later Whittlesey and co-workers[3] described ruthenium isomers resulting from the N- or C-bond tautomers of isopropyl-4,5-dimethylimidazole, in agreement with the possibility that C-bound imidazoles could have some role in metalloprotein chemistry.[4]

This type of tautomerization is important not only in biological processes, where the energetically less stable tautomer is often an active intermediate that dictates the mechanism and the formed product,[5] but also in catalytic reactions involving C−C bond formation.[6] Thus, Bergman, Ellman, and co-workers[7] have proposed that the *C*,*N*-1,2-H rearrangement is the key step for the Rh(I)-catalyzed *ortho*-alkylation of pyridines and quinolines.

Benzo[*h*]quinoline (**Hbq**) is a tricyclic planar nitrogen heterocycle, which forms *N*,*C*-cyclometalated transition metal complexes[8] with extreme ease due to the great stability[9] of the five-membered heterometallaring resulting from the C^{10}−H bond rupture (eq 1). Once the formation of the metallaring has taken place, the metalated ligand (**bq**) can undergo coordination to other metals to afford dinuclear derivatives.[10] The coordina-

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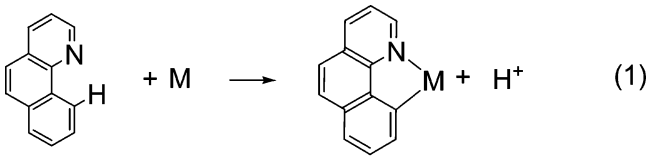
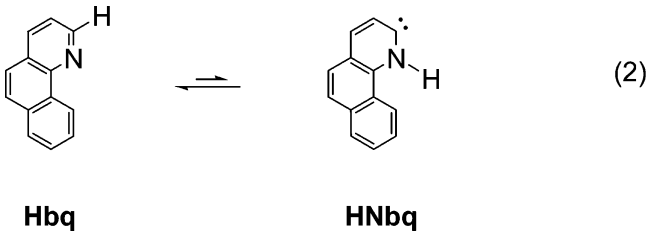
tion chemistry of benzo[*h*]quinoline also includes a few N-monodentate compounds[11] and some arene species such as $Cr(Hbq)(CO)_3$, reported by E. O. Fischer and co-workers[12] in 1968.



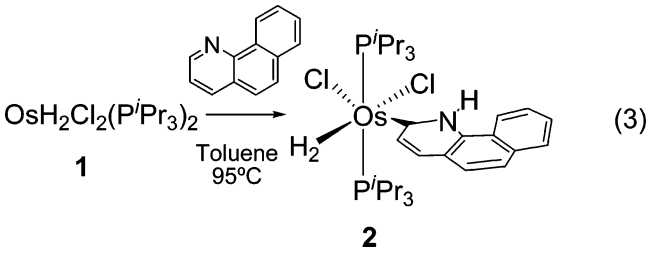
We have now studied the reactions of complexes $MH_2Cl_2(P^iPr_3)_2$ (M = Os, Ru) with benzo[*h*]quinoline and have observed that this organic molecule, in addition to metalation, undergoes tautomerization to afford a NH tautomer (**HNbq**) similar to those reported for quinoline, 8-methylquinoline, and α-pyridines (eq 2).



This paper reports, as a part of our work on the chemistry of the M−C (M = Os, Ru) bonds,[13] the stabilization of the **HNbq** tautomer by coordination to osmium and ruthenium and its transformation into the usual cyclometalated group.

Results and Discussion

1. Stabilization of an NH Tautomer of Benzo[*h*]quinoline. In spite of the marked tendency shown by benzo[*h*]quinoline to afford cyclometalated compounds in its reactions with transition metal complexes, treatment of this heterocycle with $OsH_2Cl_2(P^iPr_3)_2$ (**1**) in toluene at 95 °C produces its tautomerization as result of a 1,2-hydrogen shift between the carbon at the 2-position and the nitrogen. The resulting novel organic fragment is stabilized by coordination to the metal center. In addition, the coordination gives rise to the transformation of the OsH_2-dihydride unit of the starting complex into an elongated dihydrogen, in agreement with the trend shown by **1** to afford species with a nonclassic H−H interaction when a Lewis base is coordinated.[14] The formed complex $OsCl_2\{\kappa\text{-}C$-[HNbq]}$(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**2**) is isolated as an orange solid in 70% yield, according to eq 3.



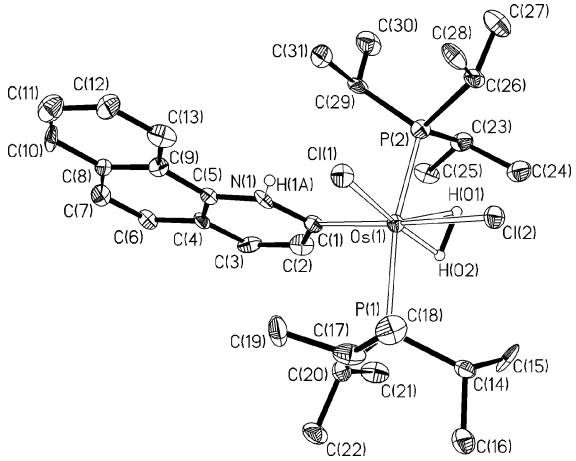


Figure 1. Molecular diagram of complex **2**. Selected bond lengths (Å) and angles (deg): Os(1)−C(1) = 2.055(11), Os(1)−Cl(1) = 2.508(3), Os(1)−Cl(2) = 2.488(3), Os(1)−P(1) = 2.406(3), Os(1)−P(2) = 2.400(3), C(1)−N(1) = 1.362(14), C(5)−N(1) = 1.363(13), C(1)−C(2) = 1.437(14), C(2)−C(3) = 1.367(15), C(3)−C(4) = 1.413(16), C(4)−C(5) = 1.373(15), Cl(1)···HN = 2.24(11); P(1)−Os(1)−P(2) = 167.70(11), Cl(1)−Os(1)−Cl(2) = 83.85(10), C(1)−Os(1)−Cl(1) = 87.1(3), C(1)−Os(1)−Cl(2) = 170.9(3), P(1)−Os(1)−C(1) = 93.3(3), P(2)−Os(1)−C(1) = 92.8(3).

Complex **2** has been characterized by elemental analysis, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. A drawing of one of them is shown in Figure 1. The study proves the stabilization of the **HNbq** tautomer, which coordinates to the metal center through the carbon atom at the 2-position (C(1)).

The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine groups occupying mutually *trans* positions (P(1)−Os−P(2): 167.70(11)° molecule *a* and 169.28(10)° molecule *b*). The metal sphere is completed by the chloride ligands mutually *cis* disposed (Cl(1)−Os−Cl(2): 83.5(10)° molecule *a* and 82.94(10)° molecule *b*), the tautomerized benzo[*h*]quinoline group *trans* disposed to Cl(2) (C(1)−Os−Cl(2): 170.9(3)° molecule *a* and 169.1(3)° molecule *b*), and the elongated dihydrogen ligand *trans* disposed to Cl(1).

The Os−C(1) bond lengths of 2.055(11) Å (molecule *a*) and 2.030(10) Å (molecule *b*) compare well with the Os−C distance in the related 8-methylquinoline derivative (2.005(6) Å)[1] and with the Os−NHC (NHC = N-heterocyclic carbene) separations in cations $[(\eta^6\text{-}p$-cymene)OsCl(=CHPh)(IPr)$]^+$ (2.090(3) Å),

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$[(\eta^6\text{-}p\text{-cymene})OsCl(IPr)]^+$ (2.078(2) Å),[15] $[(Os(=CHPh)(CH_3CN)_4(IPr)]^+$ (2.069(6) Å), $[(OsHCl(\equiv CPh)(IPr)(P^iPr_3)]^+$ (2.108(2) Å),[16] and $[OsCl\{\kappa^3\text{-}C,N,O\text{-}[=CHC(O)pyC(CH_3)O]\}(CH_3CN)(IPr)]^+$ (2.074(5) Å)[17] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene). The similarity between this **HNbq** tautomer and the NHC ligands[18] is also revealed by the $^{13}C\{^1H\}$ NMR spectra. In agreement with the chemical shifts reported for the above-mentioned compounds,[1,15−17] the $^{13}C\{^1H\}$ NMR spectrum of **2** shows the Os−C(1) resonance at 187.9 ppm. It appears as a triplet with a C−P coupling constant of 7 Hz.

The planar heterocycle lies in the plane determined by the metal and the chloride ligands with the NH-hydrogen toward Cl(1). The separation between them, 2.24(11) Å in molecule *a* and 2.14(10) Å in molecule *b*, is shorter than the sum of the van der Waals radii of hydrogen and chloride (rvdw (H) = 1.20 Å, rvdw (Cl) = 1.75 Å),[19] suggesting that there is an intramolecular Cl···H−N hydrogen bond between these atoms,[20] which contributes to the stabilization of the tautomer, as has been previously shown for quinoline and 8-methylquinoline.[1] The hydrogen bond is a consequence of the electrostatic interaction between the electronegative halogen and the acidic NH-hydrogen.[21] The Cl···H−N hydrogen bond is also supported by the IR spectrum in KBr, which shows the NH stretching frequency at 3104 cm^{-1} in accordance with the values reported for the related quinoline (3106 cm^{-1}) and 8-methylquinoline (3130 cm^{-1}) derivatives,[1] and by the ^1H NMR spectrum in dichloromethane-d_2, where the NH resonance is observed at unusually low field,[22] 15.46 ppm.

The ^1H NMR spectrum also supports the presence of an elongated dihydrogen ligand in the complex. At room temperature, this ligand displays a triplet at −10.12 ppm with a H−P coupling constant of 10.8 Hz. A variable-temperature 400 MHz T_1 study of the resonance gives a $T_{1(min)}$ value of 37 ± 1 ms, which corresponds to a hydrogen−hydrogen distance of 0.98 Å (fast spinning) or 1.24 Å (slow spinning).[23] The partially deuterated ligand η^2-HD has a H−D coupling constant of 12.2 Hz. According to eq 4,[24] this value allows us to calculate a separation between the hydrogen atoms of 1.22 Å, which agrees well with that obtained for slow spinning by means of the $T_{1(min)}$ value. The H−H distance in **2** is similar to those calculated for the related osmium complexes $OsCl_2(\eta^2\text{-}H_2)(Hpz)(P^iPr_3)_2$ (1.27 Å),[14b] $OsCl_2(\eta^2\text{-}H_2)(NH=CPh_2)(P^iPr_3)_2$ (1.24 Å),[25] $[Os(\kappa^2\text{-}O_2CCH_3)(\eta^2\text{-}H_2)\{P(OMe_3)\}(P^iPr_3)_2]BF_4$ (1.30 Å),[26] $OsX\{NH=C(Ph)C_6H_4\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (X = Cl, Br, I; 1.31 Å),[27] $[Os\{C_6H_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (1.35 Å),[21i] and $[Os\{C_6F_4C(O)CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (1.30 Å)[28] and lies in the middle of the reported range (1.0−1.5 Å) for elongated dihydrogen derivatives.[29]

$$d_{(H-H)} = -0.0167(J_{H-D}) + 1.42 \qquad (4)$$

The $^{31}P\{^1H\}$ NMR spectrum of **2** is consistent with the structure shown in Figure 1. As expected for two equivalent phosphine ligands, a singlet at 2.1 ppm is observed.

Ruthenium also promotes the tautomerization of benzo[*h*]quinoline. However, it should be taken into account that ruthenium is a poorer π-back-bonder than osmium because the osmium valence orbitals have better overlap with the ligand orbitals. Thus, the $Ru(\eta^2\text{-}H_2)$ bond is weaker than the $Os(\eta^2\text{-}H_2)$ one,[30] and as a consequence of this weakness, the dihydrogen ligand is lost during the reaction of $RuH_2Cl_2(P^iPr_3)_2$ (**1a**) with benzo[*h*]quinoline. Treatment under reflux of toluene solutions of the metal compound with 2.0 equiv of the heterocycle leads to the five-coordinate complex $RuCl_2\{\kappa\text{-}C\text{-}[HNbq]\}(P^iPr_3)_2$ (**3**), which is isolated as a green solid in 70% yield, according to Scheme 1. Under hydrogen atmosphere, this species is in equilibrium with the dihydrogen derivative $RuCl_2\{\kappa\text{-}C\text{-}[HNbq]\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**4**).

The $^{13}C\{^1H\}$, ^1H, and $^{31}P\{^1H\}$ NMR spectra of **3** are in agreement with those of the related 8-methylquinoline complex, which has been characterized by X-ray diffraction analysis. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance corresponding to the coordinated carbon atom of the heterocycle is observed at 214.3 ppm, shifted 26.4 ppm to lower field with regard to the osmium compound. It appears as a triplet with a C−P coupling constant of 11 Hz. In the ^1H NMR spectrum the most noticeable signal is that corresponding to the NH-hydrogen atom, which, in accordance with a Cl···H−N interaction, is observed at 13.84 ppm. The Cl···H−N hydrogen bond is also supported by the IR spectrum, which shows the ν(N−H) band at 3204 cm^{-1}. A singlet at 36.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of this compound.

The dihydrogen character of the RuH_2 unit in **4** is supported by the ^1H NMR spectrum of this compound in dichloromethane-

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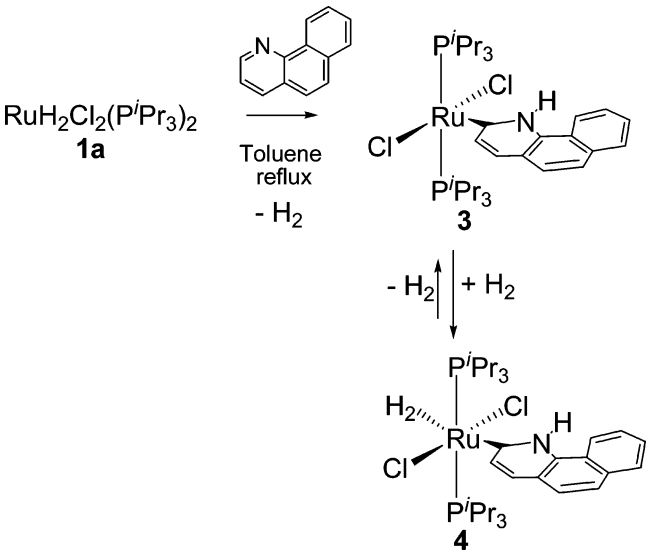
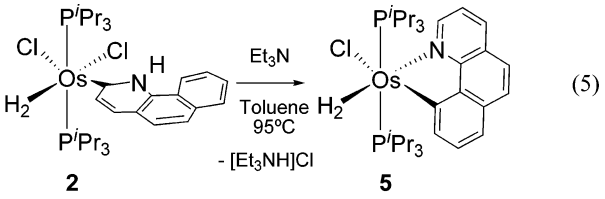
Scheme 1



d_2, which shows the dihydrogen resonance at −12.60 ppm as a triplet with a H−P coupling constant of 7.8 Hz. In this case, a $T_{1(min)}$ value of 20 ± 1 ms in the 300 MHz scale and a H−D coupling of 31.2 Hz were found. These values are consistent with a H−H separation of about 0.91 Å. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 31.5 ppm.

2. Formation of Os(II)- and Ru(II)-Metalacycle Compounds. In the presence of triethylamine the dihydride-dichloro complexes **1** and **1a** react with benzo[*h*]quinoline to afford cyclometalated species, which can also be obtained by deprotonation of **2** and **4**.

Treatment for 12 h of the osmium complex **2** with 4 equiv of triethylamine, in toluene at 95 °C, leads to the elongated dihydrogen complex $OsCl\{\kappa^2\text{-}N,C\text{-}[bq]\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**5**) containing a C^{10}-metalated benzo[*h*]quinoline group, which is isolated as an orange solid in 60% yield, according to eq 5.



(5)

Complex **5** has been characterized by elemental analysis, IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. Figure 2 shows a view of its molecular geometry.

The coordination geometry around the osmium atom can be rationalized as derived from a distorted octahedron with the phosphorus atoms of the triisopropylphosphine ligands occupying *trans* positions (P(1)−Os−P(2) = 164.11(5)°). The perpendicular plane is formed by the atoms N(1) and C(7) of the metalated heterocycle, which acts with a bite angle N(1)−Os−C(7) of 77.44(19)°, the chloride *trans* disposed to C(7) (Cl(1)−Os−C(7) = 164.18(15)°) and the elongated dihydrogen ligand *trans* located to N(1). The five-membered ring formed by the metalated benzo[*h*]quinoline group and the osmium atom is almost planar. The Os−N bond length of 2.188(5) Å and the Os−C(7) distance of 2.073(5) Å are as expected for Os−N and Os−C(sp^2) single bonds.[20d]

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **5** are in agreement with the structure shown in Figure 2. In the ^1H NMR

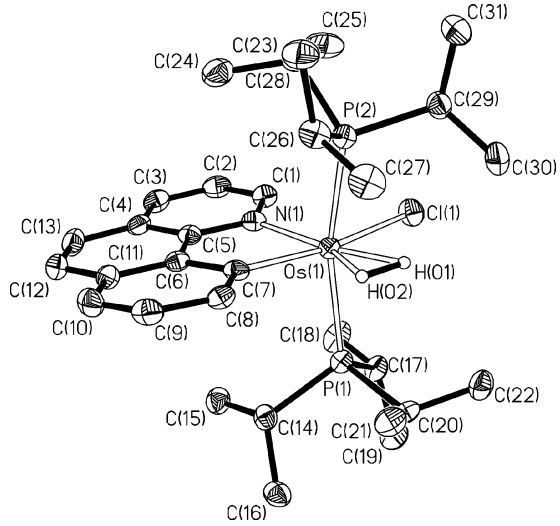
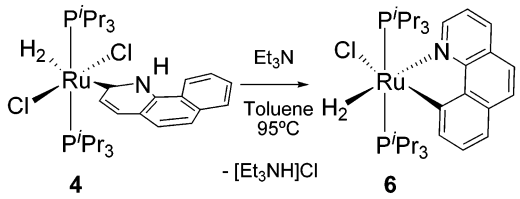


Figure 2. Molecular diagram of complex **5**. Selected bond lengths (Å) and angles (deg): Os(1)−C(7) = 2.073(5), Os(1)−Cl(1) = 2.4944(13), Os(1)−N(1) = 2.188(5), Os(1)−P(1) = 2.3856(14), Os(1)−P(2) = 2.3721(14), N(1)−C(1) = 1.352(7), C(1)−C(2) = 1.394(8), C(2)−C(3) = 1.365(8), C(3)−C(4) = 1.398(7), C(4)−C(5) = 1.422(8), C(5)−N(1) = 1.370(6), C(7)−C(6) = 1.420(7), C(7)−C(8) = 1.411(7), C(8)−C(9) = 1.398(7), C(9)−C(10) = 1.373(8), C(10)−C(11) = 1.402(7), C(11)−C(6) = 1.410(7); P(1)−Os(1)−P(2) = 164.11(5), Cl(1)−Os(1)−N(1) = 86.76(12), N(1)−Os(1)−C(7) = 77.44(19), Cl(1)−Os(1)−C(7) = 164.18(15).

spectrum in dichloromethane-d_2 at room temperature, the most noticeable resonance is that corresponding to the elongated dihydrogen ligand, which appears at −7.93 ppm as a triplet with a H−P coupling constant of 11.7 Hz. A $T_{1(min)}$ value of 38 ± 1 ms, in the 300 MHz scale, and H−D coupling constant of 7.7 Hz were found for this resonance. These values are consistent with a separation between the hydrogen atoms of the elongated dihydrogen ligand of 1.29 Å. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the metalated carbon atom of the heterocycle is observed at 165.8 ppm, shifted 22.1 ppm to higher field with regard to that of **2**. It appears as a triplet with a C−P coupling constant of 6 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 4.3 ppm.

Treatment of toluene solutions of complex **4** with 4.0 equiv of Et_3N, under the same conditions as those previously mentioned for the formation of **5**, leads to the ruthenium dihydrogen derivative $RuCl\{\kappa^2\text{-}N,C\text{-}[bq]\}(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**6**), containing a N,C^{10}-metalated heterocycle, which is isolated as an orange solid in 50% yield, according to eq 6.



(6)

Complex **6**, like **2** and **5**, has been characterized by elemental analysis, IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. A view of its molecular geometry is shown in Figure 3.

The coordination geometry around the ruthenium atom can be rationalized as a distorted octehedron with the phosphorus atoms of the triisopropylphosphine ligands occupying mutually

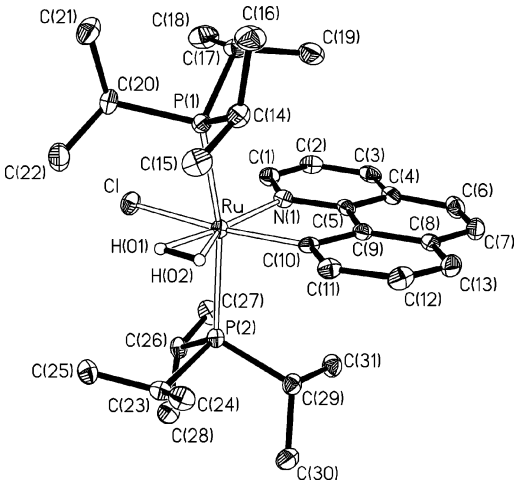


Figure 3. Molecular diagram of complex **6**. Selected bond lengths (Å) and angles (deg): Ru−C(10) = 2.047(3), Ru−Cl = 2.5135(9), Ru−N(1) = 2.144(2), Ru−P(1) = 2.3877(9), Ru−P(2) = 2.4034(9), N(1)−C(1) = 1.338(4), C(1)−C(2) = 1.401(4), C(2)−C(3) = 1.371(4), C(3)−C(4) = 1.409(4), C(4)−C(5) = 1.417(4); P(1)−Ru−P(2) = 165.57(3), Cl−Ru−N(1) = 89.10(7), N(1)−Ru−C(10) = 79.54(11), Cl−Ru−C(10) = 168.64(9).

trans positions (P(1)−Ru−P(2) = 165.57(3)°). The metal sphere is completed by the metalated group, which in this case acts with a bite angle N(1)−Ru−C(10) of 79.54(11)°, the chloride ligand *trans* disposed to C(10) (Cl−Ru−C(10) = 168.64(9)°), and the coordinated hydrogen molecule *trans* disposed to N(1). The Ru−C(10) bond length of 2.047(3) Å and the Ru−N(1) distance of 2.144(2) Å are consistent with the related parameters of **5** and agree well with the Ru−C and Ru−N distances found in the hydride-dihydrogen species RuH{κ^2-*N*,*C*-[bq]}(η^2-H_2)(P^i-Pr_3)$_2$ (2.104(3) and 2.155 Å, respectively), which has been obtained by reaction of RuH_2(η^2-H_2)$_2$(P^iPr_3)$_2$ with benzo[*h*]-quinoline.[31]

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **6** agree well with those of **5** and with the structure shown in Figure 3. In the ^{1}H NMR spectrum in dichloromethane-d_2 at room temperature, the dihydrogen ligand displays a triplet at −9.00 ppm with a H−P coupling constant of 8.0 Hz. A variable-temperature 400 MHz study of this resonance gives a $T_{1(min)}$ value of 14 ± 1 ms, whereas the partially deuterated ligand η^2-HD has a H−D coupling constant of 24.8 Hz. These values are consistent with a separation between the hydrogen atoms of 1.01 Å, which is about 0.3 Å shorter than that of **5**. This suggests a weaker metal−hydrogen bond in **6** than in **5**, in agreement with the poorer metal−dihydrogen π-back-bonder in ruthenium than in osmium. In the ^{13}C{^{1}H} NMR spectrum the resonance due to the metalated carbon atom of the heterocycle appears at 183.8 ppm, as a triplet with a C−P coupling constant of 9 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 34.6 ppm.

Concluding Remarks

This study has revealed that osmium and ruthenium compounds containing a monodentate C^2-coordinated benzo[*h*]-quinoline can be isolated, in spite of the great stability of the five-membered rings resulting from the reactions of this heterocycle with the transition metal complexes.

Benzo[*h*]quinoline undergoes a 1,2-hydrogen shift, from the carbon atom at the 2-position to the nitrogen, promoted by complexes $MH_2Cl_2(P^iPr_3)_2$ (M = Os, Ru). The formed tautomer is stabilized by coordination of the undressed carbon atom to the metal centers and by means of an intramolecular Cl···H−N hydrogen bond between the resulting NH-hydrogen atom and one of the chloride ligands. The coordination of the heterocycle produces the transformation of the MH_2 units of the starting compounds into elongated dihydrogen Os or dihydrogen Ru ligands. Thus, osmium− and ruthenium−dihydrogen complexes, containing an unprecendented N-heterocyclic carbene ligand[32] derived from benzo[*h*]quinoline, have been isolated and characterized, including by X-ray diffraction analysis. The conversion of the heterocyclic carbene into the usual cyclometalated group takes place only when the tautomer-metal species are deprotonated with triethylamine or when the reactions between $MH_2Cl_2(P^iPr_3)_2$ (M = Os, Ru) and the heterocycle are carried out in the presence of this amine.

In conclusion, these results along with those recently reported by Carmona's group[2] and by us[1] indicate that, in the presence of some transition metal complexes, the 1,2-hydrogen shift from the carbon at the 2-position to the nitrogen is energetically accessible for a very wide range of N-heterocycles. Since the coordination of the undressed carbon atom to the metal center produces the stabilization of the unfavored tautomer, one should expect a rapid growth of the number of transition metal complexes containing this novel type of N-heterocycle carbene ligand in the near future.

Experimental Section

General Information. All manipulations were performed with rigorous exclusion of air at an argon/vacuum manifold using standard Schlenk-tube techniques or in a drybox (MB-Unilab). Solvents were dried by the usual procedures and distilled under argon prior to use. Benzo[*h*]quinoline (Aldrich) was used without further purification. The starting materials $MH_2Cl_2(P^iPr_3)_2$ (M = Os (**1**),[33] Ru (**1a**))[34] were prepared in accord with methods reported in the literature.

$OsD_2Cl_2(P^iPr_3)_2$ (85−90% deuterated based on the ^{1}H NMR) was prepared by addition of CD_3OD (0.5 mL) to CD_2Cl_2 (1.0 mL) solutions of **1** (100 mg, 170 mmol). The mixture was stirred at rt for 2 h, and the solvent was removed in vacuo to give a yellow solid, which was characterized by ^{1}H and ^{2}H NMR spectroscopy as the 85−90% dideuterated derivative, and was used without further purification. ^{2}H NMR (46.97 MHz, CD_2Cl_2, 293 K): −16.58 (t, J_{P-D} = 5.2 Hz, Os−D_2).

NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300, a Bruker Avance 300 MHz, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H_3PO_4 (^{31}P{^{1}H}). Coupling constants, *J*, are given in hertz. The d_{H-H} were calculated on the basis of published methods[23,24] using both the T_{1min} and J_{HD} experimental values. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of $OsCl_2$\{κ-*C*-[HNbq]\}(η-H_2)(P^iPr_3)$_2$ (2). A Young's tap Schlenk flask was charged with benzo[*h*]quinoline (122

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mg, 0.68 mmol), **1** (200 mg, 0.34 mmol), and toluene (10 mL). The mixture was heated at 95 °C for 48 h to afford an orange suspension. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (15 mL). The solution was concentrated (to ∼4 mL). Addition of diethyl ether caused the precipitation of an orange solid, which was dried in vacuo and characterized as **2**. Yield: 180 mg (70%). Anal. Calcd for $C_{31}H_{53}Cl_2NOsP_2$: C, 48.81; H, 7.00; N, 1.84. Found: C, 48.76; H, 7.21; N, 1.77. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): 15.46 (br, 1H, NH), 8.86 (m, 1H, HNbq), 7.97 (m, 1H, HNbq), 7.84 (m, 2H, HNbq), 7.75 (m, 2H, HNbq), 7.57 (m, 1H, HNbq), 7.48 (m, 1H, HNbq), 2.30 (m, 6H, C*H*-^{i}Pr), 1.22 (m, 36H, C*H*$_3$-^{i}Pr), −10.12 (t, 2H, J_{P-H} = 10.8 Hz, OsH_2). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 293 K, plus APT, HMQC and HMBC): 187.9 (t, J_{P-C} = 7, Os−C), 148.9 (CH, HNbq), 137.6 (C_{ipso}, HNbq), 134.3 (C_{ipso}, HNbq), 132.4 (s, CH, HNbq), 129.0 (s, CH, HNbq), 128.9 (s, CH, HNbq), 128.2 (s, CH, HNbq), 125.1 (s, CH, HNbq), 124.7 (s, CH, HNbq), 123.0 (C_{ipso}, HNbq), 121.4 (s, CH, HNbq), 121.0 (s, C_{ipso}, HNbq), 25.7 (t, J_{C-P} = 12, *C*H-^{i}Pr), 19.7 and 19.2 (s, *C*H$_3$-^{i}Pr). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): 2.1 (s). IR (KBr, cm^{-1}): 3104 ν(N−H), 2264 and 2229 ν(Os−H_2), 1624, 1602, 1567, and 1503 ν(C═C). $T_{1(min)}$ (ms, CD_2Cl_2, 400 MHz, −10.13, 228 K): 37 ± 1 ⇒ d_{H-H} calc = 1.24 Å.

Determination of the J_{H-D} Value for Complex 2. A Young's tap NMR tube was charged with benzo[*h*]quinoline (30 mg, 0.17 mmol), $OsD_2Cl_2(P^iPr_3)_2$ (50 mg, 0.09 mmol), and toluene (0.75 mL). The mixture was heated at 95 °C for 48 h. After that, the solvent was removed in vacuo and CD_2Cl_2 (0.5 mL) was added. The ^{1}H-{^{31}P} NMR spectra of these solutions exhibit in the hydride region the resonances due to a mixture of the [Os](η^2-H−D) and the [Os]-(η^2-H−H) **2** species. J_{H-D} (Hz) = 12.2 ⇒ d_{H-H} calc = 1.22 Å.

Preparation of $RuCl_2\{\kappa$-*C*-[HNbq]**$\}(P^iPr_3)_2$ (3).** A Schlenk flask was charged with benzo[*h*]quinoline (143 mg, 0.80 mmol), **1a** (200 mg, 0.40 mmol), and toluene (10 mL). The mixture was refluxed for 10 h, and the resulting dark solution was filtered through Celite and concentrated (to ∼4 mL). Addition of diethyl ether (15 mL) caused the precipitation of a green solid, which was dried in vacuo and characterized as **3**. Yield: 190 mg (70%). Anal. Calcd for $C_{31}H_{51}Cl_2NRuP_2$: C, 55.43, H, 7.65; N, 2.08. Found: C, 55.21; H, 7.40; N, 2.15. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): 13.84 (br, 1H, NH), 8.60 (m, 1H, HNbq), 8.38 (m, 1H, HNbq), 7.91 (m, 1H, HNbq), 7.70 (m, 2H, HNbq), 7.67 (m, 1H, HNbq), 7.53 (m, 1H, HNbq), 7.10 (m, 1H, HNbq), 3.04 (m, 6H, C*H*-^{i}Pr), 1.25 (m, 18H, C*H*$_3$-^{i}Pr), 1.16 (m, 18H, C*H*$_3$-^{i}Pr). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 293 K, plus APT, HMQC and HMBC): 214.3 (t, J_{P-C} = 11, Ru-C), 141.8 (CH, HNbq), 136.6 (C_{ipso}, HNbq), 133.5 (C_{ipso}, HNbq), 128.6 (s, CH, HNbq), 127.9 (s, CH, HNbq), 127.4 (s, CH, HNbq), 126.7 (C_{ipso}, HNbq), 124.9 (s, CH, HNbq), 123.9 (s, CH, HNbq), 123.5 (s, CH, HNbq), 121.5 (s, C_{ipso}, HNbq), 120.1 (s, CH, HNbq), 23.2 (t, J_{C-P} = 9, *C*H-^{i}Pr), 19.9 and 19.5 (s, *C*H$_3$-^{i}Pr). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): 36.2 (s). IR (KBr, cm^{-1}): 3204 ν(N−H), 1627,[1] 1593, and 1557 ν(C═C).

Reaction of $RuCl_2\{\kappa$-*C*-[HNbq]**$\}(P^iPr_3)_2$ (3) with H_2.** A CD_2Cl_2 solution (0.5 mL) of **3** (5 mg, 0.008 mmol) was prepared under an atmosphere of H_2 in a Young's tap NMR tube. After 12 h the NMR spectra of the solution showed a 4/6 mixture of complex **3** and the dihydrogen species $RuCl_2\{\kappa$-*C*-[HNbq]$\}(\eta^2$-$H_2)(P^iPr_3)_2$ (**4**). Data for **4**: ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): 15.36 (br, 1H, NH), 8.90 (m,1H, HNbq), 8.01 (m, 1H, HNbq), 7.86 (m, 1H, HNbq), 7.78 (m,1H, HNbq), 7.75 (m, 1H, HNbq), 7.65 (m, 1H, HNbq), 7.62 (m, 1H, HNbq), 7.46 (m,1H, HNbq), 2.37 (m, 6H, CH_3, C*H*-^{i}Pr), 1.25 (m, 36H, C*H*$_3$-^{i}Pr), −12.60 (t, *J* = 7.8, 2H, RuH_2). ^{13}C{^{1}H} NMR (75.43 MHz, CD_2Cl_2, 263 K, plus APT): not observed (Ru-C), 145.2 (s, CH, HNbq), 137.5 (C_{ipso}, HNbq), 134.2 (C_{ipso}, HNbq), 130.7 (s, CH, HNbq), 129.0 (s, HNbq, CH), 128.9 (s, CH, HNbq), 128.3 (s, CH, HNbq), 125.5 (s, CH, HNbq), 124.7 (s, CH, HNbq), 122.8 (C_{ipso}, HNbq), 121.2 (s, CH, HNbq), 121.1 (C_{ipso}, HNbq), 25.4 (t, J_{C-P} = 9, *C*H-^{i}Pr), 19.8 and 19.5 (s,*C*H$_3$-^{i}Pr). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): 31.5 (s). $T_{1(min)}$ (ms, RuH_2, 300 MHz, CD_2Cl_2, 218 K, −12.88): 20 ± 1 ⇒ d_{H-H} calc = 0.93 Å.

Determination of the J_{H-D} Value for Complex 4. H−D was bubbled through CD_2Cl_2 solutions (0.5 mL) containing the **4** species. The ^{1}H{^{31}P} NMR spectra of these solutions exhibit in the hydride region the resonances due to a mixture of the [Ru](η^2-H−D) and the [Ru](η^2-H−H) **4** species. J_{HD} (Hz) = 31.2 ⇒ d_{H-H} calc = 0.90 Å.

Preparation of $OsCl\{\kappa^2$-*N*,*C*-[bq]**$\}(\eta$-$H_2)(P^iPr_3)_2$ (5).** Method A: A Young's tap Schlenk flask was charged with benzo[*h*]-quinoline (122 mg, 0.68 mmol), **1** (200 mg, 0.34 mmol), Et_3N (0.19 mL, 1.36 mmol), and toluene (10 mL). The resulting mixture was heated at 95 °C for 12 h. The red toluene solution was filtered through Celite and concentrated under reduced pressure (to×d4 ∼4 mL). Addition of diethyl ether (15 mL) caused the precipitation of an orange solid, which was dried in vacuo and characterized as **5**. Yield: 187 mg (75%). Method B: A Young's tap Schlenk flask was charged with **2** (100 mg, 0.l3 mmol), Et_3N (0.060 mL, 0.43 mmol), and toluene (10 mL). The mixture was heated at 95 °C for 12 h. The toluene solution was filtered, the solvent was removed under reduced pressure, and the residue was extracted with CH_2-Cl_2 (15 mL). The solution was concentrated (to ∼4 mL). Addition of diethyl ether caused the precipitation of an orange solid, which was dried in vacuo and characterized as **5**. Yield: 57 mg (60%). Anal. Calcd for $C_{31}H_{52}ClNOsP_2$: C, 51.26; H, 7.21; N, 1.93. Found: C, 51.35; H, 7.30; N, 2.01. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): 10.58 (m, 1H, bq), 8.11 (m, 1H, bq), 8.00 (m, 1H, bq), 7.74 (m, 1H, bq), 7.60 (m, 1H, bq), 7.53 (m, 1H, bq), 7.34 (m, 1H, bq), 7.17 (m, 1H, bq), 2.17 (m, 3H, C*H*-^{i}Pr), 0.97 (m, 18H, C*H*$_3$-^{i}Pr), 0.60 (m, 18H, C*H*$_3$-^{i}Pr) −7.93 (t, 2H, J_{P-H} = 11.7 Hz, OsH_2). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2, 293 K, plus APT, HMQC and HMBC): 165.8 (t, J_{P-C} = 6, Os-C), 155.8 (C_{ipso}, bq), 150.2 (s, CH, bq), 140.8 (s, CH, bq), 138.8 (s, C_{ipso}, bq), 134.5 (s, CH, bq), 134.1 (s, C_{ipso}, bq), 129.6 (s, CH, bq), 129.1 (s, CH, bq), 126.3 (s, C_{ipso}, bq), 123.2 (s, CH, bq), 119.1 (s, CH, bq), 116.9 (s, CH, bq), 24.7 (t, J_{C-P} = 12, *C*H-^{i}Pr), 19.1 and 18.7 (s, *C*H$_3$-^{i}Pr). ^{31}P-{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): 4.3 (s). IR (KBr, cm^{-1}): 2293 and 2203 ν(Os−H_2), 1621 and 1557 ν(C═C). $T_{1(min)}$ (ms, CD_2Cl_2, 300 MHz, −8.01, 208 K): 38 ± 1 ⇒ d_{H-H} calc = 1.30 Å.

Determination of the J_{H-D} Value for Complex 5. A Young's tap NMR tube was charged with benzo[*h*]quinoline (30 mg, 0.17 mmol), $OsD_2Cl_2(P^iPr_3)_2$, (50 mg, 0.09 mmol), Et_3N (0.34 mmol), and toluene (0.75 mL). The mixture was heated at 95 °C for 12 h. After that, the solvent was removed in vacuo and CD_2Cl_2 (0.5 mL) was added. The ^{1}H{^{31}P} NMR (300 MHz) spectra of these solutions exhibit in the hydride region the resonances due to a mixture of the [Os](η^2-H−D) and the [Os](η^2-H−H) **5** species. J_{H-D} (Hz) = 7.7 ⇒ d_{H-H} = 1.29 Å.

Preparation of $RuCl\{\kappa^2$-*N*,*C*-[bq]**$\}(\eta$-$H_2)(P^iPr_3)_2$ (6).** Method A: A Young's tap Schlenk flask was charged with benzo[*h*]-quinoline (180 mg, 1.0 mmol), **1a** (250 mg, 0.5 mmol), Et_3N (0.28 mL, 2.0 mmol), and toluene (10 mL). The resulting mixture was heated at 95 °C for 24 h. The dark solution was filtered through Celite and concentrated under reduced pressure. Addition of diethyl ether (10 mL) caused the precipitation of an orange solid, which was dried in vacuo and characterized as **6**. Yield: 200 mg (65%). Method B: A Young's tap Schlenk flask was charged, under H_2 atmosphere, with **3** (100 mg, 0.15 mmol), Et_3N (0.085 mL, 0.6 mmol), and toluene (10 mL). The resulting mixture was heated at 95 °C for 12 h. The dark solution was filtered through Celite and concentrated under reduced pressure. Addition of diethyl ether (5 mL) caused the precipitation of an orange solid, which was dried in vacuo and characterized as **6**. Yield: 47 mg (50%). Anal. Calcd for $C_{31}H_{52}ClNRuP_2$: C, 58.43; H, 8.22; N, 2.20. Found: C, 58.31; H, 8.15; N, 2.43. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): 10.46 (m,

Table 1. Crystal Data and Data Collection and Refinement for 2, 5, and 6

	2	**5**	**6**
		Crystal Data	
formula	$C_{31}H_{53}Cl_2NOsP_2$	$C_{31}H_{52}ClNOsP_2$	$C_{31}H_{52}ClNP_2Ru$
molecular wt	762.78	726.33	637.20
color and habit	orange needle	yellow plate	orange irregular block
symmetry, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	8.8270(16)	10.2474(7)	10.288(3)
b, Å	31.354(6)	10.5561(7)	10.544(3)
c, Å	23.659(4)	15.5706(11)	15.572(4)
α, deg		93.0260(10)	93.132(5)
β, deg	95.603(4)	101.4360(10)	100.966(5)
γ, deg		107.9250(10)	107.901(5)
V, Å^3	6517(2)	1559.00(18)	1566.6(7)
Z	8	2	2
D_{calc}, g cm^{-3}	1.555	1.547	1.351
		Data Collection and Refinement	
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.71073	
monochromator		graphite oriented	
scan type		ω scans	
μ, mm^{-1}	4.197	4.298	0.708
2θ range, deg	3, 57	3, 57	3, 57
temp, K	100	100	100
no. of data collected	55 095	17 182	19 524
no. of unique data	11 400 (R_{int} = 0.1593)	7348 (R_{int} = 0.0497)	13 337 (R_{int} = 0.0522)
no. of params/restraints	710/24	345/2	343/2
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0736	0.0456	0.0422
wR_2[b] [all data]	0.1355	0.0888	0.1027
S[c] [all data]	1.119	1.053	1.019

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof $= S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

1H, bq), 8.18 (m, 1H, bq), 7.96 (m, 1H, bq), 7.74 (m, 1H, bq), 7.59 (m, 1H, bq), 7.54 (m, 1H, bq), 7.34 (m, 1H, bq), 7.24 (m, 1H, bq), 2.01 (m, 6H, C*H*-^{i}Pr), 0.93 (m, 18H, C*H*$_3$-^{i}Pr), 0.65 (m, 18H, C*H*$_3$-^{i}Pr), −9.0 (t, 2H, J_{P-H} = 8.0 Hz, RuH_2). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 293 K, plus APT, HMQC and HMBC): 183.8 (t, J_{P-C} = 9, Ru-C), 155.8 (C_{ipso}, bq), 152.3 (s, CH, bq), 141.7 (s, CH, bq), 140.5 (s, C_{ipso}, bq), 134.1 (s, CH, bq), 133.7 (s, C_{ipso}, bq), 129.2 (s, CH, bq), 128.0 (s, CH, bq), 126.3 (s, C_{ipso}, bq), 123.1 (s, CH, bq), 119.3 (s, CH, bq), 117.7 (s, CH, bq), 24.2 (t, J_{C-P} = 10, *C*H-^{i}Pr), 19.1 and 19.0 (s, *C*H$_3$-^{i}Pr). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): 34.6 (s). IR (KBr, cm^{-1}): 2000 and 1915 ν(Ru−H), 1619 and 1557 ν(C═C). $T_{1(min)}$ (ms, RuH_2, CD_2Cl_2, 400 MHz, −9.04, 223 K): 14 ± 1 ⟹ d_{H-H} calc = 1.05 Å.

Determination of the J_{H-D} Value for Complex 6. CD_3OD (0.10 mL) was added to CD_2Cl_2 solutions (0.5 mL) of the **6** species. After 24 h the $^1H\{^{31}P\}$ NMR spectra of these solutions exhibit in the hydride region the resonances due to a mixture of the [Os](η^2-H−D) and the [Os](η^2-H−H) **6** species. J_{HD} (Hz) = 24.8 ⟹ d_{H-H} = 1.01 Å.

Structural Analysis of Complexes 2, 5, and 6. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (molybdenum radiation, λ = 0.71073 Å) operating at 50 kV and 40 (**2** and **5**) or 30 (**6**) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 (**6**), 20 (**5**), or 30 (**2**) s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the Sadabs[35] program. The structures for all compounds were solved by the Patterson method. Refinement, by full-matrix least-squares on F^2 with SHELXL97,[36] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. Hydride ligands were located but not all of them refined appropriately. In these cases some restraints were applied to thermal parameters and Os−H bonds (**2** and **5**). The rest of the hydrogen atoms were observed or calculated and refined using a restricted riding model or freely. All the highest electronic residuals were observed in close proximity to the Os and Ru centers and make no chemical sense (see Table 1).

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Supporting Information Available: Detailed X-ray crystallographic data (bond distances, bond angles, and anisotropic parameters) for **2**, **5**, and **6** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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