H···H Interaction in Four-Membered P−H···H−M (M = Osmium, Ruthenium) Rings

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The dihydrido-1-butene complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**1**) reacts with $PHPh_2$ to give $OsH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**2**), which can also be prepared from the reaction of $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**3**) with $PHPh_2$. Similarly, treatment of $RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**4**) with $PHPh_2$ affords $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**5**). Complex **2** reacts with HBF_4 in dichloromethane-d_2 as the solvent to give the *cis*-hydrido−dihydrogen derivative $[OsH(\eta^2\text{-}H_2)(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**6**), which in solution exchanges the relative positions of the hydrido and dihydrogen ligands. The protonation of **2** with HBF_4 in acetone affords the solvate complex $[OsH\{\eta^1\text{-}OC(CH_3)_2\}(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**7**). The reaction of **7** with carbon monoxide leads to a mixture of the *cis*-dicarbonyl-$[OsH(CO)_2(PHPh_2)(P^iPr_3)_2]BF_4$ (**8**) and *trans*-dicarbonyl-$[OsH(CO)_2(PHPh_2)(P^iPr_3)_2]BF_4$ (**9**). The reactions of **7** with CH_3CN, LiC≡CPh, and KBr give $[OsH(CH_3CN)(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**10**), $OsH(C_2Ph)(CO)(PHPh_2)(P^iPr_3)_2$ (**11**), and $OsHBr(CO)(PHPh_2)(P^iPr_3)_2$ (**12**), respectively. The structures of **5** and **8** have been determined by X-ray diffraction analysis. In both cases, the coordination geometry around the metal center is octahedral, with the two triisopropylphosphine ligands in a trans position. Also in both cases, the H−P hydrogen atom of the diphenylphosphine ligand points toward one hydrido ligand, suggesting that there is a H···H interaction between the hydrido and the HP hydrogen atom. For **5** the H−H separation is about 2.6 Å, while for **8** the H−H separation is about 2.9 Å. Spectroscopic studies also suggest that one of the hydrido ligands of **2** and the HP hydrogen atom of the diphenylphosphine interact. In this case, the estimated H−H separation is 2.5 Å. In **2** and **5**, the H···H interaction blocks the free rotation of the diphenylphosphine group around the Os−P axis, while in **8** it only permits a light oscillation.

Introduction

Hydrogen bonding is a phenomenon of wide significance; hydrogen bonding takes place between an electron-deficient hydrogen and a region of high electron density.[1]

In 1986, Milstein et al. observed that the iridium complex $[Ir(PMe_3)_4]PF_6$ reacted with H_2O and H_2S to afford the *cis*-hydrido−hydroxo compound $[IrH(OH)(PMe_3)_4]PF_6$ and the related *cis*-hydrido−mercapto derivative $[IrH(SH)(PMe_3)_4]PF_6$.[2] A comparison of the structure of the hydrido−hydroxo complex with that of the hydrido−mercapto compound shows that one of the O−H group points toward the hydrido ligand while in the sulfur analogue the S−H group is pointing away from the hydrido. Furthermore, the Ir−O−H angle (104.4(7)°) is significantly smaller than the normal tetrahedral value, as opposed to 111(3)° in $[IrH(SH)(PMe_3)_4]PF_6$ or 119.4(9)° in the analogous compound *cis*-$[IrH(OMe)(PMe_3)_4]PF_6$.[3]

These observations have been rationalized by postulating an attractive interaction between the hydridic Ir−H and the OH proton, although spectroscopic evidences in favor of such an interaction have not been found.[2,3] As a result of the interaction, the O−H···H−Ir unit forms a four-membered ring with a hydrogen−hydrogen separation of 2.40(1) Å.[3]

Recently, some examples of hydridoiridium complexes containing related intramolecular hydrogen−hydrogen interactions have been reported, where the unit involved in the interactions forms six-membered rings. As a consequence of this more favored geometry, the interactions are stronger than that in $[IrH(OH)(PMe_3)_4]PF_6$ and they can be indirectly detected by spectroscopic methods. In these cases, the estimated hydrogen−hydrogen separations are in the range 1.6−1.8 Å.[4]

(1) (a) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960. (b) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin: New York, 1968. (c) Pimentel, G. C.; McClellan, A. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 347. (d) Kollman, P. A.; Allen, L. C. *Chem. Rev.* **1972**, *72*, 283. (e) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1991. (f) Yap, G. P. A.; Rheingold, A. L.; Das, P.; Crabtree, R. H. *Inorg. Chem.* **1995**, *34*, 3474. (g) Wessel, J.; Lee, J. C.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Einsenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507. (h) Patel, B. P.; Yao, W.; Yap, G. P. A.; Rheingold, A. L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1996**, 991.

(2) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387.

(3) Stevens, R. C.; Bau, R.; Mistein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429.

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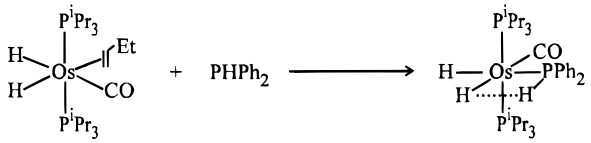
The force of an electrostatic interaction as postulated in the above-mentioned cases is proportional to the charges of the particles involved and inversily proportional to the separations between them. So, the weakness of the hydrogen−hydrogen interaction in $[IrH(OH)(PMe_3)_4]PF_6$ is not only a consequence of the long hydrogen−hydrogen separation, but also of the low charges supported by the hydrogen atoms. For a four membered ring of the type L−H···H−M, the separation between the hydrogen atoms must be necessarily long. However, one can modify the charges on them by increasing both the nucleophilic character of the hydrido ligand and the electrophilic character of the H−L hydrogen atom.

At first glance, the hydrido ligand of a neutral transition-metal hydrido compound should be more nucleophilic than that of a cationic one. This prompted us to prepare the complexes $MH_2(CO)(PHPh_2)(P^iPr_3)_2$ (M = Os, Ru) and to investigate the influence of the interaction between one of the hydrido ligands and the PH hydrogen atom on the structure and dynamic properties of the compounds. In this paper, we report the results from this study.

Results and Discussion

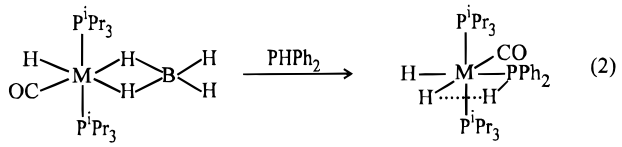
H···H Interaction in $MH_2(CO)(PHPh_2)(P^iPr_3)_2$ (M = Os, Ru). The addition of 1 equiv of diphenylphosphine to a hexane solution of the dihydrido-1-butene complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**1**) produces the displacement of the coordinated olefin and the formation of $OsH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**2**), which was isolated as a white solid in 62% yield, eq 1.



1 **2**

+ $CH_2{=}CHEt$ (1)

Complex **2** can be also prepared in 67% yield by reaction of the octahedral tetrahydrido borato compound $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**3**) with diphenylphosphine. Similarly, the treatment of $RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**4**) with this phosphine in methanol affords the related ruthenium derivative $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**5**), which was isolated as a white solid in 68% yield, eq 2.



M = Os (**3**), Ru (**4**) M = Os (**2**), Ru (**5**) (2)

(4) (a) Lee, J. C.; Rheingold, A. L.; Muller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021. (b) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (c) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201. (d) Lee, J. C.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014.

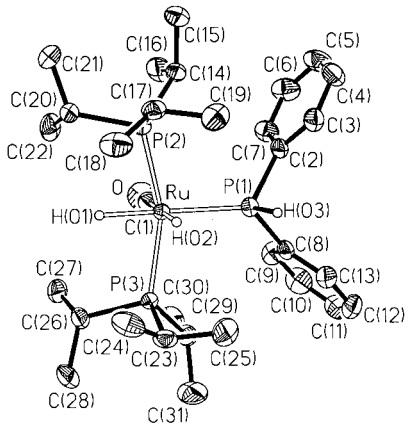


Figure 1. Molecular diagram of $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**5**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ (5)

Ru−P(1)	2.3264(8)	C(1)−O	1.158(4)
Ru−P(2)	2.3504(8)	P(1)−C(2)	1.843(3)
Ru−P(3)	2.3496(8)	P(1)−C(8)	1.847(3)
Ru−C(1)	1.896(3)	P(1)−H(03)	1.34(3)
Ru−H(01)	1.66(3)	H(02)−H(03)	2.63(5)
Ru−H(02)	1.63(4)		
P(1)−Ru−P(2)	100.74(3)	C(1)−Ru−P(3)	97.10(10)
P(1)−Ru−C(1)	97.39(10)	H(01)−Ru−H(02)	85.9(16)
P(1)−Ru−H(01)	166.2(10)	H(01)−Ru−P(3)	79.1(10)
P(1)−Ru−H(02)	80.4(12)	H(02)−Ru−P(3)	82.2(12)
P(1)−Ru−P(3)	100.68(3)	Ru−P(1)−C(2)	120.19(10)
P(2)−Ru−C(1)	97.51(10)	Ru−P(1)−H(03)	114.1(13)
P(2)−Ru−H(01)	75.9(10)	Ru−P(1)−C(8)	123.94(9)
P(2)−Ru−H(02)	84.1(12)	C(2)−P(1)−H(03)	97.5(14)
P(2)−Ru−P(3)	152.20(3)	C(2)−P(1)−C(8)	97.63(13)
C(1)−Ru−H(01)	96.3(11)	H(03)−P(1)−C(8)	98.3(13)
C(1)−Ru−H(02)	177.5(12)		

Figure 1 shows a view of the molecular geometry of **5**. Selected bond distances and angles are listed in Table 1. The hydrido ligands (H(01) and H(02)) and the hydrogen atom H(03) were located in the difference Fourier maps and refined as isotropic atoms together with the rest of the non-hydrogen atoms of the structure, giving Ru−H(01), Ru−H(02), and P(1)−H(03) distances of 1.66(3), 1.63(4) and 1.34(3) Å, respectively.

The ruthenium atom is coordinated in a somewhat octahedral fashion with the two triisopropylphosphine ligands in a pseudo-trans position (P(2)−Ru−P(3)= 152.20(3)°). The perpendicular plane is formed by the hydrido ligands H(01) and H(02), the carbonyl group trans disposed to H(02) (C(1)−Ru−H(02)= 177.5(12)°), and the diphenylphosphine trans disposed to H(01) (P(1)−Ru−H(01)= 166.2(10)°).

Without doubt, the most noticeable feature of the structure is the coplanarity of the group of atoms C(1), O, H(01), Ru, H(02), P(1), and H(03). The deviations from the best plane are −0.006(4) (C(1)), 0.002(3) (O), −0.042(32) (H(01)), 0.000(1) (Ru), 0.038(38) (H(02)), 0.000(1) (P(1)), and −0.004(34) (H(03)) and the value of the torsion angle H(02)−Ru−P(1)−H(03) is −2(2)°. This strongly supports the formation of a four-membered P(1)−H(03)···H(02)−Ru ring stabilized by electrostatic interaction between H(03) and H(02). The H(02)−H(03) separation is 2.63(5) Å.

This interaction also appears to have a significant influence on the coordination of the diphenylphosphine.

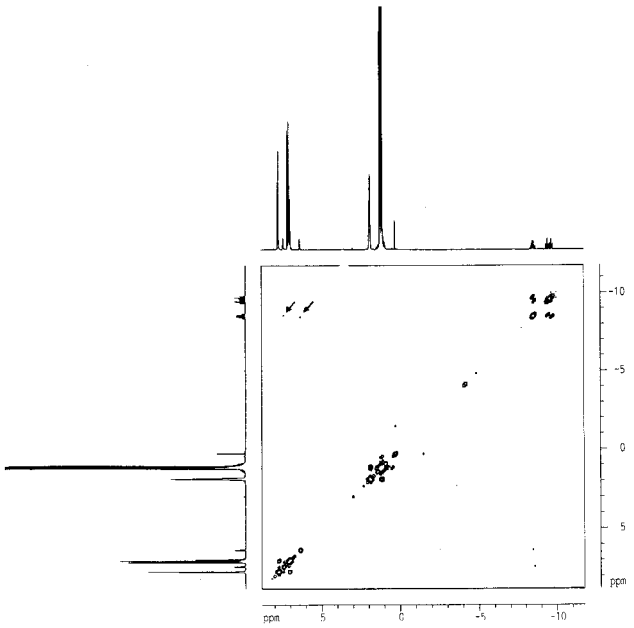


Figure 2. ^{1}H COSY NMR of the complex $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**5**).

Although the hydrido ligands show a great trans-influence and P(1) is trans disposed to H(01), the Ru−P(1) bond length (2.3264(8) Å) is about 0.03 Å shorter than the Ru−triisopropylphosphine distances (2.3504(8) and 2.3496(8) Å). The Ru−P(1) bond length is also between 0.03 and 0.04 Å shorter than the Ru−P distances found in $RuCl_2(PHPh_2)_4$ (2.3505(8) and 2.3665(8) Å).[5] The approach of the diphenylphosphine to the ruthenium atom produces a large steric hindrance between the isopropyl and phenyl groups of the phosphines. As a result, the P(2)−Ru−P(3) axis undergoes a folding toward the hydrido ligands and the C(2)−P(1)−C(8) angle (97.63(13)°) closes up slightly.[6]

The $^{31}P\{^1H\}$ and ^{1}H NMR spectra of **5** are temperature invariant between 363 and 183 K. In agreement with the disposition of the phenyl groups in Figure 1, the triisopropylphosphine ligands are chemically equivalent and, as a consequence, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 74.9 ppm for these ligands and a triplet at 20.2 ppm for the diphenylphosphine. The P−P coupling constant is 19.3 Hz. In the ^{1}H NMR spectrum, the most noticeable feature is the coupling between the resonances assigned to H(02) and H(03), as supported by the ^{1}H−COSY and selective heteronuclear $^1H\{^{31}P\}$ NMR spectra shown in Figures 2 and 3. In the $^1H\{^{31}P\}$ NMR spectrum (Figure 3a), the resonance due to H(03) appears at 6.88 ppm as a doublet with a H(03)−H(02) coupling constant of 4.1 Hz while that corresponding to H(02) is observed at −8.51 ppm as a double doublet with a H(02)−H(01) coupling constant of 6.1 Hz. The H(01) ligand gives rise to a doublet at −9.58 ppm. With P^iPr_3 coupling (Figure 3b), these resonances split into a triplet of doublets, triplet of doublets of doublets, and triplet of doublets, respectively, with H−P coupling constants of 7.8 (H(03)), 16.8 (H(02)), and 25.7 Hz (H(01)). With $PHPh_2$ coupling (Figure 3c), the resonances of the spectrum shown in Figure 3a split into a double doublet (H(03)), doublet of doublets of doublets (H(02)), and double doublet (H(01)) with H−P(1) coupling constants of 315.5 (H(03)), 28.2 (H(02)), and 77.9 Hz (H(01)). Coupling between H(01) and H(03) is not observed.

In this context, it should be mentioned that the complexes $(CO)_5W(\mu\text{-}PPh_2)OsH(CO)_2(PHPh_2)(PMePh_2)$ and $(CO)_5W(\mu\text{-}PPh_2)OsH(CO)(PHPh_2)(PMePh_2)$ containing a diphenylphosphine cis-disposed to the hydrido ligand have been previously reported.[7] While in the first of them the hydrido ligand is coupled with the HP hydrogen (J_{H-H} = 3.6 Hz), in the second one this coupling is not observed. Coupling between the HP hydrogen and the hydrido ligands in the complexes $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(PHPh_2)$ and $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}HgBr)(CO)_8(PHPh_2)$ is not observed either.[8]

At first glance, the chemical equivalence of the triisopropylphosphine ligands in the $^{31}P\{^1H\}$ NMR spectrum could be also explained in terms of an almost free rotation of the diphenylphosphine moiety with a time average C_s symmetry. However, it should be noted that in the ^{1}H NMR spectrum, neither the chemical shifts of H(02) and H(03) nor the H(02)−H(03) coupling constants can be identical in rotamers **a**, **b**, and **c** (Figure 4) and that rotamer **a** (the only one present, at least, in the solid state) is more stable than the others. If the three rotamers have different energies, in solution, the position of a possible equilibrium between them, as a result from the rotation of the diphenylphosphine group around the Ru−PH axis, should be determined by the energy difference between the rotamers. Thus, the observed chemical shifts of H(02) and H(03) and the H(02)−H(03) coupling constant should be a function of the molar fraction of each rotamer according to eqs 3 and 4.[9] Then, if the spectrum is recorded at

$$\delta = x_1\delta_{\mathbf{a}} + x_2\delta_{\mathbf{b}} + x_3\delta_{\mathbf{c}} \quad (3)$$

$$J = x_1J_{\mathbf{a}} + x_2J_{\mathbf{b}} + x_3J_{\mathbf{c}} \quad (4)$$

different temperatures, the equilibrium ratios are shifted. In such a case, one should expect changes in the spectrum, and this is not observed for our complex. So, the independence of the ^{1}H NMR spectrum with the temperature suggests that the rotation of the diphenylphosphine group around the Ru−PH bond is blocked, as a result of a strong H(02)···H(03) interaction.

The T_1 values for the resonances corresponding to H(01) and H(02) were determined over the temperature range of 293−193 K. The T_1(min) values for the two resonances were found to the same temperature, 233 K. The lower T_1(min) value at 300 MHz for H(02) (231 ms) versus H(01) (251 ms) implies an excess relaxation rate for H(02) of 0.35 s^{-1}. Using the standard equation[10] and assuming, according to a blocked rotation of the $PHPh_2$ group, that the H(02)−H(03) vector rotates with the molecule as a whole, the H(02)···H(03) separation

(5) McAslan, E. B.; Blake, A. J.; Stephenson, T. A. *Acta Crystallogr.* **1989**, *C45*, 1811.

(6) The related angles in $RuCl_2(PHPh_2)_4$ are 100.18(12)° and 101.30(11)°. See ref 5.

(7) (a) Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 5934. (b) Rosenberg, S.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1985**, *4*, 1184.

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(9) Friebolin, H. *Basic One-and Two-Dimensional NMR Spectroscopy*; VCH Verlagsgesellschaft: Weinheim, 1991.

(10) R = 129.18/r6. See ref 11.

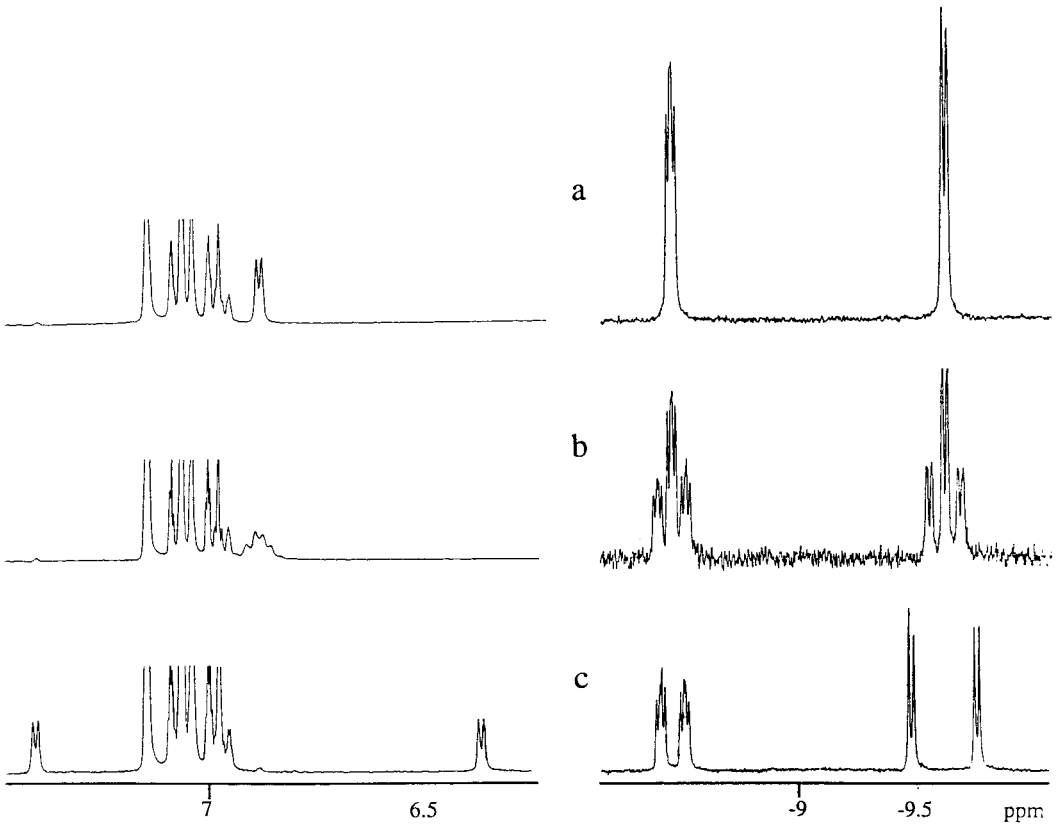

Figure 3. ^{1}H NMR spectra of $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**5**) in benzene-d_6: (a) $^1H\{^{31}P\}$; (b) $^1H\{PHPh_2\}$; (c) $^1H\{P^iPr_3\}$.

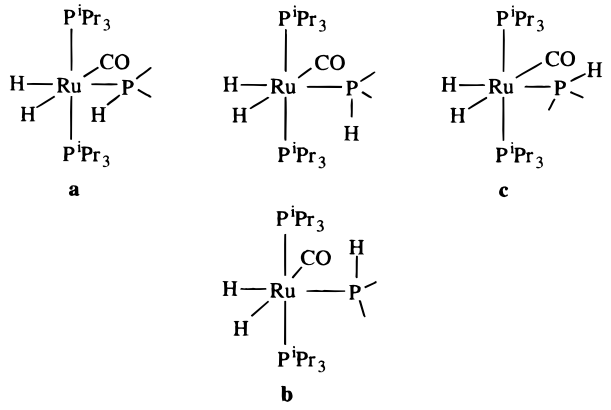

Figure 4. Possible rotamers of complex $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**5**).

can be estimated to be about 2.68 Å, which agrees very well with that determined by X-ray diffraction (2.63(5) Å).

The $^{31}P\{^1H\}$ and ^{1}H NMR spectra of $OsH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**2**) are similar to those of **5**. The $^{31}P\{^1H\}$ spectrum consists of a doublet at 35.1 ppm and a triplet at −18.6 ppm (J_{P-P} = 13.9 Hz), in agreement with a diphenylphosphine cis-disposed to two equivalent triisopropylphosphine ligands. In the ^{1}H NMR spectrum, the resonance of the HP hydrogen atom appears at 7.44 ppm as a doublet of triplets of doublets, with a H−H coupling constant of 4.5 Hz and H−P coupling constants of 331.7 ($PHPh_2$) and 6.7 (P^iPr_3) Hz. The resonance of the hydrido ligand trans-disposed to the diphenylphosphine is observed at −10.64 ppm, also as a doublet (J_{H-P} = 62.6 Hz) of triplets ($J_{H-P'}$ = 25.5 Hz) of doublets (J_{H-H} = 5.5 Hz), while that corresponding to the hydrido ligand cis-disposed to the diphenylphosphine appears at −9.94 ppm as a triplet of doublets of doublets of doublets with H−P coupling constants of 21.7 (P^iPr_3) and 21.4 ($PHPh_2$) Hz.

The T_1 values for the HP and hydrido resonances were determined over the temperature range 293−213 K. As for **2**, T_1(min) values for the three resonances were found at 233 K. At 300 MHz, the T_1(min) value of the HP resonance is 188 ms while those of hydrido resonances are 227 (hydrido cis to $PHPh_2$) and 258 ms (hydrido trans to $PHPh_2$). From these values, an excess relaxation rate for the hydrido cis to $HPPh_2$ of 0.53 s^{-1} can be calculated, which leads to an estimated H···H separation of 2.50 Å.[10,11]

The nucleophilic character of analogous hydrido complexes usually increases down a column in the periodic table.[12] In this sense, it should be noted that the calculated H···H separation in **2** is about 0.2 Å shorter than that calculated for **5**, which appears to corroborate the electrostatic character of these interactions.

H···H Interaction in $[OsHL(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (L = H_2, CO). Although the net positive charge on the complex should increase the acidity of the P−H group, it is also true that a cationic charge and the substitution of σ-donor for π-acceptor groups should decrease the nucleophilicity of the hydrido ligands.[13] The latter prompted us to prepare new cationic hydrido−

(11) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Bautista, M. T.; Earl, K. A.; Jia, J.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031. (c) Desroisiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (d) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

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(13) Labinger, J. A. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York, 1991; Chapter 10.

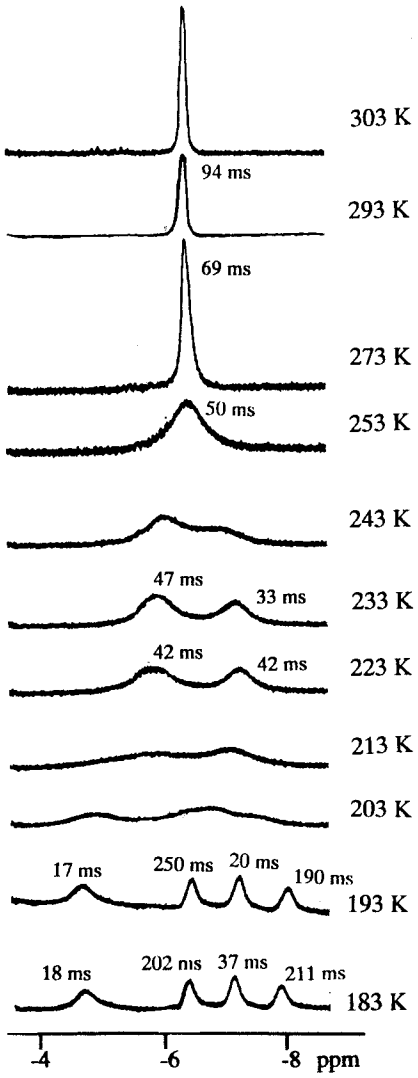


Figure 5. Variable-temperature 300-MHz ^{1}H NMR spectra in the high-field region of $[OsH(\eta^2\text{-}H_2)(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**6**) in CD_2Cl_2.

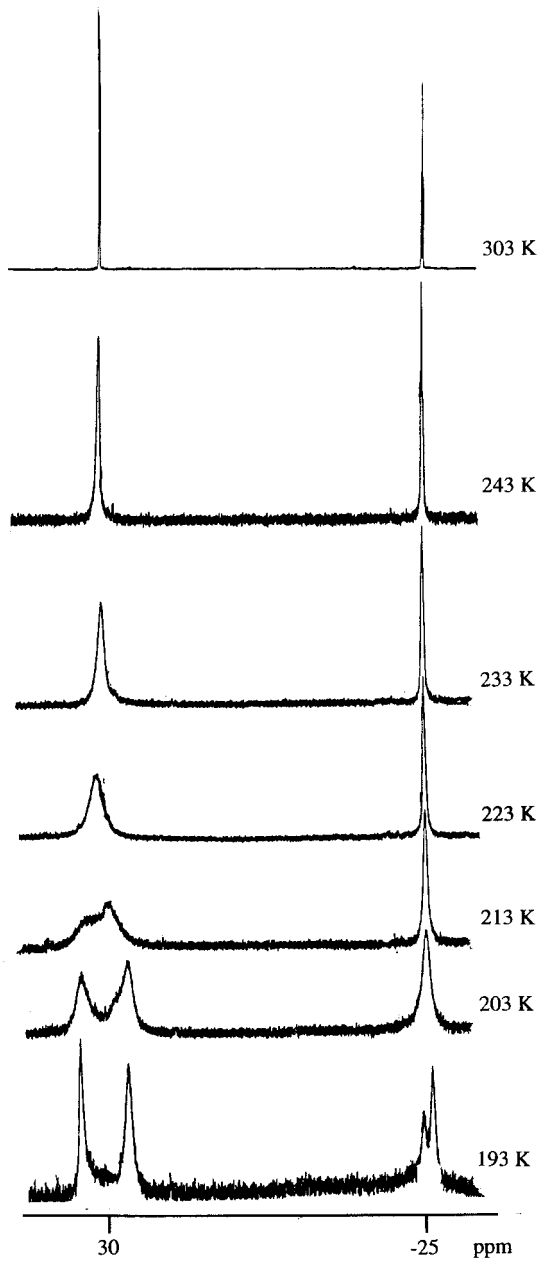


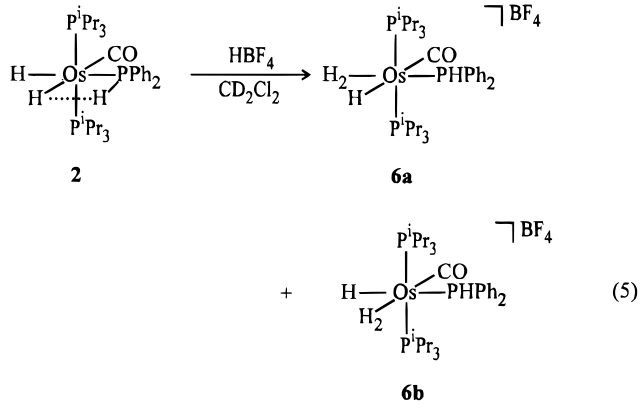
Figure 6. Variable-temperature 300-MHz $^{31}P\{^1H\}$ NMR spectra of $[OsH(\eta^2\text{-}H_2)(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**6**) in CD_2Cl_2.

diphenylphosphine complexes containing molecular hydrogen and carbon monoxide as ancillary ligands to study weaker H···H interactions.

At room temperature, the ^{1}H NMR spectrum of the solution formed by addition of 1 equiv of HBF_4 to **2** in dichloromethane-d_2 shows the resonance due to the HP proton at 6.88 ppm as a clean doublet of triplets, with P−H coupling constants of 360.0 (P = $PHPh_2$) and 6.5 (P = P^iPr_3) Hz. H−H coupling between the HP proton and the hydrido ligands is not observed. In the high-field region, the spectrum contains a broad resonance centered at −6.80 ppm. This spectrum is temperature dependent. Figure 5 shows the hydrido region as a function of the temperature. At 183 and 193 K, four broad resonances are observed, which coalesce at about 203 K to give two broad signals. Between 243 and 253 K, a second coalescence occurs and above-mentioned broad resonance is observed. With regard to the T_1 values shown in Figure 5, there is no doubt that two of the resonances observed at 183 and 193 K correspond to dihydrogen ligands while the other two resonances are due to hydrido ligands.

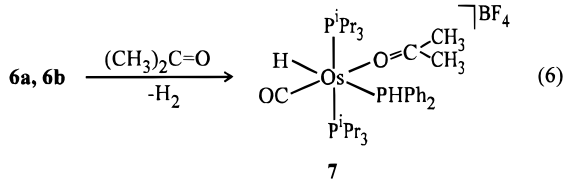
The $^{31}P\{^1H\}$ NMR spectrum is also temperature dependent. At 193 K, the spectrum shows two resonances for the triisopropylphosphine ligands and two resonances for the diphenylphosphine group. Between 193 and 203 K, the signal of the diphenylphosphine coalesce. The coalescence of resonances corresponding to the triisopropylphosphine ligands occurs between 223 and 213 K. At 303 K, the triisopropylphosphine ligands give rise to a doublet at 31.7 ppm while the resonance due to diphenylphosphine is observed as a triplet at −27.1 ppm. The P−P coupling constant is 18.6 Hz (Figure 6).

These observations can be rationalized according to the formation of two isomers of the *cis*-hydrido−dihydrogen complex $[OsH(\eta^2\text{-}H_2)(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**6a** and **6b** in eq 5), which rapidly exchange the hydrido and dihydrogen positions in solution at high temperature. Furthermore, the absence of nuclear spin coupling between the hydridos and the HP hydrogen nucleus suggests that in **6** there is no H···H interaction.



2 **6a** **6b** (5)

The addition of acetone to dichloromethane-d_2 solutions of **6** produces the displacement of the dihydrogen ligand and the formation of the solvate complex [OsH{(η^1-OC(CH$_3$)$_2$}(CO)(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (**7** in eq 6), which can be isolated as a white solid in 68% yield by protonation of **2** with HBF$_4$ in acetone and the subsequent addition of diethyl ether.

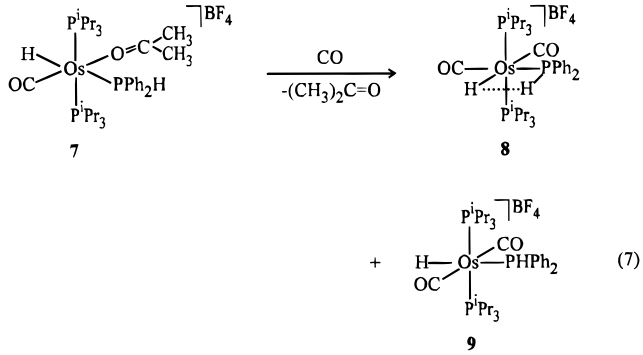


7 (6)

In the IR spectrum of **7** in Nujol, the most noticeable features are the absorption due to the [BF$_4$]$^-$ anion with T_d symmetry centered at 1075 cm^{-1}, indicating that the anion is not coordinated to the metallic center, and the ν(C═O) band of the carbonyl group of the acetone ligand at 1656 cm^{-1}, suggesting that the acetone molecule coordinates to the metal by the oxygen atom.[14] The coordination of the oxygen atom of the acetone is also supported by the ^{13}C{^{1}H} NMR spectrum at 193 K, which shows a singlet at 224.6 ppm corresponding to the carbon atom of the carbonyl group.

The ^{1}H and ^{31}P{^{1}H} NMR spectra of **7** also support the structure proposed for this compound in eq 6. The ^{31}P{^{1}H} NMR spectrum consists of a triplet at −18.3 ppm and a doublet at 29.3 ppm (J_{P-P} = 13.6 Hz), in agreement with a diphenylphosphine ligand cis-disposed to two equivalent triisopropylphosphines. The proposed trans disposition of the hydrido and diphenylphosphine ligands is supported by the ^{1}H NMR spectrum, which contains a doublet (J_{H-P} = 85.3 Hz) of triplets ($J_{H-P'}$ = 23.3 Hz) at −5.88 ppm . In the low-field region, the spectrum exhibits the expected resonance for the diphenylphosphine proton, which appears at 7.55 ppm as a doublet of triplets with H−P coupling constants of 338.2 and 5.4 Hz. In addition, it should be noted that although there are three bonds between this hydrogen atom and the hydrido ligand, coupling between them is not observed.

The acetone ligand of **7** can be easily displaced by carbon monoxide. Thus, by passing a slow stream of this gas through a dichloromethane solution of **7**, the dicarbonyl complex [OsH(CO)$_2$(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ was formed as a ca. 2:1 mixture of the cis-isomer **8** and the trans-isomer **9** (eq 7).



7 **8** **9** (7)

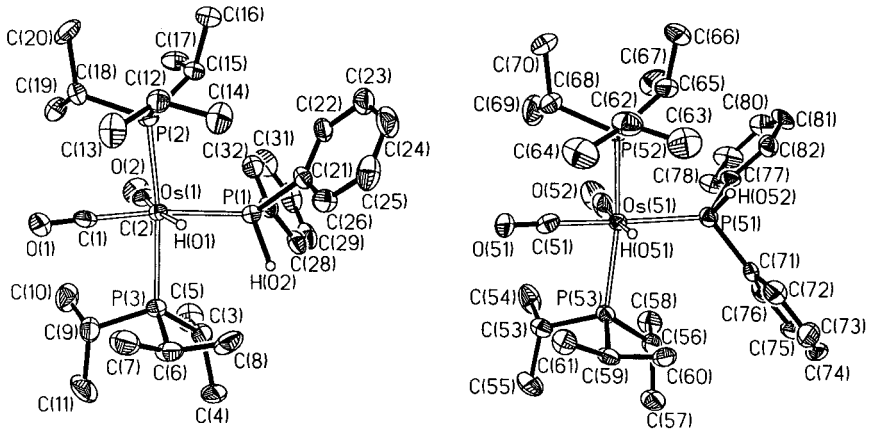
In solution, complex **9** slowly isomerizes into **8**. Thus, after 1 week, isomer **8** was obtained as a pure crystalline solid by crystallization in dichloromethane−diethyl ether and characterized by an X-ray crystallographic study. The structure has two crystallographically independent molecules of complex **8** in the asymmetric unit. Drawings of both molecules are shown in Figure 7. Selected bond distances and angles are collected in Table 2. In both molecules the hydrido ligand and the HP hydrogen atom were located in the difference Fourier maps and refined as isotropic atoms together with the rest of the non-hydrogen atoms of the structure, giving Os−H distances of 1.69(8) (molecule a) and 1.68(6) (molecule b) Å and P−H bond lengths of 1.40(5) (molecule a) and 1.39(5) (molecule b) Å.

The coordination geometry around the osmium atom is octahedral, with the two triisopropylphosphine ligands in a trans position. The perpendicular plane is formed by the carbonyl groups mutually cis-disposed and the hydrido and diphenylphosphine ligands also cis-disposed.

In both molecules the P−H group lies in quadrants bordered on the hydrido ligand. However, the four atoms forming the four-membered P−H···H−Os ring are not coplanar, the values of the torsion angle H(01)−Os−P(1)−H(02) are 66(3)° (molecule a) and −36(2)° (molecule b). This seems to indicate that although there is a H···H interaction, it is significantly weaker than those in **2** and **5**. In agreement with this, the metal−diphenylphosphine separation is longer in **8** than in **5** (2.429(2) and 2.433(2) Å versus 2.3264(8) Å). The estrangement of the diphenylphosphine from the metal produces a decrease of the steric hindrance between the isopropyl and phenyl groups of the phosphines. As a result, the folding of the phosphorus−metal−phosphorus axis in **8** is smaller than in **5** (167.96(6)° and 165.04(7)° versus 152.20(3)°) and the angle formed by phosphorus and the *ipso*-carbon atoms of the diphenylphosphine is bigger in **8** than in **5** (105.5(3)° and 101.2(3)° versus 97.63(13)°). The H···H separation also seems to be longer in **8** than in **5** (3.04(9) and 2.83(8) Å versus 2.63(5) Å).

From the X-ray analysis of the structure of **8**, it is inferred that this complex has more than one stable conformer and that the difference in energy between them must be small. Furthermore, it should be noted that the main difference between molecules a and b of **8** is the disposition of the phenyl groups and the HP

(14) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 1669.



(a) **(b)**

Figure 7. Molecular diagrams for the two independent molecules (a and b) of the cation $[OsH(CO)_2(PHPh_2)(P^iPr_3)_2]^+$ (**8**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[OsH(CO)_2(PHPh_2)(P^iPr_3)_2]BF_4$ (8)[a]

	a	b		a	b
Os−P(1)	2.429(2)	2.433(2)	C(1)−O(1)	1.148(8)	1.152(8)
Os−P(2)	2.430(2)	2.436(2)	C(2)−O(2)	1.151(8)	1.158(9)
Os−P(3)	2.431(2)	2.438(2)	P(1)−C(21)	1.829(7)	1.832(6)
Os−C(1)	1.893(8)	1.893(8)	P(1)−C(27)	1.826(7)	1.834(7)
Os−C(2)	1.939(8)	1.910(9)	P(1)−H(02)	1.40(5)	1.39(5)
Os−H(01)	1.69(8)	1.68(6)	H(01)−H(02)	3.04(9)	2.83(8)
P(1)−Os−P(2)	98.84(6)	89.94(7)	C(1)−Os−P(3)	85.3(2)	84.1(2)
P(1)−Os−C(1)	168.9(2)	166.9(2)	C(2)−Os−H(01)	172(2)	176(2)
P(1)−Os−C(2)	93.4(2)	95.1(2)	C(2)−Os−P(3)	94.5(2)	95.3(3)
P(1)−Os−H(01)	79(3)	84.3(19)	H(01)−Os−P(3)	87(3)	89(2)
P(1)−Os−P(3)	89.45(6)	99.60(6)	Os−P(1)−C(21)	124.5(2)	125.6(2)
P(2)−Os−C(1)	85.0(2)	84.2(2)	Os−P(1)−H(02)	108.2(18)	106.2(18)
P(2)−Os−C(2)	93.8(2)	95.3(3)	Os−P(1)−C(27)	116.7(2)	119.3(2)
P(2)−Os−H(01)	86(3)	81(2)	C(21)−P(1)−H(02)	98.7(18)	98.0(18)
P(2)−Os−P(3)	167.96(6)	165.04(7)	C(21)−P(1)−C(27)	105.5(3)	101.2(3)
C(1)−Os−C(2)	96.7(3)	97.1(3)	H(02)−P(1)−C(27)	98.7(19)	102(2)
C(1)−Os−H(01)	91(3)	83.2(19)			

[a] The first set of values (a) corresponds to the bond distances and angles of molecule a in Figure 7; the second set of values (b) corresponds to the related parameters observed in the second independent molecule (b in Figure 7).

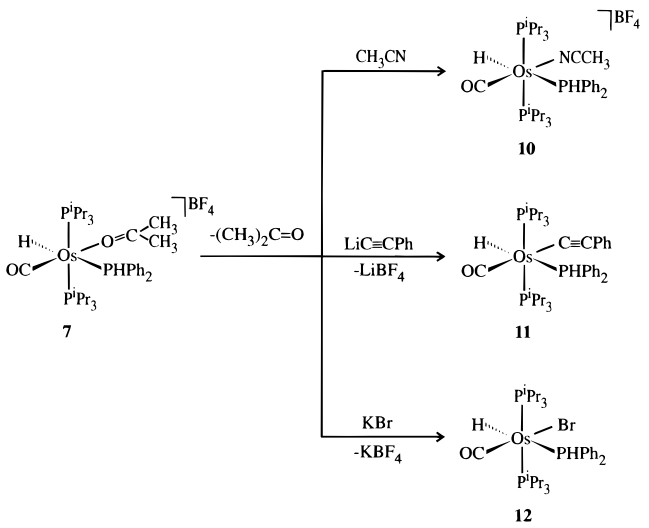
hydrogen atom, which produce a loss of the symmetry. As a result, the triisopropylphosphine ligands of both conformers are chemically inequivalent while the chemical environment of the phosphorus atom of the diphenylphosphine group is always the same. Accordingly, if the NMR spectra were recorded at different temperatures, one should expect changes in the signal corresponding to the triisopropylphosphine ligands in the $^{31}P\{^1H\}$ NMR spectrum and in the resonances of the hydrido ligand and the HP hydrogen atom in the ^1H spectrum. In fact, the $^{31}P\{^1H\}$ and ^1H NMR spectra of **8** are temperature dependent. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet ($J_{P-P} = 25.7$ Hz) at 15.1 ppm corresponding to the triisopropylphosphine ligands and a triplet at −35.8 ppm for the diphenylphosphine. Although decoalescence is not observed, lowering the sample temperature leads to broadening of the triisopropylphosphine resonance while the diphenylphosphine signal does not change. In the ^1H NMR spectrum at room temperature, the hydrido ligand, which is coupled with the HP proton, gives rise to a doublet ($J_{H-P} = 27.9$ Hz) of triplets ($J_{H-P'} = 18.0$ Hz) of doublets ($J_{H-H} = 4.5$ Hz) at −8.10 ppm. The resonance of the HP proton appears at 7.19 ppm, also as a doublet of triplets of doublets but with H−P coupling constants of 378.0 and 9.3 Hz. Lowering the sample temperature also produces broadening of both resonances.

In contrast to the NMR spectra of **8**, the $^{31}P\{^1H\}$ and ^1H NMR spectra of the *trans*-dicarbonyl isomer **9** are temperature invariant. The $^{31}P\{^1H\}$ NMR spectrum contains a doublet at 19.0 ($J_{P-P} = 11.5$ Hz) ppm for the triisopropylphosphine ligands and a triplet at −42.0 ppm for the diphenylphosphine. In the ^1H NMR spectrum, the resonance of the hydrido ligand, which is not coupled with the HP proton, appears at −10.31 ppm as a doublet ($J_{H-P} = 39.9$ Hz) of triplets ($J_{H-P'} = 20.4$ Hz) and the HP proton is observed at 7.48 ppm, also as a doublet ($J_{H-P} = 362.4$ Hz) of triplets ($J_{H-P'} = 5.4$ Hz).

In the *trans*-dicarbonyl isomer **9**, which does not possess a H···H interaction, the free rotation of the diphenylphosphine group around the Os−PH axis must occur. Furthermore, the independence of its spectra (^1H and $^{31}P\{^1H\}$) from temperature suggests that this rotation is fast at each temperature.

In contrast to the spectra of **9**, the ^1H and $^{31}P\{^1H\}$ NMR spectra of **8** are temperature dependent. The independence of the spectra of **9** from temperature shows that the broadening observed in the Os−H and PH signals in the ^1H NMR spectrum and the broadening of the signal of the triisopropylphosphine in the $^{31}P\{^1H\}$

Scheme 1



NMR spectrum of **8** can be only due to a hindered rotation around the Os−PH bond. Thus, the comparison between the spectra of **8** and **9** indicates that in **8** the H···H interaction persists in solution and, therefore, the fluxional process in the *cis*-dicarbonyl isomer most probably consists of an oscillation of the diphenylphosphine group around the Os−PH axis. In addition, comparison of the structural parameters of **8** and **5** clearly shows that the H···H interaction in **5** is stronger than in **8**. So, the independence of the spectra (^{1}H and ^{31}P{^{1}H}) of **2** and **5** with the temperature can be only rationalized by accepting that in these compounds the rotation of the diphenylphosphine around the M−PH axis is blocked.

The T_1 values for the hydrido resonances of **8** and **9** were determined over the range of 293−188 K. The T_1(min) values at 300 MHz for both resonances (271 ms for the hydrido ligand of **8** and 288 ms for the hydrido ligand of **9**) were found at the same temperature, 198 K. Assuming that the excess relaxation rate for the hydrido resonance of **8** (0.22 s^{-1}) is a result of the proximity of the HP proton in this compound, we can estimate a H···H separation of 2.9 Å,[10] which is the average value of those found by X-ray diffraction (3.04(9) and 2.83(8) Å), in agreement with the proposed oscillation.

Inside of this range, we attempted to tune the H···H interaction by replacement of one carbonyl group by σ-donor ligands. Thus, we carried out the reactions of the acetone complex **7** with acetonitrile, lithium phenylacetylide, and potassium bromide (Scheme 1). Unfortunately, in the three new compounds, [OsH(CO)(CH$_3$CN)(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (**10**), OsH(C$_2$Ph)(CO)(PHPh$_2$)(P^{i}Pr$_3$)$_2$ (**11**), and OsHBr(CO)(PHPh$_2$)(P^{i}Pr$_3$)$_2$ (**12**), the hydrido and diphenylphosphine ligands are mutually trans-disposed and a H···H interaction is not observed. This suggests that although the H···H interaction can contribute to the stability of a particular complex, it is not sufficient to determine its stereochemistry.

Complexes **10**−**12** were obtained in 50−70% yield as white solids. The proposed trans disposition of the hydrido and diphenylphosphine ligands is supported by the ^{1}H NMR spectra, which contain doublets of triplets between −7.56 and −9.07 ppm with H−P coupling constants between 74.4 and 93.6 (PHPh$_2$) Hz and between 22.5 and 23.7 (P^{i}Pr$_3$) Hz. H−H coupling between these hydridos and the HP hydrogen atoms is not observed.

Conclusion

This study has revealed that in the solid state as well as in solution an intramolecular interaction between nucleophilic and electrophilic hydrogen atoms of a transition-metal complex can take place, even when the separation between the hydrogen atoms is more than 2.4 Å. Because the interaction is electrostatic in character, it can be modulated by tuning the nucleophilicity and electrophilicity of the hydrogen atoms.

Although the interaction does not impose the stereochemistry of a particular complex, it favors the formation of determined conformers. Some unusual distortions of the structure of the complex can also be rationalized on the basis of this interaction. In solution, it reduces the dynamic properties of the complexes, in particular those of the ligands supporting the interaction.

In conclusion, we report the characterization of a new intramolecular H···H interaction (long distance H···H interaction) which for transition-metal hydrido compounds has a significant influence in the structural parameters of the molecule and, in solution, in the dynamic behavior of the ligands.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere by using Schlenk techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complexes OsH$_2$(η^2-CH$_2$=CHEt)(CO)(P^{i}Pr$_3$)$_2$ (**1**),[15] OsH(η^2-H$_2$BH$_2$)(CO)(P^{i}Pr$_3$)$_2$ (**3**),[16] and RuH(η^2-H$_2$BH$_2$)(CO)(P^{i}Pr$_3$)$_2$ (**5**)[16] were prepared by a published method.

Physical Measurements. NMR spectra were recorded on a Varian UNITY 300 or on a Bruker ARX 300 spectrometer at room temperature unless otherwise stated. Chemical shifts are expressed in parts per million, upfield from Si(CH$_3$)$_4$ (^{1}H, ^{13}C{^{1}H}) and 85% H$_3$PO$_4$ (^{31}P{^{1}H} NMR spectra). Coupling constants J and N ($N = J$(HP) + J(HP′) for ^{1}H; and $N = J$(CP) + J(CP′) for ^{13}C) are given in hertz. The probe temperature of the NMR spectrometers was calibrated at each temperature against a methanol standard. The T_1 experiments were performed on a Varian UNITY 300 spectrometer or on a Bruker AXR 300 spectrometer with a standard 180°−τ−90° pulse sequence. T_1 values are given in milliseconds (ms). Infrared spectra were recorded on a Nicolet 550 spectrometer using Nujol mulls on polyethylene sheets. C and H analyses were carried out on a Perkin-Elmer 240C microanalyzer.

Preparation of OsH$_2$(CO)(PHPh$_2$)(P^{i}Pr$_3$)$_2$ (2). The complex can be prepared by two different procedures.

(a) A solution of OsH$_2$(η^2-CH$_2$=CHEt)(CO)(P^{i}Pr$_3$)$_2$ (ca. 160 mg, 0.28 mmol) in 5 mL of pentane was treated with PHPh$_2$ (59 μL, 0.34 mmol). The mixture was stirred for 30 min at room temperature and concentrated in vacuo to dryness. Addition of methanol to the resulting residue gave a white solid. The mixture was decanted, and the resulting white solid was washed with methanol and dried in vacuo. Yield: 125 mg (62%).

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(16) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

(b) To a stirred suspension of $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**3**) (115 mg, 0.21 mmol) in 5 mL of methanol was added $PHPh_2$ (36 μL, 0.21 mmol). The mixture was stirred for 1 h at room temperature. A white solid was formed. The solution was decanted, and the white solid was washed with methanol and dried in vacuo. Yield: 102 mg (67%). Anal. Calcd for $C_{31}H_{55}OOsP_3$: C, 51.22; H, 7.62. Found: C, 50.71; H, 8.10.

IR (Nujol, cm^{-1}): $\nu(PPh_2-H)$ 2334, $\nu(Os-H)$ 1984, $\nu(CO)$ 1853. ^1H NMR (300 MHz, C_6D_6): δ 7.72 (vt, 4H, $N = J_{H-H} + J_{H-P} = 17.4$ Hz, *o*-C_6H_5), 7.44 (dtd, 1H, $J_{H-P} = 331.7$ Hz, $J_{H-P'} = 6.7$ Hz, $J_{H-H} = 4.5$ Hz, P*H*Ph_2), 7.07 (ddd, 4H, $J_{H-H} = J_{H-H'} = 7.0$ Hz, $J_{H-P} = 1.5$ Hz, *m*-C_6H_5), 6.98 (dd, 2H, $J_{H-H} = 7.0$ Hz, $J_{H-H'} = 1.4$ Hz, *p*-C_6H_5), 1.94 (m, 6H, PC*H*CH_3), 1.19 (dvt, 18H, $J_{H-H} = 7.1$ Hz, $N = 13.5$ Hz, PCHC*H*$_3$), 1.09 (dvt, 18H, $J_{H-H} = 6.9$ Hz, $N = 12.6$ Hz, PCHC*H*$_3$), −9.94 (tddd, 1H, $J_{H-P} = 21.7$ Hz, $J_{H-P'} = 21.4$ Hz, $J_{H-H} = 5.5$ Hz, $J_{H-H'} = 4.5$ Hz, Os-*H*), −10.64 (dtd, 1H, $J_{H-P} = 62.6$ Hz, $J_{H-P'} = 25.5$ Hz, $J_{H-H} = 5.5$ Hz, Os-*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 35.1 (d, $J_{P-P'} = 13.9$ Hz), −18.6 (t, $J_{P-P'} = 13.9$ Hz).

Preparation of $RuH_2(CO)(PHPh_2)(P^iPr_3)_2$ (5). A stirred suspension of $RuH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**4**) (120 mg, 0.26 mmol) in 5 mL of methanol was treated with $PHPh_2$ (45 μL, 0.26 mmol). The mixture was stirred for 4 h at room temperature. A white solid was formed. The solution was decanted, and the white solid was washed with methanol and dried in vacuo. Yield: 113 mg (68%). Anal. Calcd for $C_{31}H_{55}OP_3Ru$: C, 58.38; H, 8.69. Found: C, 58.46; H, 8.11.

IR (Nujol, cm^{-1}): $\nu(PPh_2\text{-}H)$ 2336, $\nu(Ru-H)$ 1949, $\nu(CO)$ 1845. ^1H NMR (300 MHz, C_6D_6): δ 7.74 (vt, 4H, $N = J_{H-P} + J_{H-H} = 18.3$ Hz, *o*-C_6H_5), 7.07 (vt, 4H, $N = J_{H-H} + J_{H-H'} = 14.4$ Hz, *m*-C_6H_5), 6.99 (d, 2H, $J_{H-H} = 7.1$ Hz, *p*-C_6H_5), 6.88 (dtd, 1H, $J_{H-P} = 315.5$ Hz, $J_{H-P'} = 7.8$ Hz, $J_{H-H} = 4.1$ Hz, P*H*Ph_2), 1.88 (m, 6H, PC*H*CH_3), 1.23 (dvt, 18H, $J_{H-H} = 7.2$ Hz, $N = 13.5$ Hz, PCHC*H*$_3$), 1.12 (dvt, 18H, $J_{H-H} = 6.8$ Hz, $N = 12.7$ Hz, PCHC*H*$_3$), −8.51 (dtdd, 1H, $J_{H-P} = 28.2$ Hz, $J_{H-P'} = 16.8$ Hz, $J_{H-H} = 6.1$ Hz, $J_{H-H'} = 4.1$ Hz, Ru−*H*), −9.58 (dtd, 1H, $J_{H-P} = 77.9$ Hz, $J_{H-P'} = 25.7$ Hz, $J_{H-H} = 6.1$ Hz, Ru−*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, C6D6): δ 74.9 (d, $J_{P-P'} = 19.3$ Hz), 20.2 (t, $J_{P-P'} = 19.3$ Hz).

Preparation of $[OsH(\eta^2\text{-}H_2)(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (6). A solution of $OsH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**2**) (10 mg, 0.014 mmol) in 0.5 mL of CD_2Cl_2 in a NMR tube was treated with $HBF_4{\cdot}OEt_2$ (2 μL, 0.014 mmol). The NMR tube was sealed under argon.

^1H NMR (300 MHz, 293 K, CD_2Cl_2): δ 7.52−7.41 (m, 10H, C_6H_5), 6.59 (dt, 1H, $J_{H-P} = 361.5$ Hz, $J_{H-P'} = 6.5$ Hz, P*H*Ph_2), 2.19 (m, 6H, PC*H*CH_3), 1.20 (dvt, 18H, $J_{H-H} = 6.0$ Hz, $N = 13.2$ Hz, PCHC*H*$_3$), 1.16 (dvt, 18H, $J_{H-H} = 6.6$ Hz, $N = 13.8$ Hz, PCHC*H*$_3$), −6.67 (br, 3H, Os−*H*$_3$). ^1H NMR (300 MHz, 183 K, CD_2Cl_2): δ 7.88−7.32 (br, 20H, C_6H_5), 6.38, 6.06 (both br, each 1H, P*H*Ph_2), 2.48−2.08 (br, 12H, PC*H*CH_3), 1.55−0.80 (br, 72H, PCHC*H*$_3$), −4.75 (br, 2H, Os(η^2-*H*$_2$)), −6.44 (br, 1H, Os−*H*), −7.15 (br, 2H, Os(η^2-*H*$_2$)), −7.92 (br, 1H, Os−*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 31.7 (d, $J_{P-P} = 18.6$ Hz), −27.1 (t, $J_{P-P} = 18.6$ Hz).

Preparation of $[OsH\{\eta^1\text{-}OC(CH_3)_2\}(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (7). A solution of $OsH_2(CO)(PHPh_2)(P^iPr_3)_2$ (**2**) (100 mg, 0.14 mmol) in 5 mL of acetone was treated with $HBF_4{\cdot}OEt_2$ (19.2 μL, 0.14 mmol). The mixture was stirred for 1 h at room temperature. The solution was concentrated to ca. 0.5 mL, and after the addition of diethyl ether, a white solid was formed. The solution was decanted, and the white solid was washed with diethyl ether and dried in vacuo. Yield: 83 mg (68%). Anal. Calcd for $C_{34}H_{60}BF_4O_2OsP_3$: C, 46.89; H, 6.94. Found: C, 46.65; H, 6.86.

IR (Nujol, cm^{-1}): $\nu(PPh_2-H)$ 2333 $\nu(Os-H)$ 2061(s), $\nu(CO)$ 1915 (s), $\nu(OC(CH_3)_2)$ 1656, $\nu(BF_4)$ 1075. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.60−7.44 (m, 10H, C_6H_5), 7.55 (dt, 1H, $J_{H-P} = 338.2$ Hz, $J_{H-P'} = 5.4$ Hz, P*H*Ph_2), 2.35 (m, 6H, PC*H*CH_3), 2.14 (s, 6H, OC(C*H*$_3$)$_2$), 1.15 (dvt, 18H, $J_{H-H} = 6.8$ Hz, $N = 13.1$ Hz, PCHC*H*$_3$), 1.10 (dvt, 18H, $J_{H-H} = 7.1$ Hz, $N = 14.0$ Hz, PCHC*H*$_3$), −5.88 (dt, ^1H, $J_{H-P} = 85.3$ Hz, $J_{H-P'} = 23.3$ Hz, Os−*H*). $^{13}C\{^1H\}$ NMR (75.43 MHz, 193 K, CD_2Cl_2): δ 224.6 (s, {η^1-OC(CH$_3$)$_2$}), 182.1 (dt, $J_{C-P} = 8.1$ Hz, $J_{C-P'} = 7.1$ Hz, *C*O), 132.4 (d, $J_{C-P} = 9.4$ Hz, C_{ipso}), 131.8 (s, *p*-C_6H_5), 131.1 (s, *m*-C_6H_5), 128.8 (d, $J_{C-P} = 8.7$ Hz, *o*-C_6H_5), 30.8 (s, {η^1-OC-(C*H*$_3$)$_2$}), 23.4 (br, P*C*HCH$_3$), 19.4 (s br, PCH*C*H$_3$), 18.1 (s br, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 29.3 (d, $J_{P-P'} = 13.6$ Hz), −18.3 (t, $J_{P-P'} = 13.6$ Hz).

Preparation of the Isomeric Mixture *cis*-, *trans*-$[OsH(CO)_2(PHPh_2)(P^iPr_3)_2]BF_4$ (8, 9). CO was bubbled through a stirred solution of $[OsH\{\eta^1\text{-}OC(CH_3)_2\}(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**7**) (100 mg, 0.12 mmol) in 6 mL of CH_2Cl_2 for 90 min. The solution was concentrated to ca. 0.5 mL, and after the addition of diethyl ether a white solid was formed. The solution was decanted, and the white solid was washed with diethyl ether and dried in vacuo. The solid obtained was a mixture of two isomers **8:9** in a 2:1 molar ratio.Yield: 91 mg (90%). Anal. Calcd for $C_{32}H_{54}BF_4O_2OsP_3$: C, 45.72; H, 6.47. Found: C, 46.04; H, 6.42.

IR (Nujol, cm^{-1}): $\nu(PPh_2-H)$ 2325, $\nu(Os-H)$ 2000, $\nu(CO)$ 1980, 1950, 1910. Spectroscopic data of **8(*cis*)** ^1H NMR (300 MHz, $CDCl_3$): δ 7.55−7.37 (m, 10H, C_6H_5), 7.19 (dtd, ^1H, $J_{H-P} = 378.0$ Hz, $J_{H-P'} = 9.3$ Hz, $J_{H-H'} = 5.4$ Hz, P*H*Ph_2), 2.35 (m, 6H, PC*H*CH_3), 1.21 (dvt, 18H, $J_{H-H} = 7.2$ Hz, $N = 14.4$ Hz, PCHC*H*$_3$), 1.11 (dvt, 18H, $J_{H-H} = 6.9$ Hz, $N = 12.9$ Hz, PCHC*H*$_3$), −8.10 (dtd, ^1H, $J_{H-P} = 27.9$ Hz, $J_{H-P'} = 18.0$ Hz, $J_{H-H'} = 4.5$ Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 15.1 (d, $J_{P-P'} = 25.7$ Hz), −35.8 (t, $J_{P-P'} = 25.7$ Hz). Spectroscopic data of **9(*trans*)** ^1H NMR (300 MHz, $CDCl_3$): δ 7.58−7.44 (m, 10H, C_6H_5), 7.48 (dt, 1H, $J_{H-P} = 362.4$ Hz, $J_{H-P'} = 5.4$ Hz, P*H*Ph_2), 2.23 (m, 6H, PC*H*CH_3), 1.16 (dvt, 36H, $J_{H-H} = 7.5$ Hz, N = 14.7 Hz, PCHC*H*$_3$), −10.31 (dt, 1H, $J_{H-P} = 39.9$ Hz, $J_{H-P'} = 20.4$ Hz, Os−*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 19.0 (d, $J_{P-P'} = 11.5$ Hz), −42.0 (t, $J_{P-P'} = 11.5$ Hz). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$) of **8** and **9**: δ 185.3 (dt, $J_{C-P} = 10.0$ Hz, $J_{C-P'} = 9.1$ Hz, *C*O), 184.7 (dt, $J_{C-P} = 10.5$ Hz, $J_{C-P'} = 9.0$ Hz, *C*O), 179.4 (dt, $J_{C-P} = 71.5$ Hz, $J_{C-P'} = 10.2$ Hz, *C*O), 133.3 (d, $J_{C-P} = 9.8$ Hz, C_{ipso}), 132.6 (d, $J_{C-P} = 9.8$ Hz, C_{ipso}), 131.8, 131.4, 130.8, 130.2, 129.5, 129.4, 129.25, 120.1, 127.4 (all s, C_6H_5), 27.4 (vt, $N = 28.5$ Hz, P*C*HCH$_3$), 26.9 (vt, $N = 28.1$ Hz, P*C*HCH$_3$), 19.5 (s, PCH*C*H$_3$), 19.2 (s, PCH*C*H$_3$), 19.0 (s, PCH*C*H$_3$).

Preparation of $[OsH(NCCH_3)(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (10). A solution of $[OsH\{\eta^1\text{-}OC(CH_3)_2\}(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**7**) (120 mg, 0.14 mmol) in 5 mL of CH_2Cl_2 was treated with CH_3CN (7.2 μL, 0.14 mmol). The mixture was stirred for 1 h at room temperature. The solution was concentrated to ca. 0.5 mL, and after the addition of diethyl ether, a white solid was formed. The solution was decanted, and the white solid was washed with diethyl ether and dried in vacuo. Yield: 84 mg (70%). Anal. Calcd for $C_{33}H_{57}BF_4ONOsP_3$: C, 46.43; H, 6.73; N, 1.64. Found: C, 46.32; H, 7.12; N, 1.62.

IR (Nujol, cm^{-1}): $\nu(PPh_2-H)$ 2333, $\nu(Os-H)$ 2097(s), $\nu(CO)$ 1926 (s), $\nu(BF_4)$ 1050. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.61−7.40 (m, 10H, C_6H_5), 7.51 (dt, 1H, $J_{H-P} = 342.9$ Hz, $J_{H-P'} = 5.8$ Hz, P*H*Ph_2), 2.51 (s, 3H, NCC*H*$_3$), 2.35 (m, 6H, PC*H*CH_3), 1.19 (dvt, 36H, $J_{H-H} = 6.9$ Hz, $N = 13.5$ Hz, PCHC*H*$_3$), −8.26 (dt, 1H, $J_{H-P} = 74.7$ Hz, $J_{H-P'} = 22.5$ Hz, Os−*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 19.5 (d, $J_{P-P'} = 13.0$ Hz), −30.0 (t, $J_{P-P'} = 13.0$ Hz).

Preparation of $OsH(C{\equiv}CPh)(CO)(PHPh_2)(P^iPr_3)_2$ (11). A stirred suspension of $[OsH\{\eta^1\text{-}OC(CH_3)_2\}(CO)(PHPh_2)(P^iPr_3)_2]BF_4$ (**7**) (100 mg, 0.12 mmol) in 5 mL of toluene was treated with PhC≡CLi (13.7 mg, 0.13 mmol). The mixture was stirred for 2 h at room temperature. The mixture was filtered through Kieselguhr. The resulting solution was concentrated to ca. 0.5 mL, and after the addition of methanol, a white solid was formed. The solution was decanted, and the white solid was washed with methanol and dried in vacuo. Yield: 51 mg (50%). Anal. Calcd for $C_{39}H_{59}OOsP_3{\cdot}CH_3OH$: C, 55.92; H, 7.39. Found: C, 55.60; H, 7.08.

IR (Nujol, cm^{-1}): $\nu(PPh_2-H)$ 2330, $\nu(Os-H)$ 2093(s), $\nu(CO)$ 1898 (s), $\nu(C\equiv C)$ 1591. ^1H NMR (300 MHz, C_6D_6): δ 7.91 (vt, 4H, $N = J_{H-H} + J_{H-P} = 18.1$ Hz, *o*-P(C_6H_5)), 7.61 (dt, ^1H, $J_{H-P} = 342.1$ Hz, $J_{H-P'} = 5.4$ Hz, P*H*Ph_2), 7.54 (dd, 2H, $J_{H-H} = 7.2$ Hz, $J_{H-H'} < 1$ Hz, *o*-C_6H_5), 7.21−6.96 (m, 9H, C_6H_5), 2.45 (m, 6H, PC*H*CH_3), 1.24 (dvt, 18H, $J_{H-H} = 6.9$ Hz, $N = 12.9$ Hz, PCHC*H*$_3$), 1.18 (dvt, 18H, $J_{H-H} = 7.0$ Hz, $N = 13.3$ Hz, PCHC*H*$_3$), −9.07 (dt, 1H, $J_{H-P} = 74.4$ Hz, $J_{H-P'} = 23.7$ Hz). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 189.8 (dt, $J_{C-P} = 9.1$ Hz, $J_{C-P'} = 7.5$ Hz, *C*O), 137.7 (d, $J_{C-P} = 33.9$ Hz, *C*ipso), 134.3−124.4 (C_6H_5), 112.2 (s, $C_\beta\equiv$), 108.6 (dt, $J_{C-P} = J_{C-P'} = 17.4$ Hz, $C_\alpha\equiv$), 26.7 (vt, $N = 26.3$ Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$), 20.2 (s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 16.8 (d, $J_{P-P'} = 13.4$ Hz), −31.6 (t, $J_{P-P'} = 13.4$ Hz).

Preparation of OsHBr(CO)(PHPh$_2$)(P^{i}Pr$_3$)$_2$ (12). A stirred suspension of [OsH{η^1-OC(CH$_3$)$_2$}(CO)(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (**7**) (150 mg, 0.17 mmol) in 5 mL of THF was treated with KBr (23 mg, 0.19 mmol). The mixture was stirred for 5 h at room temperature. The mixture was filtered through Kieselguhr. The resulting solution was concentrated to dryness, and after the addition of methanol, a white solid was formed. The solution was decanted, and the white solid was washed with methanol and dried in vacuo. Yield: 51 mg (50%). Anal. Calcd for $C_{31}H_{54}OBrOsP_3$: C, 46.21; H, 6.75. Found: C, 45.81; H, 6.20.

IR (Nujol, cm^{-1}): $\nu(PPh_2-H)$ 2355, $\nu(Os-H)$ 2091(s), $\nu(CO)$ 1902 (s). ^1H NMR (300 MHz, C_6D_6): δ 7.88 (vt, 4H, $N = J_{H-H} + J_{H-P} = 18.3$ Hz, *o*-C_6H_5), 7.85 (dt, 1H, $J_{H-P} = 345.9$ Hz, $J_{H-P'} = 4.8$ Hz, P*H*Ph_2), 7.07 (dd, 4H, $J_{H-H} = J_{H-H'} = 7.2$ Hz, *m*-C_6H_5), 7.21 (d, 2H, $J_{H-H} = 6.9$ Hz, *p*-C_6H_5), 2.58 (m, 6H, PC*H*CH_3), 1.25 (dvt, 18H, $J_{H-H} = 6.9$ Hz, $N = 13.2$ Hz, PCHC*H*$_3$), 1.11 (dvt, 18H, $J_{H-H} = 6.9$ Hz, $N = 12.9$ Hz, PCHC*H*$_3$), −7.56 (dt, 1H, $J_{H-P} = 93.6$ Hz, $J_{H-P'} = 23.4$ Hz, Os−*H*). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 15.0 (d, $J_{P-P'} = 14.2$ Hz), −29.2 (t, $J_{P-P'} = 14.2$ Hz).

Crystal Data for 5 and 8. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of methanol into a concentrated solution of **5** in toluene or from dichloromethane/ether for **8**. A summary of crystal data and refinement parameters is reported in Table 3. The colorless crystals (0.52 × 0.45 × 0.32 mm (**5**) and 0.32 × 0.28 × 0.22 mm (**8**)) were glued on a glass fiber and mounted on a Siemens STOE AED (**5**) or Siemens P4 four-circle (**8**) diffractometer, with graphite-monochromated Mo Kα radiation. A group of 46 reflections in the range 20° ≤ 2θ ≤ 40° (**5**) or 52 reflections in the range 30° ≤ 2θ ≤ 42° (**8**) was carefully centered at 173 K and used to obtain by the unit cell dimensions least-squares methods. Three standard reflections were monitored at periodic intervals thoughout data collection: no significant variations were observed. All data were corrected for absorption using a semiempirical method.[17] The structures were solved by Patterson (Ru or Os atoms, SHELXTL-PLUS[18]) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL93[19]). The BF_4^- anion of one of the independent molecules of **8** was found to be disordered.

Table 3. Crystal Data and Data Collection and Refinement Parameters for RuH$_2$(CO)(PHPh$_2$)(P^{i}Pr$_3$)$_2$ (5) and [OsH(CO)$_2$(PHPh$_2$)(P^{i}Pr$_3$)$_2$]BF$_4$ (8)

	5	**8**
formula	$C_{31}H_{55}OP_3Ru$	$C_{32}H_{54}BF_4O_2Os$
mol wt	637.73	840.67
color and habit	colorless, prismatic block	colorless, irregular block
cryst size, mm	0.52 × 0.45 × 0.32	0.32 × 0.28 × 0.22
symmetry	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	22.419(3)	17.487(2)
b, Å	9.173(1)	12.293(1)
c, Å	17.084(2)	34.284(3)
β, deg	108.980(10)	99.232(7)
V, Å^3	3322.3(7)	7274.5(12)
Z	4	8
D_{calc}, g cm^{-3}	1.275	1.535
μ, mm^{-1}	0.64	3.69
scan type	$w/2\theta$	w
2θ range, deg	4 ≤ 2θ ≤ 50	4 ≤ 2θ ≤ 50
temp, K	173	173
no. of data collcd	6048	14 560
no. of unique data	5865($R_{int} = 0.0270$)	12 769($R_{int} = 0.0354$)
no. of params refined	350	792
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0321	0.0377
wR_2[b] [all data]	0.0909	0.0748
S[c] [all data]	1.043	0.825

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] w$R_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

This group was refined with common restrained B−F and F−F distances (1.20(1) and 1.96(1) Å). Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed (hydrido and hydrogen atoms bonded to P) or calculated and refined riding on carbon atoms with common isotropic thermal parameters. Atomic scattering factors, corrected for anomalous dispersion for Ru, Os, and P, were implemented by the program. The refinements converge to R_1 [$F^2 > 2\sigma(F^2)$] = 0.0321 (**5**) or 0.0377 (**8**) and wR_2 [all data] = 0.0909 (**5**) or 0.0748 (**8**), with weighting parameters $x = 0.0503$, $y = 1.25$ (**5**) and $x = 0.0264$, $y = 0$ (**8**).

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray study, bond distances and angles, and least-squares planes for **5** and **8** (30 pages). Ordering information is given on any current masthead page.

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