Reactivity of $MH(\eta^2\text{-}H_2BH_2)(CO)(P\textit{i}Pr_3)_2$ (M = Os, Ru) toward Electrophiles: Synthesis of New Hydridocarbonylosmium(II) and -ruthenium(II) Complexes Containing Triisopropylphosphine as Ligand

Miguel A. Esteruelas,[†] Maria P. García,[†] Ana M. López,[†] Luis A. Oro,*[,†] Natividad Ruiz,[†] Christoph Schlünken,[†,‡] Cristina Valero,[†] and Helmut Werner*[,‡]

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain, and Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, W-8700 Würzburg, Germany

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The complexes $[(P\textit{i}Pr_3)_2(CO)HM(\mu,\eta^4\text{-}BH_4)MH(CO)(P\textit{i}Pr_3)_2]BF_4$ (**5**, **6**), $MH(\eta^2\text{-}O_2CR^*)(CO)(P\textit{i}Pr_3)_2$ (**7–13**) and $MH(pz)(CO)(Hpz)(P\textit{i}Pr_3)_2$ (**14**, **15**) (M = Os, Ru) have been prepared by reaction of $MH(\eta^2\text{-}H_2BH_2)(CO)(P\textit{i}Pr_3)_2$ (M = Os, Ru) with HBF_4, R^*CO_2H (R* = (*S*)-CH(NaphOMe)Me, (*R*)-CH(OMe)Ph, (*R*)-C(CF_3)(OMe)Ph, (*S*)-CHOC(=O)CH_2CH_2) and Hpz (pyrazole), respectively. **5** and **6** react with molecular hydrogen, tetrafluorobenzobarrelene (TFB), methyl vinyl ketone, acetonitrile, and acetone to give $[OsH(\eta^2\text{-}H_2)(CO)(P\textit{i}Pr_3)_2]^+$ (**16**), $[OsH(\eta^2\text{-}H_2)(CO)(OH_2)(P\textit{i}Pr_3)_2]^+$ (**17**), $[OsH(CO)(TFB)(P\textit{i}Pr_3)_2]^+$ (**18**), $[OsH(CO)(\pi\text{-}CH_2{=}CHC(=O)CH_3)(P\textit{i}Pr_3)_2]^+$ (**19**), $[MH(CO)(CH_3CN)_2(P\textit{i}Pr_3)_2]^+$ (M = Os (**20**), Ru (**21**)) and $[RuH(CO)(\eta^1\text{-}(CH_3)_2CO)_2(P\textit{i}Pr_3)_2]^+$ (**22**). In solution **22** dissociates an acetone molecule to give $[RuH(CO)(\eta^1\text{-}(CH_3)_2CO)(P\textit{i}Pr_3)_2]^+$ (**23**). The cations $[MH(CO)(Hpz)_2(P\textit{i}Pr_3)_2]^+$ (M = Os (**24**), Ru (**25**)) were obtained by addition of HBF_4 to diethyl ether solutions of **14** and **15**. The latter react with HCl to give a mixture of two isomers of $MHCl(CO)(Hpz)(P\textit{i}Pr_3)_2$ (M = Os (**26**), Ru (**27**)). The catalytic activity of **7–13** in asymmetric hydrogen transfer from 2-propanol to acetophenone is also described. The osmium carboxylates lead to considerably higher optical yields than ruthenium complexes.

Introduction

We have recently reported that the five-coordinated hydridoosmium and -ruthenium complexes $MHCl(CO)(P\textit{i}Pr_3)_2$ (M = Os (**1**), Ru (**2**)) react with $NaBH_4$ in benzene/methanol to give the octahedral compounds $MH(\eta^2\text{-}H_2BH_2)(CO)(P\textit{i}Pr_3)_2$ (M = Os (**3**), Ru (**4**)), which possess a rigid structure in solution only at low temperatures. Above ca. −30 °C exchange processes take place which involve the bridging and terminal hydrogen atoms attached to boron but not the metal hydride ligand. **3** and **4** react with Lewis bases such as CO, $P(OMe)_3$, PMe_3, and $P\textit{i}Pr_3$ to form species of formula $MH_2(CO)L(P\textit{i}Pr_3)_2$.[1] In the reaction with PhC_2H the five-coordinated bis(alkynyl) complexes $M(C{\equiv}CPh)_2(CO)(P\textit{i}Pr_3)_2$ are produced.[2]

There is considerable experimental evidence indicative of the action of tetrahydroborate compounds as effective catalyst precursors for isomerization, oligomerization, and hydrogenation of olefins.[3] In this line, **3** and **4** serve as catalyst precursors for hydrogen transfer reactions from 2-propanol to cyclohexanone, acetophenone,[4] benzylideneacetone, benzylideneacetophenone[5] and phenylacetylene.[2] Under catalytic conditions, **3** and **4** decompose to $MH_4(CO)(P\textit{i}Pr_3)_2$ which leads to $MH_2(CO)(P\textit{i}Pr_3)_2$ that presumably acts as the active catalyst.[6]

When we attempted to replace 2-propanol by methanol, ethanol, or 2-methoxyethanol as the hydrogen source, for the reduction of cyclohexanone in the presence of **3**, we observed that a rapid deactivation of the catalyst occurred. This unexpected finding prompted us to explore the reactivity of **3** toward CH_3OH, C_2H_5OH, and $MeOC_2H_4OH$ in more detail. During these studies we discovered an unusual fragmentation of the alcohols, which was accompanied by the formation of $OsH_2(CO)_2(P\textit{i}Pr_3)_2$, $OsH(CH_3)(CO)_2(P\textit{i}Pr_3)_2$, and $OsH(CH_2OMe)(CO)_2(P\textit{i}Pr_3)_2$, respectively.[7]

As a continuation of our work on the chemical properties of **3** and **4**, we describe, in the present paper, the results of a study on the reactivity of these compounds toward electrophiles such as HBF_4, R^*CO_2H (R* = (*S*)-CH(NaphOMe)Me, (*R*)-CH(OMe)Ph, (*R*)-C(CF_3)(OMe)Ph, (*S*)-CHOC(=O)CH_2CH_2), and Hpz (pyrazole), and reactions of some complexes obtained in this way.

Results and Discussion

Reactions of Complexes 3 and 4 with Electrophiles. The investigations aimed to elucidate the reactivity of **3** and **4** toward electrophiles are summarized in Scheme I. Whereas both compounds react with HBF_4 in diethyl ether at room temperature to give the binuclear complexes **5** and **6**, the reactions with (*R*)-(+)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid, (*S*)-5-oxotetrahydrofuran-2-carboxylic acid, *R*(−)-α-methoxyphenylacetic acid, (*S*)-(+)-2-(6-methoxy-2-naphthyl)propionic acid, and pyrazole in methanol lead to the mononuclear compounds **7–15**. These compounds have been fully characterized by elemental analysis and spectroscopically by IR and ^1H and ^{31}P NMR. The presence of the $[BH_4]^-$ anion in **5** and **6** was also confirmed by ^{11}B NMR spectroscopy (see Experimental Section).

[†] Universidad de Zaragoza.
[‡] Universität Würzburg.

(1) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.
(2) Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187.
(3) (a) Green, M. L. H.; Munakata, H. *J. Chem. Soc. A* **1974**, 269. (b) Miller, R. G.; Pinke, P. A.; Stauffer, R. D.; Golden, H. J.; Baker, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 4211. (c) Holah, D. G.; Hughes, A. N.; Hui, B. C.; Kan, C. T. *J. Catal.* **1977**, *48*, 340. (d) Letts, J. B.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 3898.
(4) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1.
(5) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1989**, *43*, 53.
(6) Esteruelas, M. A.; Valero, C.; Oro, L. A.; Werner, H.; Meyer, U. *Inorg. Chem.* **1991**, *30*, 1159.
(7) Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Schlünken, Ch.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034.

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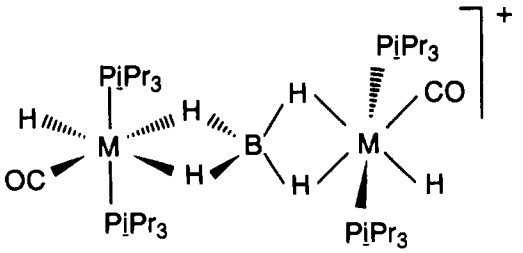
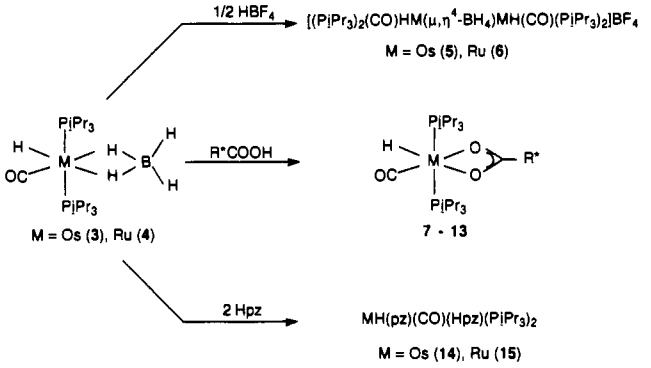


Figure 1. Proposed structure for the cations $[(PiPr_3)_2(CO)HM(\mu\text{-}\eta^4\text{-}BH_4)\ MH(CO)(PiPr_3)_2]^+$ (M = Os (**5**), Ru (**6**)).

Scheme I



Complex	M	R*
7	Os	(S)-CH(NaphOMe)Me
8	Ru	(S)-CH(NaphOMe)Me
9	Os	(R)-CH(OMe)Ph
10	Ru	(R)-CH(OMe)Ph
11	Os	(R)-C(CF3)(OMe)Ph
12	Ru	(R)-C(CF3)(OMe)Ph
13	Os	(S)-CHO(C=O)CH2CH2

Figure 1 shows a geometry for the cations **5** and **6** in accordance with the obtained spectroscopic data. It consists of two $MH(CO)(PiPr_3)_2$ fragments bridged by a tetrahedral BH_4 unit. The six donor atoms around each metal define two octahedra with the CO and hydride ligands trans to the BH_4 unit. This disposition leads to a situation where the two phosphine ligands of each metal are not equivalent. Consistently, the $^{31}P\{^1H\}$NMR spectra of **5** and **6** in chloroform show four well-separated resonances of relative intensities 1:2:2:1 (AB splitting pattern) which are temperature invariant down to −55 °C. However, the ^1H NMR spectra are temperature dependent. At room temperature the spectra contain a virtual triplet in the hydride region at $\delta = -12.0$ for **5** and at $\delta = -12.95$ for **6** with P–H coupling constants of about 19 Hz. At −50 °C, new broad signals assigned to the ligand $[BH_4]^-$ appear (Figure 2). This behavior suggests the intervention of a quadrupole-induced ^{10}B and ^{11}B spin relaxation ("thermal" decoupling)[8,9b] and a slow (on the NMR time scale) intramolecular exchange process which involves the bridging hydrogen atoms but not the metal hydride ligands.

The preparation of the ruthenium compound $[(tripod)HRu(\mu,\eta^4\text{-}BH_4)\ RuH(tripod)]^+$ (tripod = $MeC(CH_2PPh_2)_3$) comparable in structure to

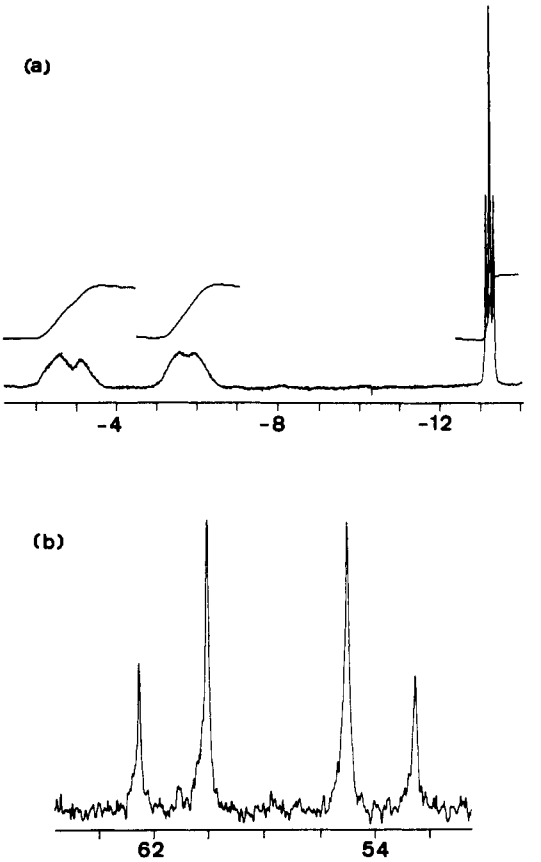


Figure 2. (a) ^1H NMR spectrum of $[(PiPr_3)_2(CO)HRu(\mu\text{-}\eta^4\text{-}BH_4)\text{-}RuH(CO)(PiPr_3)_2]^+$ (**6**) in the hydride region at −50 °C. (b) ^{31}P NMR spectrum of $[(PiPr_3)_2(CO)HRu(\mu\text{-}\eta^4\text{-}BH_4)RuH(CO)(PiPr_3)_2]^+$ (**6**) at 20 °C.

5 and **6** has been previously reported by Venanzi et al.[9a] This complex was obtained by decomposition of $RuH(\eta^2\text{-}H_2BH_2)$(tripod) in methanol. Interestingly, the decomposition of **3** and **4** in methanol leads to $MH_2\text{-}(CO)_2(PiPr_3)_2$.[1,7] For the metals in the iron triad, the covalent tetrahydroborate complexes are usual for iron and ruthenium.[9] Osmium is the only member of this triad for which the number of such complexes remains small. Two mononuclear compounds have been previously reported, $OsH_3(\eta^2\text{-}H_2BH_2)(P(c\text{-}C_5H_9)_3)_2$[10] and **3**, and to the best of our knowledge, **5** represents the first example of a binuclear osmium complex containing a $\mu,\eta^4\text{-}BH_4$ ligand.

The complexes **7**–**13** are formulated as octahedral derivatives containing chelating carboxylate ligands on the basis of assignments for ν_{asym} (OCO) and ν_{sym} (OCO) at ca. 1590–1535 and 1450–1430 cm^{-1} respectively. In this line, the values found for $\Delta\nu$ (ν_{asym} (OCO) − ν_{sym} (OCO)) coincide with those established by Deacon[11] et al. for the chelating coordination of the acetate group. The related acetate complexes were already known and had been prepared by displacement of chloride in **1** and **2** by the acetate anion.[12]

The compounds **14** and **15** contain formally a pyrazole group and a pyrazolide ion.[13] The ^1H and $^{31}P\{^1H\}$ NMR spectra (see Experimental Section) suggest that the molecular structures of these compounds are octahedra with equivalent phosphines cis disposed to the hydride ligands. Although the N–H proton of the pyrazole group was not found in the IR and ^1H NMR spectra, its presence is strongly supported by the reactions shown in eq 3 (see below). A similar compound of formula $RuH(pz)\text{-}(CO)(Hpz)(PPh_3)_2$ has been recently reported by us. In this case, it was prepared by treatment of $RuHCl(CO)(Hpz)(PPh_3)_2$ with the stoichiometric amount of KOH (methanolic solution) and pyrazole.[15]

(8) Beall, H.; Bushweller, C. H.; Dewkett, W. J.; Grace, M. *J. Am. Chem. Soc.* **1970**, *92*, 3484.
(9) (a) Rhodes, L. F.; Venanzi, L. M.; Sorato, C.; Albinati, A. *Inorg. Chem.* **1986**, *25*, 3335. (b) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263. (c) Crabtree, R. H.; Pearman, A. J. *J. Organomet. Chem.* **1978**, *157*, 335. (d) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *Inorg. Chim. Acta* **1984**, *89*, 167. (e) Vites, J. C.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633. (f) Ghilardi, C. A.; Innocenti, P.; Midollini, S.; Orlandini, A. *J. Chem. Soc., Dalton Trans.* **1985**, 605. (g) Rhodes, L. F.; Venanzi, L. M. *Inorg. Chem.* **1987**, *26*, 2692. (h) Jia, G.; Meek, D. W.; Gallucci, J. C. *Inorg. Chem.* **1991**, *30*, 403. (i) Bianchini, C.; Perez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279.
(10) Frost, P. W.; Howard, J. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1362.
(11) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.
(12) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.
(13) The pyrazole ligand can act as nucleophile using the electron pair of N(2) or alternatively as electrophile using the acidic N–H group. When pyrazole is deprotonated, the pyrazolide ion is formed.[14]
(14) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.
(15) Garcia, M. P.; López, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3465.

Scheme II

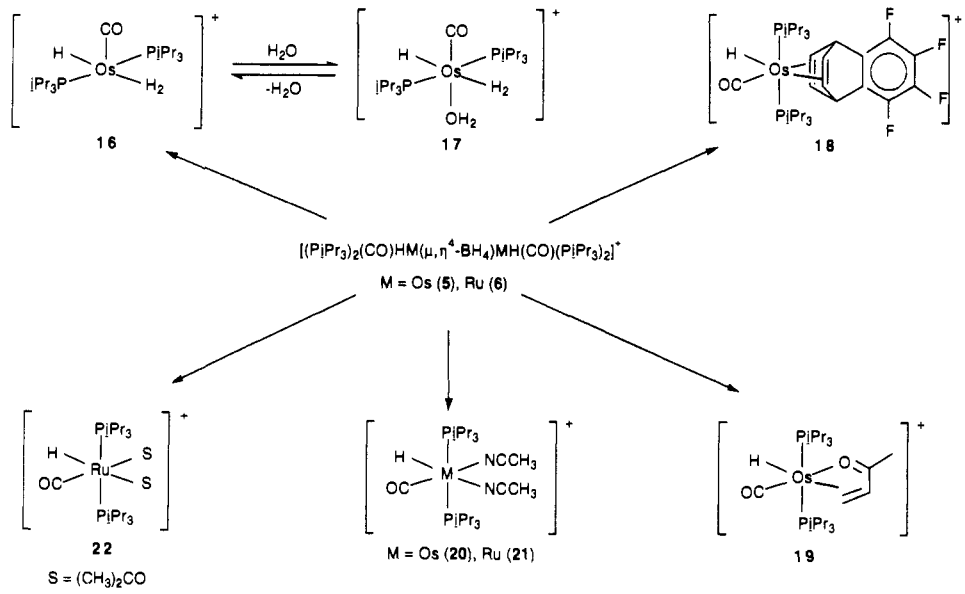


Figure 3. ^1H NMR spectrum for the conversion of $[OsH(\eta^2\text{-}H_2)(CO)(OH_2)(P\textit{i}Pr_3)_2]BF_4$ (○, **17**) into $[OsH(\eta^2\text{-}H_2)(CO)(P\textit{i}Pr_3)_2]BF_4$ (●, **16**) in chloroform-d_1.

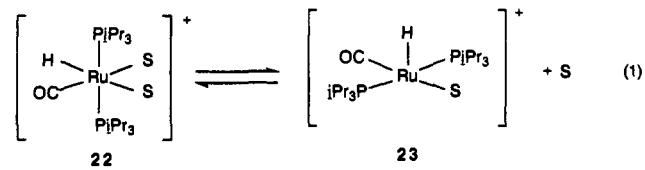
Ligand Substitution Reactions of Complexes 5 and 6. **5** and **6** can be considered as the result of the stabilization of the unsaturated $[MH(CO)(P\textit{i}Pr_3)_2]^+$ (M = Ru, Os) fragments by **3** and **4**. From this point of view, **3** and **4** are metalloligands that could be displaced by other coordinating molecules. Furthermore, we were interested in investigating the reactivity of **5** and **6** toward molecules which could be involved in catalytic processes (hydrogen, substrates, and solvent), as a part of a broad study on the catalytic properties of osmium and ruthenium systems containing phosphine ligands.[2,4-7,16] Thus, we have carried out a first exploration of the reactivity of **5** and **6** toward molecular hydrogen, tetrafluorobenzobarrelene, methyl vinyl ketone, acetonitrile, and acetone. The results are summarized in Scheme II.

Under normal conditions (25 °C, 1 atm of hydrogen), **5** reacts with hydrogen. When a suspension of **5** in diethyl ether is stirred under hydrogen atmosphere for 36 h, the yellow starting solid turns into a white solid. The ^1H NMR spectrum of this new solid, in chloroform-d_1, contains the signals corresponding to the $P\textit{i}Pr_3$ ligand together with a triplet at $\delta = -5.8$ ($J(HP) = 17.7$ Hz) and a broad resonance at $\delta = -1.2$ ($T_1 = 8$ ms) characteristic of a η^2-H_2 ligand. Integration of the latest two signals gives an intensity ratio of 1:2. The $^{31}P\{^1H\}$ spectrum shows a singlet at $\delta = 42.6$. These spectroscopic data indicate that the compound formed under these conditions is **16** (Scheme II). The addition of water to a chloroform solution of **16** leads to **17**, which can be isolated as a white solid. In chloroform-d_1 as solvent, **17** is converted into **16** by dissociation of the water molecule (ca. 20% in 1 h). Figure 3 shows spectroscopic evidence for this transformation.

16 is a rare example of a 16-electron hydride–dihydrogen complex, which demonstrates that electron saturation is not a necessary condition for the stabilization of a η^2-H_2 ligand. In this line, the synthesis and X-ray molecular structure of the related $RuHI(\eta^2\text{-}H_2)(PCy_3)_2$ complex has been reported.[17] In this case, in contrast to **16**, the hydride and dihydrogen ligands are mutually cis-disposed. On the other hand, it should be mentioned that Caulton and co-workers[18] have speculated that the deuteration of the $[OsH_5(PMe_2Ph)_3]^+$ cation involves an $[OsH_3(PMe_2Ph)_3]^+$ intermediate similar to **16**.

3 can be also displaced from **5** by tetrafluorobenzobarrelene and methyl vinyl ketone to give **18** and **19** respectively. The IR and NMR spectra of **18** and **19** are in good agreement with the proposed structures in Scheme II. Thus the IR spectra in Nujol show the absorptions due to the $[BF_4]^-$ anion with T_d symmetry along with bands characteristic of coordinated ligands. In particular, the IR spectrum of **19** contains a C=O stretching band at 1560 cm^{-1} suggesting that the methyl vinyl ketone coordinates to the osmium atom via the oxygen atom of the C=O bond.[19] This proposal is also supported by the $^{13}C\{^1H\}$ NMR spectrum, which show a singlet at 177.3 ppm assigned to the carbonyl group of the olefinic ligand. On the other hand, the trans configuration of the hydride ligand and α,β-unsaturated ketone C=C bond is mainly supported by the chemical shift of the Os–H signal in the ^1H NMR spectrum, which appears at $\delta = -3.5$. A similar δ value for Os–H has been found in the compound $OsHCl(CO)(\eta^2\text{-}CH_2{=}CH_2)(P\textit{i}Pr_3)_2$ containing the ethylene ligand trans to hydride.[12]

5 and **6** each react with coordinating solvents such as acetonitrile and acetone to give the cationic monohydrides **20–22**. Figure 4 suggests that in solution, **22** is stable only at low temperatures. From −55 to +17 °C, it is in a dynamic equilibrium with **23** (eq 1). At 50 °C **23**, characterized



(1)

by a triplet at −22.2 ppm with a P–H coupling constant of 17.5 Hz, is the main species in solution and can be isolated as a white solid when a solution of **22** in dichloromethane is evaporated to dryness. The methyl

(16) (a) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295. (b) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563. (c) Garcia, M. P.; López, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Chem. Commun.* **1988**, 793. (d) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (e) Garcia, M. P.; López, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Organomet. Chem.* **1990**, *388*, 365. (f) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Meyer, U.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288. (g) Esteruelas, M. A.; Garcia, M. P.; López, A. M.; Oro, L. A. *Organometallics* **1991**, *10*, 127. (h) Esteruleas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1991**, *10*, 462. (e) Esteruelas, M. A.; Garcia, M. P.; López, A. M.; Oro, L. A. *Organometallics* **1992**, *11*, 702.

(17) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; López, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314.

(18) Johnson, T. J.; Huffman, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073.

(19) It has been reported the methyl vinyl ketone reacts with $[RuH(\eta^2\text{-}H_2BH_2)(triphos)]$ to give $[Ru(\pi\text{-}CH_2{=}CHC(=O)Me)(triphos)]$ (triphos = $PhP(CH_2CH_2PR_2)_2$). In this case, no infrared bands above 1500 cm^{-1} assigned to $\nu(C{=}O)$ were observed[20]. However, the IR spectrum of $W(\pi\text{-}CH_2{=}CHC(=O)Me)_3$ contains a band at 1495 cm^{-1}.[21]

(20) Jia, G.; Meek, D. W.; Gallucci, J. C. *Organometallics* **1990**, *9*, 2549.

(21) King, R. B.; Fronzaglia, A. *J. Chem. Soc., Chem. Commun.* **1966**, 274.

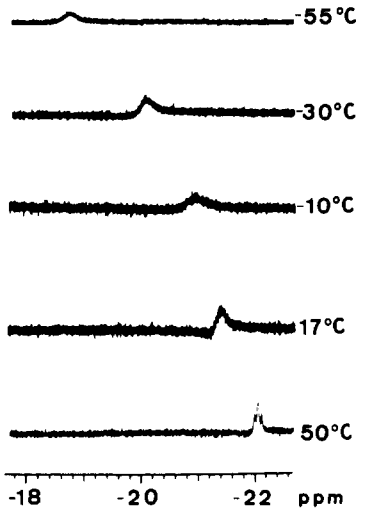


Figure 4. ^1H NMR ($CDCl_3$) spectra of $[RuH(\eta^1\text{-}(CH_3)_2CO)_2(CO)(PiPr_3)_2]BF_4$ (**22**) in the hydride region as a function of temperature.

signals of the acetone ligand also undergo significant changes with the temperature. At 50 °C, the spectrum contains a single peak at $\delta = 2.10$. In contrast, the spectrum recorded at −55 °C shows two methyl singlets at $\delta = 2.43$ and 2.36 in an approximately 1:1 ratio. The IR spectra of **22** and **23** in dichloromethane at room temperature also provide clear evidence for the equilibrium shown in eq 1. The IR spectrum of **23** contains a band due to the carbonyl group of the acetone ligand at 1675 cm^{-1}, which strongly supports a Ru(η^1-acetone) bonding mode.[22] The IR spectrum of **22** shows in the same region, a band at 1675 cm^{-1} and another at 1715 cm^{-1}, which can be assigned to free acetone. The coordination η^1-bonding mode of acetone to the ruthenium atom in this type of compounds is also supported by the $^{13}C\{^1H\}$ NMR spectrum of **23**, that contains a singlet at 209.7 ppm, due to the carbonyl group of the acetone.

In summary, the weak Lewis base character of **3** and **4** allows stabilization of **5** and **6** without interfering with the coordination of molecules which could be involved in catalytic processes.[23]

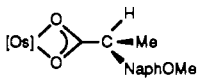
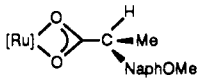
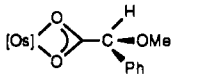
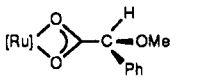
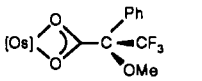
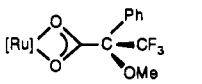
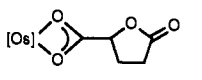
Asymmetric Reduction of Acetophenone Catalyzed by 7–13. The preparation of optically active hydroxy organic compounds by catalytic asymmetric hydrogenation of ketones is an important process in organic synthesis. However, only a very limited number of active catalyst complexes have been found. In some cases the use of hydrogen transfer catalysts can be a viable alternative to the classical reduction with molecular hydrogen.[24] This prompted us to explore the catalytic activity of compounds **7–13** in asymmetric hydrogen transfer reactions from 2-propanol to acetophenone (eq 2). The reactions were carried out in a

$$(CH_3)_2CHOH + Ph(CO)CH_3 \rightarrow (CH_3)_2CO + PhC^*H(OH)(CH_3) \quad (2)$$

mixture of 2-propanol/toluene (2:1) at 85 °C, under a strict argon atmosphere. The results are listed in Table I. Osmium carboxylate complexes result in considerably higher optical yields than ruthenium complexes.

Asymmetric hydrogen transfer catalysts have already been described for rhodium, iridium and ruthenium complexes containing chiral phosphine,[25] Schiff base,[26] carboxylate,[27] and amine[28] ligands. For these systems, the presence of potassium hydroxide is necessary for the formation

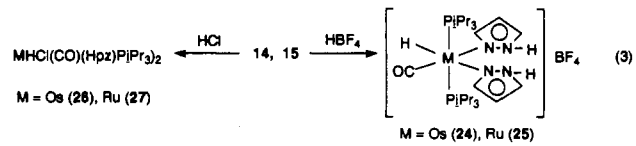
Table I. Asymmetric Hydrogen Transfer from 2-Propanol to Acetophenone Catalyzed by $MH(\eta^2\text{-}O_2CR^*)(CO)(PiPr_3)_2$ (M = Os, Ru) Complexes

catalyst	time	conv (%)	ee (%)	config
 **7**	8 d, 16 h	41	6.6	*R*-(+)
 **8**	10 d	20		
 **9**	5 d, 16 h	60	12.5	*S*-(−)
 **10**	46 h	46	0.7	*R*-(+)
 **11**	2 d, 16 h	82	12	*R*-(+)
 **12**	3 d, 2 h	44	0.3	*R*-(+)
 **13**	9 d, 21 h	22	1	*S*-(−)

of a coordinated isopropoxide group that leads to the formation of intermediate hydrides by a β-elimination reaction.[29] In contrast, for the hydrides **7–13**, the presence of potassium hydroxide or other cocatalysts is not necessary.

We have recently reported accumulating evidences that in the iron triad not only ruthenium but also osmium form a variety of complexes that behave as good catalysts for the reduction of nonprochiral unsaturated organic substrates.[4-6,16b,d,f] We now describe the first examples of osmium compounds that are active catalysts for the asymmetric reduction of prochiral unsaturated organic substrates, although the ee's are not very high.

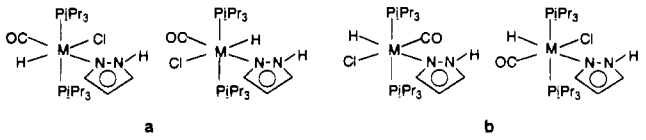
Pyrazole Compounds. We have previously mentioned that **3** and **4** react with pyrazole to give **14** and **15**. With **14** and **15** as starting materials new pyrazole compounds were obtained (eq 3). Reactions with HBF_4



lead to the cations **24** and **25**, which can be deprotonated with NaH; while treatment with HCl leads to the neutral hydrido–chloro complexes **26** and **27** which can also be prepared by addition of pyrazole to **1** and **2**, respectively.[16e]

(22) Huang, Y. H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298.
(23) Complexes **3** or **4** were isolated from diethyl ether solutions obtained in the preparation of **17–23**.
(24) Mestroni, G.; Camus, A.; Zassinovich, G. In *Aspects of Homogeneous Catalysis*; Ugo, R., Eds.; D. Reidel Publishing Company: Boston, MA, 1981; Vol. 4, pp 71–89.
(25) (a) Spogliarich, R.; Zassinovich, G.; Kaspar, J.; Graziani, M. *J. Mol. Catal.* **1982**, *16*, 359. (b) Bianchi, M.; Matteoli, U.; Frediani, P.; Menchi, G.; Piacenti, F. *J. Organomet. Chem.* **1982**, *236*, 375. (c) Kvintovics, P.; Bakos, J.; Heil, B. *J. Mol. Catal.* **1985**, *32*, 111. (d) Spogliarich, R.; Kaspar, J.; Graziani, M.; Morandini, F. *J. Organomet. Chem.* **1986**, *306*, 407. (e) Krause, H. W.; Bhatnagar, A. K. *J. Organomet. Chem.* **1986**, *302*, 265. (f) Spogliarich, R.; Farnetti, E.; Kaspar, J.; Graziani, M.; Cesarotti, E. *J. Mol. Catal.* **1989**, *50*, 19. (g) Chauvin, R. *J. Mol. Catal.* **1990**, *62*, 147.
(26) (a) Zassinovich, G.; Grisoni, F. *J. Organomet. Chem.* **1983**, *247*, C24. (b) Zassinovich, G.; Mestroni, G. *J. Mol. Catal.* **1987**, *42*, 81. (c) Zassinovich, G.; Bettella, R.; Mestroni, G.; Bresciani-Pahor, N.; Geremia, S.; Randaccio, L. *J. Organomet. Chem.* **1989**, *370*, 187. (d) De Martin, S.; Zassinovich, G.; Mestroni, G. *Inorg. Chim. Acta* **1990**, *174*, 9.
(27) Kvintovics, P.; James, B. R.; Heil, B. *J. Chem. Soc., Chem. Commun.* **1986**, 1810.
(28) (a) Kvintovics, P.; Heil, B. *J. Organomet. Chem.* **1989**, *361*, 117. (b) Botteghi, C.; Chelucci, G.; Chessa, G.; Delogu, G.; Gladiali, S.; Soccolini, F. *J. Organomet. Chem.* **1986**, *304*, 217.
(29) Fernández, M. J.; Esteruelas, M. A.; Covarrubias, M.; Oro, L. A. *J. Organomet. Chem.* **1986**, *316*, 343.

Scheme III



a b

M = Os (26), Ru (27)

The NMR spectra of **26** and **27** show that there are two isomers of each compound in solution. In the hydride region of the ^1H NMR spectrum of **26** in chloroform-d_1 at room temperature, the isomers are characterized by triplets at $\delta = -14.50$ and $\delta = -17.20$ with P–H coupling constants of about 17 Hz. In toluene-d_8, the ^1H NMR of **27** in the hydride region contains a broad signal at $\delta = -13.42$ and a triplet at $\delta = -14.94$ with a P–H coupling constant of about 20 Hz. The ^{31}P NMR spectra of **26** and **27** show two signals for each compound, indicating that the phosphine ligands are equivalent.

Three isomers are possible for a formulation $MHCl(CO)(Hpz)(PiPr_3)_2$ with equivalent phosphines cis disposed to the hydride ligand: hydride trans to chloro (a), hydride trans to pyrazole (b), and hydride trans to carbonyl group (c). According to the observed ^1H NMR spectra, isomer c can be rejected. It is known, from previous studies[1,12] that chemical shifts of hydride ligands trans to carbonyl groups appear at lower field than those observed for **26** and **27**. For each isomer, furthermore, the existence of two conformers may be ascribed to hindered rotations about the M–N axis (Scheme III). In the light of the structures shown in Scheme III, it is clear that the hydride signal of isomer a depends strongly on the conformer structure. Thus, the slow rotation of the pyrazole ligand on the Ru–N axis in **27a** could lead to a broadening of the hydride signal as it is experimentally observed for the signal at $\delta = -13.42$ in the ^1H NMR spectrum of **27**. In accordance with this, we have assigned the signals at $\delta = -14.50$ and $\delta = -13.42$ to isomers **26a** and **27a**, and the signals at $\delta = -17.20$ and $\delta = -14.94$ to **26b** and **27b** respectively.

Figure 5 shows the ^1H NMR spectrum of **27** in the N–H and hydride regions with toluene-d_8 as solvent, at temperature ranging from −70 to +60 °C. At temperatures lower than 0 °C, the broad signal resolves into a triplet with a P–H coupling constant of about 20 Hz, suggesting that, at low temperatures, the rotation about the Ru–N axis is stopped. Consequently, for **27a** a single conformer of the two possible ones is present at these temperatures.

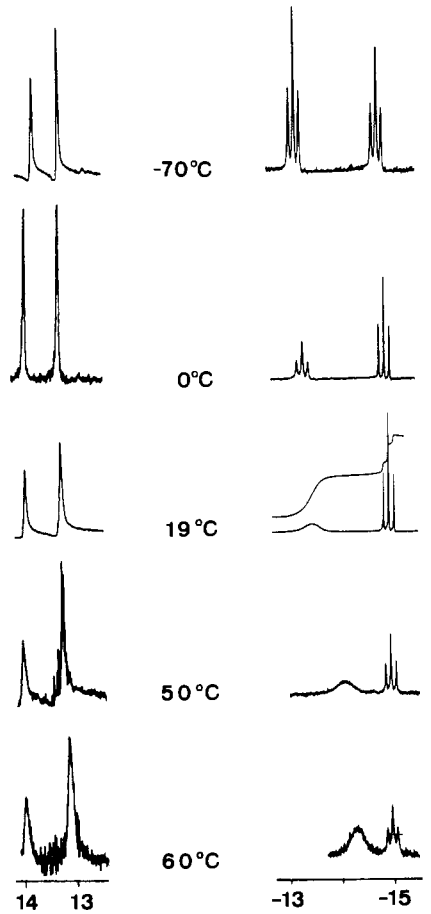


Figure 5. ^1H NMR (toluene-d_8) spectrum of $RuHCl(CO)(Hpz)(PiPr_3)_2$ (**27a**, **27b**) in the NH and hydride regions as a function of temperature.

Concluding Remarks

The results reported in this work and reported previously show that the complexes $MH(\eta^2\text{-}H_2BH_2)(CO)(PiPr_3)_2$ (M = Os (**3**), Ru (**4**)) are not only catalyst precursors for hydrogen transfer reactions from 2-propanol to unsaturated organic substrates but also useful starting materials for the synthesis of new five and six-coordinated hydridocarbonylosmium and -ruthenium compounds containing triisopropylphosphine as ligand.

Both compounds react with HBF_4 to give the binuclear complexes $[(PiPr_3)_2(CO)HM(\mu,\eta^4\text{-}BH_4)MH(CO)(PiPr_3)_2]BF_4$ (M = Os (**5**), Ru (**6**)). These compounds can be considered as the results of the stabilization of the very unsaturated $[MH(CO)(PiPr_3)_2]^+$ fragments by **3** and **4**. Consequently, the metalloligands **3** and **4** are displaced by neutral molecules such as hydrogen, tetrafluorobenzobarrelene, methyl vinyl ketone, acetonitrile, and acetone. While the resulting cations $[MH(CO)(PiPr_3)_2L_2]^+$ (L_2 = TFB, $CH_2{=}CHC(=O)CH_3$; L = CH_3CN) (**18–21**) are stable in solution, $[RuH(CO)(\eta^1\text{-}(CH_3)_2CO)_2(PiPr_3)_2]^+$ (**22**) dissociates one molecule of acetone to give the five-coordinated solvato species $[RuH(CO)(\eta^1\text{-}(CH_3)_2CO)(PiPr_3)_2]^+$ (**23**). The five-coordinated dihydrogen cation $[OsH(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]^+$ (**16**) is also stable in solution and does not react with molecular hydrogen under normal conditions, suggesting that no steric arguments can be used to justify the unusual coordination of the ligands around the osmium atom.

5 and **6** react also with chiral carboxylates to give $MH(\eta^2\text{-}O_2CR^*)(CO)(PiPr_3)_2$ (M = Os, Ru) (**7–13**). These compounds catalyze the asymmetric hydrogen transfer reactions from 2-propanol to acetophenone, indicating that in the iron triad not only ruthenium but also osmium form complexes that behave as good catalysts for the asymmetric reduction of prochiral unsaturated organic substrates.

The reactions of **5** and **6** with the dual pyrazole (nucleophile, electrophile) lead to $MH(pz)(CO)(Hpz)(PiPr_3)_2$ (M = Os (**14**), Ru (**15**)), which contain formally a pyrazole ligand and a pyrazolide anion. These compounds react with HCl to give a mixture of two isomers of $MHCl(CO)(Hpz)(PiPr_3)_2$ (M = Os (**26**), Ru (**27**)).

In summary we report overwhelming evidence showing the versatility of the chemistry of the complexes $MH(\eta^2\text{-}H_2BH_2)(CO)(PiPr_3)_2$ (M = Os, Ru) and their derivatives.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of argon by using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. Carboxylic acids were used as purchased from Fluka. The starting materials tetrafluorobenzobarrelene (TFB)[30], $MHCl(CO)(PiPr_3)_2$ (M = Os (**1**), Ru (**2**)),[12] and $MH(\eta^2\text{-}H_2BH_2)(CO)(PiPr_3)_2$ (M = Os (**3**), Ru (**4**))[1] were prepared by published methods.

Physical Measurements. NMR spectra were recorded on a Varian 200 XL or on a Varian UNYT 300 spectrophotometer. Chemical shifts are expressed in parts per million upfield from $Si(CH_3)_4$ (^1H and ^{13}C), 85% H_3PO_4 (^{31}P), and $BF_3{\cdot}Et_2O$ (^{11}B). Coupling constants J and N [$N = J(PH) + J(P'H)$] are given in hertz. The T_1 experiment was performed at 20 °C on a 200-MHz Varian XL with a standard 180°–τ–90° pulse sequence. Infrared spectra were recorded with a Perkin-Elmer 783 instrument. C, H, and N analyses were carried out with a Perkin-Elmer 240 C microanalyzer.

Hydrogen Transfer Reactions. The catalytic reactions were carried out under an atmosphere of argon in a mixture of 2-propanol/toluene (2:1) at 85 °C, with magnetic stirring, in a 50-mL round-bottomed flask

(30) Roe, D. M.; Massey, A. G. *J. Organomet. Chem.* **1970**, *23*, 547.

fitted with a condenser and provided with a serum cap. In a typical procedure, a solution of the catalyst (0.1 mmol) in 12.5 mL of toluene and 12.5 mL of 2-propanol was stirred for 1 h, and 10 mmol of acetophenone in 12.5 mL of 2-propanol was injected. The progress of the reaction was monitored by using a Perkin-Elmer 8900 gas chromatograph with a flame ionization detector and an FFAP on Chromosorb GHP 80/100-mesh (3.6 × 1/8 in.) column at 160 °C. The solvents were evaporated off, and the residual mixture (alcohol and ketone) was isolated by distillation at reduced pressure. The ee was calculated from its optical rotation in ethanol solution using a value of $[\alpha]_D^{19}$ +42.9 (undil.)[31] for the (*R*)-(+)-1-phenylethanol isomer, and corrected to the composition of the distillate. Optical rotations were measured with a Perkin-Elmer 241 polarimeter.

Preparation of $[(PiPr_3)_2(CO)HOs(\mu\text{-}\eta^4\text{-}BH_4)OsH(CO)(PiPr_3)_2]BF_4$ (5). A solution of **3** (128 mg, 0.23 mmol) in 15 mL of diethyl ether was treated with a diethyl ether solution of HBF_4 ($HBF_4{\cdot}Et_2O$; 38 μL, 0.28 mmol). After the mixture was stirred for 5 h at room temperature, a pale yellow solid precipitated, which was filtered off, repeatedly washed with diethyl ether, and dried in vacuo; yield 119 mg (88%). Anal. Calcd for $Os_2C_{38}H_{90}B_2F_4O_2P_4$: C, 38.65; H, 7.68. Found: C, 38.82; H, 8.05. IR (Nujol): ν(OsH) 2130 (w), ν(CO) 1940 (s) cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2, −50 °C): δ 2.50 and 2.30 (both m, each 6 H, $PCHCH_3$), 1.26 (m, 72 H, $PCHCH_3$), −3.82 and −5.39 (both br, each 2 H, μ-BH_4), −12.11 (vt, 2 H, *J* (HP) = 20.6, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 34.0, 26.8 (AB-system, *J*(PP′) = 172.7). ^{11}B NMR (89.55 MHz, CH_2Cl_2/C_6D_6): δ 28.58 (br, BH_4), −0.67 (s, BF_4).

Preparation of $[(PiPr_3)_2(CO)HRu(\mu\text{-}\eta^4\text{-}BH_4)RuH(CO)(PiPr_3)_2]BF_4$ (6). This was prepared in a manner analogous to that described for **5** starting from **4** (175 mg, 0.38 mmol) and $HBF_4{\cdot}Et_2O$ (57 μL, 0.41 mmol). After 2 h it was worked up as described for **5**. Pale yellow solid, yield 143 mg (75 %). Anal. Calcd for $Ru_2C_{38}H_{90}B_2F_4O_2P_4$: C, 45.51; H, 9.05. Found: C, 45.87; H, 9.54. IR (Nujol): ν(CO) 1940 (s) cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2, −50 °C): δ 2.38 and 2.11 (both m, each 6 H, $PCHCH_3$), 1.20 (m, 72 H, $PCHCH_3$), −2.85 and −5.76 (both br, each 2 H, μ-BH_4), −13.26 (vt, 2 H, *J* (HP) = 18.7, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CH_2Cl_2/CDCl_3$): δ 61.08, 54.00, (AB-system, *J*(PP′) = 201). ^{11}B NMR (89.55 MHz, CH_2Cl_2/C_6D_6): δ 14.38 (br, BH_4), −1.60 (s, BF_4).

Preparation of $OsH(\eta^2\text{-}O_2C\{(S)\text{-}CH(NaphOMe)Me\})(CO)(PiPr_3)_2$ (7). A solution of **3** (200 mg, 0.36 mmol) in 10 mL of methanol was treated with $\{(S)\text{-}CH(NaphOMe)Me\}CO_2H$ (92 mg, 0.40 mmol) and 0.1 mL of methanol. After being stirred for 2 h at room temperature, the solution was concentrated to ca. 4 mL and cooled to −78 °C. Colorless crystals were formed which were filtered off, repeatedly washed with methanol, and dried in vacuo; yield 227 mg (82 %). Anal. Calcd for $OsC_{33}H_{57}O_4P_2$: C, 51.47; H, 7.48. Found: C, 51.55; H, 7.80. IR (Nujol): ν(OsH) 2170 (w), ν (CO) 1900 (s), ν (OCO) 1535 (asym) and 1430 (sym) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.37 (m, 6 H, $C_{10}H_6$), 3.52 (q, 1 H, *J*(HH) = 7.0, CH), 3.43 (s, 3 H, OCH_3), 2.21 (m, 6 H, $PCHCH_3$), 1.61 (d, 3 H, *J*(HH) = 7.0, CH_3), 1.24 (m, 36 H, $PCHCH_3$), −20.96 (t, *J*(HP) = 16.0, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 39.41 (s).

Preparation of $RuH(\eta^2\text{-}O_2C\{(S)\text{-}CH(NaphOMe)Me\})(CO)(PiPr_3)_2$ (8). This was prepared analogously as described for **7** starting from **4** (168 mg, 0.36 mmol) and $\{(S)\text{-}CH(NaphOMe)Me\}CO_2H$ (92 mg, 0.40 mmol): pale yellow crystals; yield 191 mg (70%). Anal. Calcd for $RuC_{33}H_{57}O_4P_2$: C, 58.22; H, 8.43. Found: C, 58.24; H, 8.76. IR (Nujol): ν(OsH) 2070 (w), ν(CO) 1900 (s), ν(OCO) 1545 (asym) and 1430 (sym) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.40 (m, 6 H, $C_{10}H_6$), 3.67 (q, 1 H, *J*(HH) = 7.0, CH), 3.44 (s, 3 H, OCH_3), 2.06 (m, 6 H, $PCHCH_3$), 1.67 (d, 3 H, *J*(HH) = 7.0, CH_3), 1.23 (m, 36 H, signals are overlapped, $PCHCH_3$), −17.74 (t, 1 H, *J*(HP) = 19.0, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 57.38 (s).

Preparation of $OsH(\eta^2\text{-}O_2C\{(R)\text{-}\{CH(OMe)Ph\})(CO)(PiPr_3)_2$ (9). This was prepared analogously as described for **7** starting from **3** (200 mg, 0.36 mmol) and $\{(R)\text{-}CH(OMe)Ph\}CO_2H$ (66 mg, 0.40 mmol). After the mixture was stirred for 2 h under reflux, it was worked up as described for **7**: colorless crystals; yield 203 mg (80%). Anal. Calcd for $OsC_{28}H_{52}O_4P_2$: C, 47.71; H, 7.58. Found: C, 47.96; H, 7.95. IR (Nujol): ν(OsH) 2155 (w), ν(CO) 1900 (s), ν(OCO) 1590 (asym) and 1450 (sym) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.45 (m, 5 H, C_6H_5), 4.44 (s, 1 H, CH), 3.18 (s, 3 H, OCH_3), 2.22 (m, 6 H, $PCHCH_3$), 1.26 (m, 36 H, $PCHCH_3$), −21.25 (t, 1 H, *J*(HP) = 16.0, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 40.06 (s).

(31) *Handbook of Chemistry and Physics* Weast, R. C., Ed., CRC Press: Boca Raton, FL, 1988; 1st Student Edition.

Preparation of $RuH(\eta^2\text{-}O_2C\{(R)\text{-}CH(OMe)Ph\})(CO)(PiPr_3)_2$ (10). This was prepared analogously as described for **9** starting from **4** (168 mg, 0.36 mmol) and $\{(R)\text{-}CH(OMe)Ph\}CO_2H$ (66 mg, 0.40 mmol): pale yellow crystals; yield 177 mg (80%). Anal. Calcd for $RuC_{28}H_{52}O_4P_2$: C, 54.62; H, 8.51. Found: C, 54.34; H, 8.91. IR (Nujol): ν(OsH) 2040 (w), ν(CO) 1875 (s), ν(OCO) 1565 (asym) and 1440 (sym) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.50 (m, 5 H, C_6H_5), 4.65 (s, 1 H, CH), 3.24 (s, 3 H, OCH_3), 2.14 (m, 6 H, $PCHCH_3$), 1.24 (m, 36 H, $PCHCH_3$), −17.89 (t, 1 H, *J*(HP) = 18.0, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 57.46 (s).

Preparation of $OsH(\eta^2\text{-}O_2C\{(R)\text{-}C(CF_3)(OMe)Ph\})(CO)(PiPr_3)_2$ (11). This was prepared analogously as described for **9** starting from **3** (200 mg, 0.36 mmol) and $\{(R)\text{-}C(CF_3)(OMe)Ph\}CO_2H$ (94 mg, 0.40 mmol): colorless crystals; yield 206 mg (74%). Anal. Calcd for $OsC_{29}H_{51}F_3O_4P_2$: C, 45.07; H, 6.65. Found: C, 45.40; H, 7.00. IR (Nujol): ν(OsH) 2175 (w), ν(CO) 1895 (s), ν(OCO) 1590 (asym) and 1450 (sym) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.54 (m, 5 H, C_6H_5), 3.65 (s, 3 H, OCH_3), 2.23 (m, 6 H, $PCHCH_3$), 1.12 (m, 36 H, $PCHCH_3$), −22.04 (t, 1 H, *J*(HP) = 18.0, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 41.63 (s).

Preparation of $RuH(\eta^2\text{-}O_2C\{(R)\text{-}C(CF_3)(OMe)Ph\})(CO)(PiPr_3)_2$ (12). This was prepared analogously as described in **9** starting from **4** (168 mg, 0.36 mmol) and $\{(R)\text{-}C(CF_3)(OMe)Ph\}CO_2H$ (94 mg, 0.40 mmol): pale yellow crystals; yield 172 mg (70%). Anal. Calcd for $RuC_{29}F_3H_{51}O_4P_2$: C, 50.94; H, 7.52. Found: C, 51.36; H, 7.71. IR (Nujol): ν(OsH) 2070 (w), ν(CO) 1895 (s), ν(OCO) 1590 (asym) and 1450 (sym) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.55 (m, 5 H, C_6H_5), 3.65 (s, 3 H, OCH_3), 2.05 (m, 6 H, $PCHCH_3$), 1.20 (m, 36 H, $PCHCH_3$), −18.43 (t, 1 H, *J*(HP) = 19.0, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 57.72 (s).

Preparation of $OsH(\eta^2\text{-}O_2C\{(S)\text{-}CHOC(=O)CH_2CH_2\})(CO)(PiPr_3)_2$ (13). This was prepared analogously as described in **9** starting from **3** (200 mg, 0.36 mmol) and $\{(S)\text{-}CHOC(=O)CH_2CH_2\}CO_2H$ (52 mg, 0.40 mmol): colorless crystals; yield 171 mg (71%). Anal. Calcd for $OsC_{24}H_{48}O_5P_2$: C, 43.10; H, 7.23. Found: C, 43.22; H, 7.76. IR (Nujol): ν(OsH) 2170 (w), ν(CO) 1890 (s), ν(OCO) 1560 (asym) and 1450 (sym) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 4.18 (m, 3 H, CHOC(=O) and OC(=O)CH_2), 2.25 (m, 6 H, $PCHCH_3$), 1.78 (m, 2 H, CH_2), 1.22 (m, 36 H, $PCHCH_3$), −21.62 (t, 1 H, *J*(HP) = 16.0, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 39.78 (s).

Preparation of $OsH(pz)(CO)(Hpz)(PiPr_3)_2$ (14). A solution of **3** (55 mg, 0.10 mmol) in 8 mL of toluene was treated with pyrazole (15 mg, 0.22 mmol) and 0.1 mL of methanol. After being stirred for 30 min at room temperature, the solution was concentrated to ca 0.5 mL and 5 mL of methanol was added. A white solid precipitated, which was filtered off, repeatedly washed with methanol, and dried in vacuo; yield 55 mg (83%). Anal. Calcd for $OsC_{25}H_{50}N_4OP_2$: C, 44.57; H, 7.48; N, 8.31. Found: C, 44.22; H, 7.92; N, 8.12. IR (Nujol): ν(OsH) 2070 (w), ν(CO) 1875 (s) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 8.08 (br, 1 H), 7.75 (br, 2 H) and 7.28 (br, 1 H) (H^3, $H^{3'}$, H^5, and $H^{5'}$, pz, Hpz), 6.35 and 6.32 (both br, each 1 H, H^4 and $H^{4'}$, pz, Hpz), 2.1 (m, 6 H, $PCHCH_3$), 1.09 (dvt, 36 H, *N* = 13.0, *J*(HH) = 7.6, $PCHCH_3$), −15.80 (t, 1 H, *J*(HP) = 18.6, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, C_6D_6): δ 20.98 (s).

Preparation of $RuH(pz)(CO)(Hpz)(PiPr_3)_2$ (15). A suspension of **4** (94.5 mg, 0.2 mmol) in 10 mL of methanol was treated with pyrazole (35.5 mg, 0.52 mmol); the mixture was stirred at room temperature for 2 h. During the first hour a clear solution was obtained, and then the complex began to precipitate as a white solid, which was filtered off, repeatedly washed with methanol, and dried in vacuo; yield 75 mg (64%). Anal. Calcd for $RuC_{25}H_{50}N_4OP_2$: C, 51.27; H, 8.60; N, 9.57. Found: C, 51.02; H, 9.18; N, 9.60. IR (Nujol): ν(RuH) 2030 (w), ν(CO) 1990 (s) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 8.01, 7.83, 7.67, and 7.39 (all d, each 1 H, *J*(HH) = 2, H^3, $H^{3'}$, H^5, and $H^{5'}$, pz, Hpz), 6.41 and 6.25 (both t, each 1 H, *J*(HH) = 2, H^4 and $H^{4'}$, pz, Hpz), 1.97 (m, 6 H, $PCHCH_3$), 1.10 (dvt, 18 H, *N* = 12.4, *J*(HH) = 7.1, $PCHCH_3$), 1.08 (dvt, 18 H, *N* = 12.8, *J*(HH) = 6.9, $PCHCH_3$), −13.24 (t, 1 H, *J*(HP) = 21.8, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CH_2Cl_2/CDCl_3$): δ 48.45 (s).

Preparation of $[OsH(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]BF_4$ (16). Route a. A suspension of **5** (142 mg, 0.12 mmol) in 5 mL of diethyl ether was stirred under hydrogen atmosphere. After 36 h the white solid formed was filtered off, repeatedly washed with diethyl ether, and dried by a soft stream of hydrogen. Yield: 68 mg (90%).

Route b. A solution of **3** (194 mg, 0.35 mmol) in 5 mL of dichloroethane was treated with $HBF_4{\cdot}Et_2O$ (58 μL, 0.42 mmol) and stirred under hydrogen at room temperature. After 15 min the solution was concen-

trated to ca. 1 mL by passing a stream of H_2 (g) through it. Addition of 10 mL of diethyl ether led to the formation of a white precipitate, which was stirred under hydrogen atmosphere. After 36 h the solid was worked up as described in route a. Yield: 86 mg (78%). Anal. Calcd for $OsC_{19}H_{45}BF_4OP_2$: C, 36.31; H, 7.21. Found: C, 36.36; H, 7.44. IR (Nujol): ν(OsH) 2080 (w), ν(CO) 1930 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.4 (m, 6 H, PC*H*CH_3), 1.3 (dvt, 36 H, N = 15.0, J(HH) = 7.0, PCHC*H*$_3$), -1.2 (br, 2 H, Os(H_2), T_1 = 8 ms), -5.8 (t, 1 H, J(HP) = 17.7, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 42.6 (s).

Reaction of 16 with H_2O: Preparation of [OsH(η^2-H_2)(CO)(OH_2)-(P*i*Pr$_3$)$_2$]BF$_4$ (17). Distilled water (3.8 μL, 0.21 mmol) was added to a solution of **16** (107 mg, 0.17 mmol) in 5 mL of chloroform. After 1 h the solution was concentrated to ca. 0.5 mL. Addition of 5 mL of diethyl ether led to the formation of a white precipitate, which was worked up as described for **16**. Yield: 92 mg (84%). Anal. Calcd for $OsC_{19}H_{47}BF_4O_2P_2$: C, 35.30; H, 7.33. Found: C, 35.02; H, 7.04. IR (Nujol): ν(OH) 3500 (m), ν(OsH) 2080 (w), ν(CO) 1930 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 4.06 (br, 2 H, OH_2), 2.4 (m, 6 H, PC*H*CH_3), 1.3 (dvt, 36 H, N = 15.0, J(HH) = 7.0, PCHC*H*$_3$), -1.1 (br, 2 H, Os(H_2), T_1 = 8 ms), -5.4 (t, 1 H, J(HP) = 18.3, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 43.5 (s).

Preparation of [OsH(CO)(TFB)(P*i*Pr$_3$)$_2$]BF$_4$ (18). Route a. A solution of **3** (133 mg, 0.24 mmol) in 15 mL of diethyl ether was first treated with tetrafluorobenzobarrelene (TFB; 63 mg, 0.28 mmol) and then with HBF_4·Et_2O (38 μL, 0.28 mmol). After the mixture was stirred for 30 min at room temperature, a white solid precipitated, which was filtered off, repeatedly washed with diethyl ether, and dried in vacuo; yield 87 mg (85%).

Route b. A solution of **5** (105 mg, 0.09 mmol) in 5 mL of dichloromethane was treated with TFB (38 mg, 0.17 mmol). After being stirred for 30 min at room temperature, the solution was concentrated to ca. 0.5 mL and 10 mL of diethyl ether was added. A white solid precipitated, which was worked up as described in route a. Yield: 66 mg (87%). Anal. Calcd for $OsC_{31}H_{49}BF_8OP_2$: C, 43.66; H, 5.79. Found: C, 43.49; H, 6.08. IR (Nujol): ν(OsH) 2060 (w), ν(CO) 1960 (s), ν(CF) 1500 (vs) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 5.14 (br, 2 H, -CH, TFB), 4.85 and 3.72 (both br, each 2 H, =CH, TFB), 2.9 (m, 6 H, PC*H*CH_3), 1.5 and 1.3 (both dvt, each 18 H, N = 14.3, J(HH) = 7.5, PCHC*H*$_3$), -8.45 (t, 1 H, J(HP) = 28.9, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 13.07 (s).

Preparation of [OsH(CO)(π-CH_2=CHC(=O)CH_3)(P*i*Pr$_3$)$_2$]BF$_4$ (19). This was prepared analogously as described for **18** in route b starting from **5** (140 mg, 0.12 mmol) and methyl vinyl ketone (24.0 μL, 0.28 mmol). After 3 h it was worked up as described for **18** in route b: white solid; yield 68 mg (81%). Anal. Calcd for $OsC_{23}H_{49}BF_4O_2P_2$: C, 39.66; H, 7.09. Found: C, 39.40; H, 7.52. IR (Nujol): ν(OsH) 2010 (w), ν(C=O) 1940 (s), ν(C=O) 1560 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 4.92, 3.74, and 3.32 (all m, each 1 H, H_2C=C*H*C(O)CH_3), 3.14 and 2.86 (both m, each 3 H, PC*H*CH_3), 2.76 (s, 3 H, -C(O)C*H*$_3$), 1.6 and 1.7 (both dvt, each 18 H, N = 13.8, J(HH) = 7.2, PCHC*H*$_3$), -3.5 (dd, 1 H, J(HP) = 24.3, J(HP') = 29.4, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 31.8, 24.4 (AB-system, J(PP') = 130.5). $^{13}C\{^1H\}$ NMR (75.33 MHz, $CDCl_3$): δ 177.3 (s, *C*(O)CH_3), 175.9 (t, J(PC) = 8.3, CO), 45.4 (br, =CH-), 44.3 (t, J(PC) = 6.0, $=CH_2$), 31.7 (s, OCH_3), 28.3 (vt, N(PC) = 26.7, P*C*HCH$_3$), 19.9, 19.7, 19.0, 18.9 (all s, PCH*C*H$_3$).

Preparation of [OsH(CO)(CH_3CN)$_2$(P*i*Pr$_3$)$_2$]BF$_4$ (20). This was prepared analogously as described for **19** starting from **5** (118 mg, 0.10 mmol) and acetonitrile (CH_3CN; 8.6 μL, 0.20 mmol): white solid; yield 47 mg (67%). Anal. Calcd for $OsC_{23}H_{49}N_2BF_4OP_2$: C, 38.99; H, 6.97; N, 3.95. Found: C, 39.30; H, 7.47; N, 3.80. IR (Nujol): ν(CN) 2330 (w), 2290 (w), ν(OsH) 2140 (w), ν(CO) 1925 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.53 and 2.50 (both s, each 3 H, CH_3CN), 2.4 (m, 6 H, PC*H*CH_3), 1.30 (dvt, 36 H, N = 13.5, J(HH) = 7.0, PCHC*H*$_3$), -14.87 (t, 1 H, J(HP) = 17.0, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 24.94 (s).

Preparation of [RuH(CO)(CH_3CN)$_2$(P*i*Pr$_3$)$_2$]BF$_4$ (21). To a suspension of **6** (103 mg, 0.10 mmol) in 10 mL of diethyl ether was added an excess of CH_3CN (0.1 mL, 1.9 mmol) dropwise. The addition of the first drop gave a colorless solution, and further addition caused precipitation of **21** as a white solid. The suspension was stirred at room temperature for 30 min. The mixture was evaporated under vacuo to about one-third of its volume. The solid was filtered off, repeatedly washed with diethyl ether, and dried in vacuo; yield 87 mg (70%). Anal. Calcd for $RuC_{23}H_{49}N_2BF_4OP_2$: C, 44.59; H, 7.97; N, 4.52. Found: C, 45.18; H, 8.04; N, 4.31. IR (Nujol): ν(CN) 2310 (w), 2285 (w), ν(RuH) 2040 (w), ν(CO) 1935 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.39 (s, 6 H, CH_3CN), 2.34 (m, 6 H, PC*H*CH_3), 1.30 (dvt, 36 H, N = 13.6, J(HH) = 7.2, PCHC*H*$_3$), -14.17 (t, 1 H, J(HP) = 19.0, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 52.23 (s).

Preparation of [RuH(CO)(η^1-$(CH_3)_2CO$)$_2$(P*i*Pr$_3$)$_2$]BF$_4$ (22). Route a. A suspension of complex **6** (90 mg, 0.09 mmol) in 4 mL of diethyl ether was treated with acetone (0.5 mL). The mixture was stirred, and immediately the initial yellow solid turned white in color. The product was filtered off and repeatedly washed with diethyl ether, and it slowly became pale yellow. The very air-sensitive pale yellow complex was dried in vacuo.

Route b. Addition of diethyl ether (8 mL) to a solution of complex **6** (90 mg, 0.09 mmol) in acetone (1 mL) caused the precipitation of a white solid, which was filtered off and washed with diethyl ether three times, after which **22** was obtained as a pale yellow solid which was dried in vacuo. IR (Cl_2CH_2): ν(C=O) 1925 (s), ν(C=O) 1715 (m) and 1675 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, -55 °C): δ 2.43 (s, 6 H, Me_2CO), 2.36 (s, 6 H, Me_2CO), 2.1 (m, 6 H, PC*H*CH_3), 1.2 (m, 36 H, PCHC*H*$_3$), -18.65 (br, 1 H, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 52.81 (s).

Preparation of [RuH(CO)(η^1-$(CH_3)_2CO$)(P*i*Pr$_3$)$_2$]BF$_4$ (23). Complex **22** was dissolved in dichloromethane, and the solution was evaporated to dryness. The resulting white solid was dried in vacuo for 2 h. IR (Cl_2CH_2): ν(C=O) 1925 (s), ν(C=O) 1675 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 20 °C): δ 2.44 (m, 6 H, PC*H*CH_3), 2.20 (s, 6 H, Me_2CO), 1.31 (dvt, 18 H, N = 13.9, J(HH) = 7.1, PCHC*H*$_3$), 1.31 (dvt, 18 H, N = 13.1, J(HH) = 6.9, PCHC*H*$_3$), -21.32 (t, 1 H, J(HP) = 18.5, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 54.26 (s). $^{13}C\{^1H\}$ NMR (75.33 MHz, $CDCl_3$): δ 209.7 (s, Me_2CO), 205.0 (t, J(PC) = 13.3, CO), 31.2 (s, *Me*$_2$CO), 24.7 (vt, N = 10.0, P*C*HCH$_3$), 19.9, 19.4 (both s, PCH*C*H$_3$).

Preparation of [OsH(CO)(Hpz)$_2$(P*i*Pr$_3$)$_2$]BF$_4$ (24). A solution of **14** (70 mg, 0.10 mmol) in 15 mL of diethyl ether was treated with HBF_4·Et_2O (18 μL, 0.13 mmol). After the mixture was stirred for 30 min at room temperature, a white solid precipitated, which was filtered off, repeatedly washed with diethyl ether, and dried in vacuo. Yield: 68 mg (90%). Anal. Calcd for $OsC_{25}H_{51}N_4BF_4OP_2$: C, 39.37; H, 6.74; N, 7.34. Found: C, 39.40; H, 6.98; N, 7.44. IR (Nujol): ν(NH) 3410 (m), ν(OsH) 2130 (w), ν(CO) 1945 (s). ^1H NMR (200 MHz, $CDCl_3$): δ 11.0 (br, 2 H, NH), 8.05, 8.01, 7.96 and 7.7 (all br, each 1 H, H^3, $H^{3'}$, H^5, and $H^{5'}$, H*pz*), 6.44 and 6.34 (both br, each 1 H, H^4 and $H^{4'}$, H*pz*), 2.0 (m, 6 H, PC*H*CH_3), 1.02 (dvt, 36 H, N = 14.0, J(HH) = 6.6, PCHC*H*$_3$), -15.80 (t, 1 H, J(HP) = 18.6, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 22.26 (s).

Reaction of 24 with NaH: Preparation of 14. A solution of **24** (90 mg, 0.12 mmol) in 5 mL of THF was treated with NaH (5.74 mg, 0.24 mmol). After being stirred for 1 h the solution was concentrated to dryness, 5 mL of toluene was added, and the solution was filtered. The colorless filtrate was concentrated to ca. 0.1 mL, and 4 mL of methanol was added. Then it was worked up as described for **14**: white solid; yield 60 mg (75%). The solid was identified spectroscopically as **14**.

Preparation of [RuH(CO)(Hpz)$_2$(P*i*Pr$_3$)$_2$]BF$_4$ (25). A solution of **15** (76 mg, 0.13 mmol) in 4 mL of dichloromethane was treated with HBF_4·Et_2O (19 μL, 0.14 mmol). After being stirred for 30 min, the solution was concentrated to ca. 0.75 mL. A white-yellowish product was precipitated by addition of diethyl ether. The solid was filtered off, repeatedly washed with diethyl ether, and dried in vacuo; yield 65 mg (74%). Anal. Calcd for $RuC_{25}H_{51}N_4BF_4OP_2$: C, 44.58; H, 7.63; N, 8.32. Found: C, 44.69; H, 8.11; N, 8.20. IR (Nujol): ν(NH) 3400 (m), ν(RuH) 2045 (w), ν(CO) 1915 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 11.58 (s, 2 H, NH), 7.94, 7.82, 7.54 and 7.35 (all br, each 1 H, H^3, $H^{3'}$, H^5, and $H^{5'}$, H*pz*), 6.41 and 6.24 (both br, each 1 H, H^4 and $H^{4'}$, H*pz*), 1.95 (m, 6 H, PC*H*CH_3), 1.21 (dvt, 18 H, N = 13.2, J(HH) = 7.0, PCHC*H*$_3$), 1.10 (dvt, 18 H, N = 13.2, J(HH) = 6.6, PCHC*H*$_3$), -13.58 (t, 1 H, J(HP) = 19.8, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 49.39 (s).

Preparation of OsHCl(CO)(Hpz)(P*i*Pr$_3$)$_2$ (26). Route a. A suspension of **1** (80 mg, 0.14 mmol) in 5 mL of hexane was treated with pyrazole (11 mg, 0.17 mmol). After the mixture was stirred for 15 min at room temperature, a white solid was formed, which was filtered off, washed with hexane and dried in vacuo; yield 76 mg (85%).

Route b. A solution of **14** (80 mg, 0.12 mmol) in 4 mL of toluene was treated with HCl (d = 1.18; 41.3 μL, 0.48 mmol). The reaction mixture was heated for 12 h under reflux and then was filtered. It was concentrated to ca. 0.5 mL, and 5 mL of methanol was added. A white solid precipitated, which was worked up as described in route a. Owing to the IR and NMR spectra the white solid turned out to be a mixture of two isomers **26a** and

26b in a 2:1 ratio. Yield: 62 mg (80%). Anal. Calcd for $OsC_{22}H_{47}N_2ClOP_2$: C, 41.07; H, 7.30; N, 4.35. Found: C, 41.63; H, 7.73; N, 4.49.

26a. IR (Nujol): δ(NH) 3250 (m), ν(OsH) 2130 (w), ν(CO) 1905 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 12.8 (s, 1 H, NH), 7.87, 7.49 (both br, each 1 H, H^3, H^5, H*pz*), 6.40 (br, 1 H, H^4, H*pz*), 2.6 (m, 6 H, PC*H*CH_3), 1.20 (dvt, 18 H, *N* = 13, *J*(HH) = 7, PCHC*H*$_3$), −14.50 (t, 1 H, *J*(HP) = 16.8, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 22.98 (s).

26b. IR (Nujol): ν(NH) 3190 (m), ν(OsH) 2130 (w), ν(CO) 1885 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 13.2 (s, 1 H, NH), 7.50 (br, 2 H, H^3, H^5, H*pz*), 6.30 (br, 1 H, H^4, H*pz*), 2.0 (m, 6 H, PC*H*CH_3), 1.00 (dvt, 18 H, *N* = 13, *J*(HH) = 7, PCHC*H*$_3$), −17.20 (t, 1 H, *J*(HP) = 16.8, OsH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 21.26 (s).

Preparation of RuHCl(CO)(Hpz)($PiPr_3$)$_2$ (27). A solution of **15** (76 mg, 0.13 mmol) in 4 mL of dichloromethane was treated with a solution of HCl in methanol (0.3 mL, 0.47 N, 0.14 mmol). After being stirred for 1 h, the solution was concentrated to ca. 0.5 mL, and methanol was added to precipitate **27** as a white solid, which was filtered off, repeatedly washed with methanol, and dried in vacuo; yield 47 mg (65%). Anal. Calcd for $RuC_{22}H_{47}N_2ClOP_2$: C, 47.69; H, 8.55; N, 5.06. Found: C, 47.66; H, 9.19; N, 5.01. IR (Nujol): ν(NH) 3200 (m), ν(RuH) 2025 (w), ν(CO) 1910 (s) cm^{-1}. A mixture of two isomers was observed in solution in the ratio **27a**:**27b** = 1:1.

27a. ^1H NMR (200 MHz, $CDCl_3$): δ 13.3 (s, 1 H, NH), 7.39, 6.66 (both br, each 1 H, H^3, H^5, H*pz*), 5.93 (br, 1 H, H^4, H*pz*), 2.8 (m, 6 H, PC*H*CH_3), 1.30 (m, 18 H, PCHC*H*$_3$), −13.42 (br, 1 H, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 49.10 (br).

27b. ^1H NMR (200 MHz, $CDCl_3$): δ 13.9 (s, 1 H, NH), 7.88, 6.85 (both br, each 1 H, H^3, H^5, H*pz*), 6.13 (br, 1 H, H^4, H*pz*), 2.0 (m, 6 H, PC*H*CH_3), 1.30 (m, 18 H, PCHC*H*$_3$), −14.94 (t, 1 H, *J*(HP) = 20.2, RuH). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 47.20 (s).

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