$(Me_4Cp)_2TiBr$ corroborates their assignment to halogen-localized orbitals.

The average values ΔIE of methyl group are (within the experimental error) identical with those for the chloro derivatives. Thus, the same assignment of the PE bands is adopted as for the $Cp'_2TiCl$ species.

No spin–orbital splitting of bromine p(π) ionizations has been resolved in the above PE spectra, in spite of the atomic spin–orbit coupling parameter of 0.305 eV for bromine. Reduction of the spin–orbit splitting is approximately proportional to the decrease of the electron density on the atomic center. Bonding interactions bring about broadening of the vibrational envelope of lone-pair ionizations. Thus, unresolved spin–orbit components within band e indicate some interaction of bromine p(π) orbitals with the $Cp'_2Ti$ fragment. This interaction seems to be of comparable extent for the two symmetry species of p(π) orbitals. No spectral feature indicating the presence of the dimerized species was detected in the PE spectra.

## Conclusions

The effect of methyl groups upon ionization energies is additive. Variations of photoionization cross sections with photon energy and band shifts provide a consistent assignment. According to the classification of the bonding situation in bis(cyclopentadienyl)metal halides introduced by Cauletti and co-workers,[6] the $Cp'_2TiX$ complexes adhere to the class A systems; i.e., the cyclopentadienyl $e_1(\pi)$ orbitals lie above the halogen lone pairs. The extent of the delocalization of the halogen p orbitals seems to be comparable for Cl and Br. No dimer species were detected in the PE spectra of the $Cp_2TiX$ and $(MeCp)_2TiX$ complexes.

**Registry No.** $Cp_2TiCl$, 60955-54-6; $(MeCp)_2TiCl$, 32698-18-3; $(Me_3Cp)_2TiCl$, 120325-58-8; $(Me_4Cp)_2TiCl$, 120325-59-9; $(Me_5Cp)_2TiCl$, 73348-99-9; $Cp_2TiBr$, 128467-43-6; $(MeCp)_2TiBr$, 137045-86-4; $(Me_3Cp)_2TiBr$, 140167-91-5; $(Me_4)_2TiBr$, 140167-90-4; $(Me_5Cp)_2TiBr$, 107495-35-2.

OM910308M

# Synthesis, Molecular Structure, and Reactivity of Octahedral Alkylhydridoosmium(II) Complexes $[OsH(R)(CO)_2(PR'_3)_2]$

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In contrast to the reaction of $[OsH(\eta^2\text{-}BH_4)(CO)(PR'_3)_2]$ (**2a,b**) with methanol under reflux, which gives the dihydrides *cis,cis,trans*-$[OsH_2(CO)_2(PR'_3)_2]$ (**4a,b**), the corresponding reaction with ethanol or 2-methoxyethanol under the same conditions leads to the formation of the alkylhydridoosmium(II) complexes $[OsH(R)(CO)_2(PR'_3)_2]$ (**5a,b** (R = $CH_3$), **6a,b** (R = $MeOCH_2$)) in good yields. The X-ray structural analysis of **5a** reveals an octahedral coordination sphere around the osmium center with the CO ligands in cis and the phosphines in trans positions. Reactions of **5a,b** with electrophiles preferentially leads to cleavage of the Os–$CH_3$ bond; thus, on treatment with HX (X = Cl, $CH_3CO_2$, $CF_3CO_2$) the monohydrides $[OsHX(CO)_2(PR'_3)_2]$ (**11**, **12**, **13a,b**) are formed. Protonation of **5a** with $HBF_4$ in ether/acetone yields quantitatively the cationic hydrido complex $[OsH(acetone)(CO)_2(P^iPr_3)_2]BF_4$ (**15**) whereas from **5a,b** and $HBF_4$ in the presence of water the compounds $[OsH(H_2O)(CO)_2(PR'_3)_2]BF_4$ (**16a,b**) are obtained. Complex **15** reacts with acetonitrile, trimethyl phosphite, or pyrazole by displacement of the acetone ligand to give the compounds $[OsH(L)(CO)_2(P^iPr_3)_2]BF_4$ (**17–19**). Subsequent reaction of **19** (L = pyrazole) with the dimers $[M(\mu\text{-}OMe)(diolefin)]_2$ (**20**, **22**, M = Rh; **21**, M = Ir) produces the heterobinuclear complexes **23–25**; in these the metal centers (Os and Rh or Ir) are bridged by a hydride and a pyrazolyl group. Treatment of **15** with methyl vinyl ketone and $CO_2Me$-substituted alkynes $RC{\equiv}CO_2Me$ gives cationic four- and five-membered metallacycles **26–29** which are formed by a Markovnikov or an anti-Markovnikov type of insertion of the unsaturated substrate into the Os–H bond.

We have recently reported that the five-coordinate hydridoosmium complex $[OsHCl(CO)(P^iPr_3)_2]$ (**1a**) under hydrogen not only catalyzes the reduction of cyclohexene, 1,3- and 1,4-cyclohexadiene, styrene, and diphenyl- and phenylacetylene[1,2] but in presence of $NaBH_4$ also serves as a catalyst for hydrogen transfer from 2-propanol to cyclohexanone, acetophenone, benzylideneacetone, benzylideneacetophenone, and phenylacetylene.[3-5] It was shown that compound **1a** reacts with $NaBH_4$ to give initially the tetrahydridoborate complex **2a**, which in the presence of 2-propanol decomposes to the tetrahydride **3a** (Scheme I).[6] If $[OsHCl(CO)(PMe^tBu_2)_2]$ is used as starting material, in a similar reaction sequence complex

[†] Universidad de Zaragoza.
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(1) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem.* **1988**, *100*, 1621; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563.
(2) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431.
(3) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1.
(4) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1989**, *53*, 43.
(5) Werner, H.; Meyer, U.; Esteruelas, M. A.; Sola, E.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187.
(6) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

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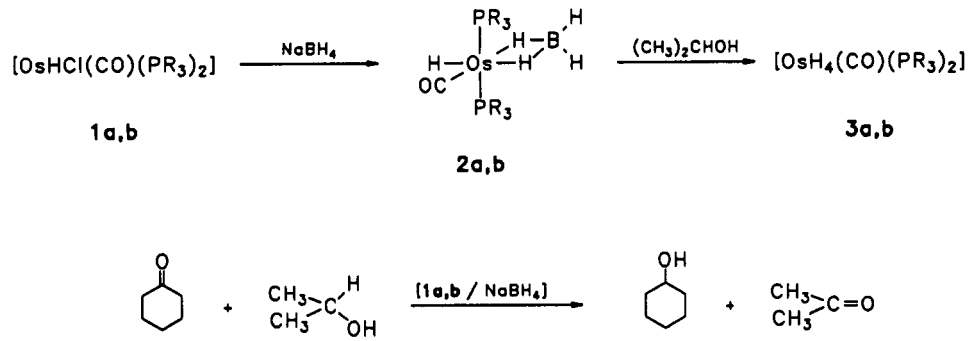
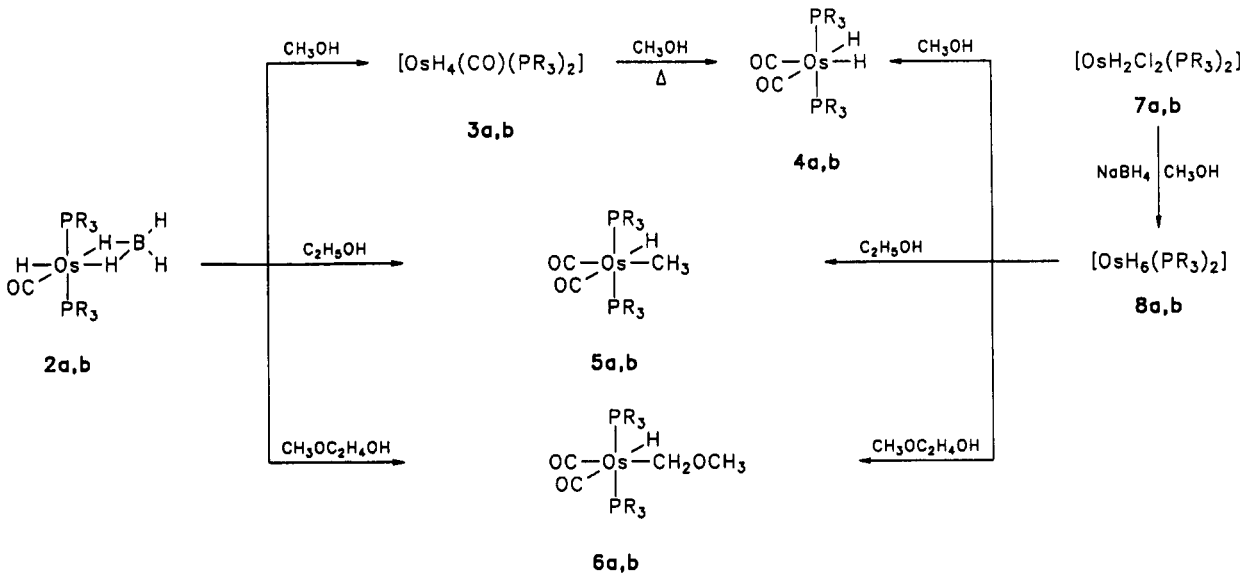
**Scheme I**




(a: $PR_3 = P\text{i}Pr_3$; b: $PR_3 = PMe\text{t}Bu_2$)

**Scheme II**




(a: $PR_3 = P\text{i}Pr_3$; b: $PR_3 = PMe\text{t}Bu_2$)

**3b** is obtained.[6,7] Kinetic investigations suggest[8] that, in the hydrogen-transfer processes catalyzed by **1a,b** and $NaBH_4$, the coordinatively unsaturated dihydrides $[OsH_2(CO)(PR_3)_2]$, which are generated from **3a,b** by loss of $H_2$, are the active catalytic species.

When we attempted in the reduction of cyclohexanone to replace 2-propanol by methanol, ethanol, or 2-methoxyethanol as a hydrogen source, we observed that a rapid deactivation of the catalyst occurred. Whereas with 0.02 mmol of the catalyst, prepared from **1a** and $NaBH_4$ in 2-propanol, in 4 h at room temperature, a 34% conversion of cyclohexanone to cyclohexanol could be obtained, with the same catalyst (or catalyst precursor) under analogous conditions in methanol, ethanol, or 2-methoxyethanol the yield of cyclohexanol was almost zero.

This unexpected finding prompted us to explore the reactivity of **2a,b** 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 $[OsH_2(CO)_2(PR_3)_2]$ (**4a,b**) and the novel alkylhydridoosmium complexes $[OsH(CH_3)(CO)_2(PR_3)_2]$ (**5a,b**) and $[OsH(CH_2OMe)(CO)_2(PR_3)_2]$ (**6a,b**). The present paper describes the preparation and structure of these compounds and illustrates their remarkable reactivity by choosing **5a** and **5b** as representative examples.

## Results

**1. Preparation of the Alkyl Hydrido Complexes $[OsH(R)(CO)_2(PR_3)_2]$ (5a,b, 6a,b).** We have already described that the $OsH(\eta^2\text{-}BH_4)$ complexes **2a,b** react with methanol *at room temperature* to give the osmium tetrahydrides **3a,b**.[6,7] If the reaction, however, is carried out in $CH_3OH$ *under reflux*, the six-coordinate dihydrido compounds **4a,b** are formed in 70–75% yield (see Scheme II). Whereas complex **4a** is also accessible from **3a** upon treatment with carbon monoxide,[6] the corresponding $PMe^tBu_2$ derivative **4b** has not been obtained by this route. In contrast, the isomer of **4b**, *all-trans*-$[OsH_2(CO)_2(PMe^tBu_2)_2]$ is known and has been prepared by chloride substitution from *all-trans*-$[OsCl_2(CO)_2(PMe^tBu_2)_2]$ and $LiAlH_4$.[2] Regarding the reaction conditions, it seems obvious that the cis,cis,trans compound **4b** is thermodynamically more stable than the all-trans isomer, which might be due to the more favorable arrangement H–Os–CO

(7) Meyer, U. Dissertation, Universität Würzburg, 1988.
(8) Esteruelas, M. A.; Valero, C.; Meyer, U. Unpublished results. See: Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288.

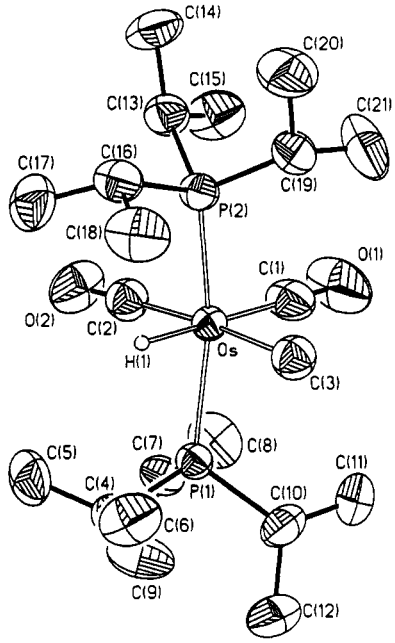



**Figure 1.** Crystal structure of complex **5a**. Hydrogen atoms of the phosphine ligands and the $OsCH_3$ group were omitted for clarity. There is a disorder between the $CH_3$ ligand and its trans CO group (see also the text).

compared with H–Os–H and CO–Os–CO.

Treatment of **2a,b** with *ethanol* under reflux does not lead to the formation of **4a,b** but instead gives the hydridomethylosmium compounds **5a,b** in good yields. As there is no doubt that both the methyl and the second carbonyl ligand are generated from $C_2H_5OH$, the formation of **5a,b** parallels that of the mesityleneosmium complex [(mes)OsH($CH_3$)(CO)] (mes = mesitylene = 1,3,5-trimethylbenzene), which has been prepared from [(mes)$OsCl_2]_n$ and $Na_2CO_3$/EtOH in presence of 3.3-dimethyl-1-butene.[9]

2-Methoxyethanol behaves similarly to $C_2H_5OH$ and reacts with **2a,b** to yield **6a,b**. These compounds as well as the hydrido methyl derivatives **5a,b** are also obtained from the dichloro dihydrido complexes **7a,b** on stepwise treatment with $NaBH_4/CH_3OH$ and $RC_2H_4OH$ (R = H, OMe). We have recently shown that the reaction of **7a,b** with $NaBH_4$ in methanol/benzene gives the compounds **8a,b**, which in agreement with the work of Koetzle and Spencer et al.[10] probably contain no ($\eta^2$-$H_2$) ligands but are "classical" hydrides.[11] They react with $C_2H_5OH$ and $MeOC_2H_4OH$ to form the alkyl hydrido complexes **5a,b** and **6a,b**. On this alternative route, *both* CO ligands are generated by controlled fragmentation from the alcohol. **5a,b** and **6a,b** are colorless solids which are significantly more stable than the very labile tetracarbonyl derivative [OsH($CH_3$)$(CO)_4$].[12]

As far as the spectroscopic data of the new alkyl hydrido compounds are concerned, the most characteristic features are the high-field signal at $\delta$ −7.6 to −7.8 in the $^1H$ NMR (assigned to the osmium-bound hydride) and the two CO absorptions in the $^{13}C$ NMR spectra at $\delta$ 183–191 indicating the presence of two chemically different carbonyl ligands in the metal coordination sphere.

**Table I. Final Atomic Coordinates (×10⁴) for Refined Atoms of Complex 5a**

| atom | x/a | y/b | z/c |
|---|---|---|---|
| Os[a] | 18157 (2) | 12301 (1) | −15830 (2) |
| P(1) | 3328 (2) | 1161 (1) | 570 (1) |
| P(2) | 980 (2) | 1320 (1) | −3747 (1) |
| O(1) | −1643 (7) | 1091 (3) | −1549 (5) |
| O(2)[b] | 1936 (13) | 2301 (3) | −1319 (7) |
| O(2′)[b] | 2133 (23) | 183 (4) | −1904 (11) |
| C(1) | −333 (9) | 1148 (3) | −1544 (6) |
| C(2)[b] | 1821 (22) | 1907 (5) | −1404 (14) |
| C(2′)[b] | 1780 (28) | 554 (5) | −1790 (20) |
| C(3)[b] | 2217 (19) | 453 (6) | −1782 (13) |
| C(3′)[b] | 1929 (36) | 2023 (6) | −1403 (23) |
| C(4) | 5604 (7) | 1230 (2) | 1007 (6) |
| C(5) | 6054 (9) | 1737 (3) | 672 (7) |
| C(6) | 6317 (9) | 833 (3) | 420 (7) |
| C(7) | 2867 (7) | 1642 (2) | 1503 (5) |
| C(8) | 1083 (10) | 1668 (3) | 1361 (7) |
| C(9) | 3934 (11) | 1672 (3) | 2858 (6) |
| C(10) | 3193 (9) | 558 (2) | 1240 (5) |
| C(11) | 1418 (10) | 435 (3) | 1146 (7) |
| C(12) | 4388 (11) | 444 (3) | 2526 (7) |
| C(13) | −328 (8) | 1865 (2) | −4388 (6) |
| C(14) | −808 (10) | 1953 (3) | −5767 (6) |
| C(15) | −1819 (9) | 1909 (3) | −4027 (7) |
| C(16) | 2740 (7) | 1411 (3) | −4269 (5) |
| C(17) | 3713 (10) | 1871 (3) | −3715 (7) |
| C(18) | 3898 (10) | 973 (3) | −3975 (7) |
| C(19) | −59 (9) | 776 (2) | −4662 (5) |
| C(20) | −263 (12) | 762 (3) | −6012 (6) |
| C(21) | −1665 (11) | 654 (3) | −4503 (8) |
| H(1) | 3644 (71) | 1257 (18) | −1668 (50) |

[a] Atomic coordinates for this atom × $10^5$. [b] These atoms are involved in a disorder. Unprimed atoms correspond to the molecule with higher occupancy (0.61 (1)); the primed ones have an occupancy factor of 0.39 (1).

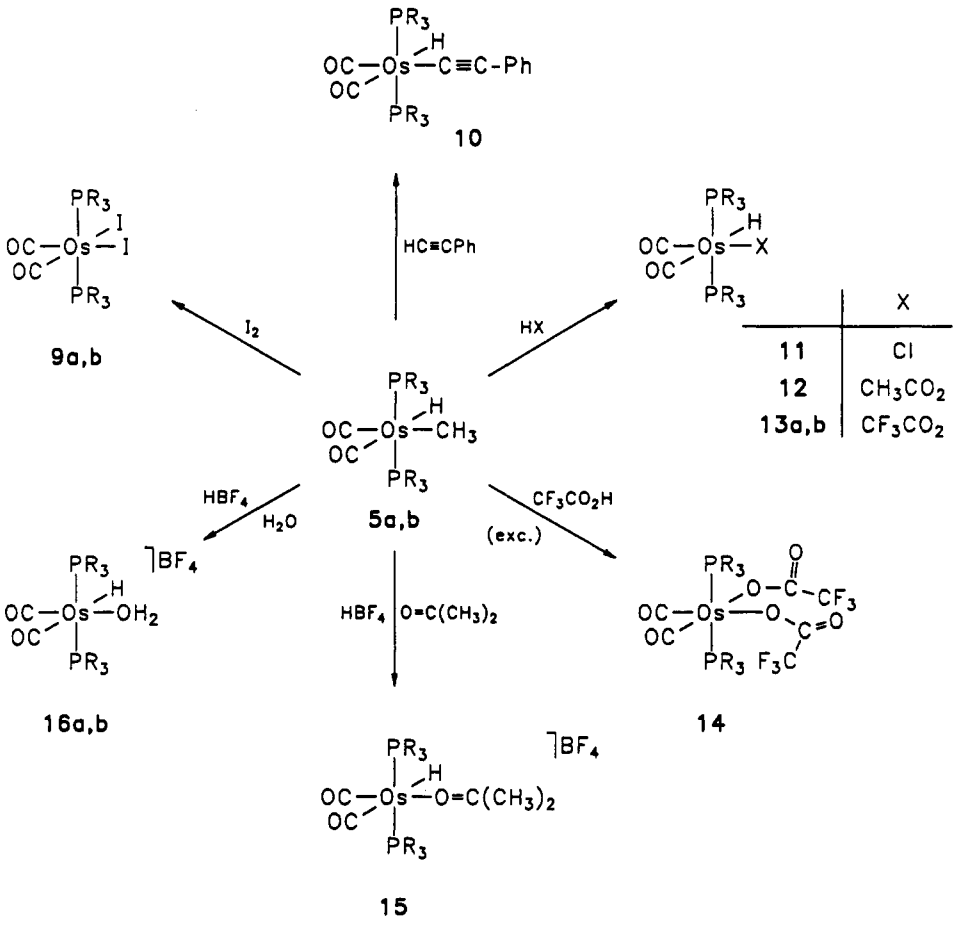
**Table II. Selected Bond Distances (Å) and Angles (deg) for Complex 5a**

| | | | |
|---|---|---|---|
| Os–P(1) | 2.384 (1) | C(2)–O(2) | 1.093 (16) |
| Os–P(2) | 2.377 (1) | C(2′)–O(2′) | 1.091 (20) |
| Os–C(1) | 1.901 (8) | P(1)–C(4) | 1.865 (6) |
| Os–C(2) | 1.879 (14) | P(1)–C(7) | 1.854 (7) |
| Os–C(2′) | 1.880 (14) | P(1)–C(10) | 1.861 (6) |
| Os–C(3) | 2.198 (17) | P(2)–C(13) | 1.869 (6) |
| Os–C(3′) | 2.197 (17) | P(2)–C(16) | 1.863 (7) |
| Os–H(1) | 1.63 (7) | P(2)–C(19) | 1.873 (6) |
| C(1)–O(1) | 1.149 (11) | | |
| P(1)–Os–P(2) | 165.6 (1) | P(2)–Os–H(1) | 82 (2) |
| P(1)–Os–C(1) | 97.6 (2) | C(1)–Os–C(2) | 94.5 (6) |
| P(1)–Os–C(2) | 89.1 (5) | C(1)–Os–C(2′) | 85.1 (6) |
| P(1)–Os–C(2′) | 91.9 (5) | C(1)–Os–C(3) | 94.7 (5) |
| P(1)–Os–C(3) | 89.2 (4) | C(1)–Os–C(3′) | 97.3 (6) |
| P(1)–Os–C(3′) | 89.5 (5) | C(1)–Os–H(1) | 175 (2) |
| P(1)–Os–H(1) | 84 (2) | C(2)–Os–C(3) | 170.8 (8) |
| P(2)–Os–C(1) | 96.8 (2) | C(2)–Os–H(1) | 90 (2) |
| P(2)–Os–C(2) | 90.1 (5) | C(2′)–Os–C(3′) | 177 (1) |
| P(2)–Os–C(2′) | 89.0 (6) | C(2′)–Os–H(1) | 90 (2) |
| P(2)–Os–C(3) | 89.3 (4) | C(3)–Os–H(1) | 81 (2) |
| P(2)–Os–C(3′) | 89.1 (5) | C(3′)–Os–H(1) | 87 (2) |

**2. Molecular Structure of 5a.** The crystal structure of the hydrido methyl complex is made up of discrete molecules separated by normal van der Waals distances. Figure 1 shows the molecular structure and the numbering scheme of one of the two disordered molecules that form the crystal (see Experimental Section). Atomic coordinates are listed in Table I, and derived bond distances and angles are summarized in Table II. The molecule contains an osmium atom in a distorted octahedral environment. This distortion probably arises from the different steric requirements of the coordinated ligands which causes displacements of the more bulky groups ($P^iPr_3$, $CH_3$, CO)

(9) Stahl, S.; Werner, H. *J. Am. Chem. Soc.* **1991**, *113*, 2944.
(10) (a) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930. (b) Connelly, N. G.; Howard, J. A. K.; Spencer, J. L.; Woodley, P. K. *J. Chem. Soc., Dalton Trans.* **1984**, 2003.
(11) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1.
(12) (a) Evans, J.; Okrasinski, S. J.; Pribula, A. J.; Norton, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 4000. (b) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

**Scheme III**




(a: $PR_3 = P^iPr_3$; b: $PR_3 = PMe^tBu_2$; for **10–12**, **14**, **15**: R = iPr)

toward the "small" hydride. As a consequence, the L–Os–H(1) angles differ from the ideal value of 90° and are 84 (2)° for P(1)–Os–H(1), 82 (2)° for P(2)–Os–H(1), and 81 (2)° for C(3)–Os–H(1), respectively.

With regard to the $P^iPr_3$ ligands, the molecular structure of **5a** is quite similar to that of the five-coordinate osmium(II) complex $[Os(CH{=}CHPh)Cl(CO)(P^iPr_3)_2]$ insofar as both molecules share a trans disposition of the two phosphine groups with almost equivalent P–Os–P angles, 165.6 (1)° in **5a** and 167.4 (5)° in the vinyl derivative.[13] The Os–P distances in the two compounds are also comparable, being in **5a** slightly shorter (2.384 (1) and 2.377 (1) Å) than in $[Os(CH{=}CHPh)Cl(CO)(P^iPr_3)_2]$ (2.398 (2) and 2.395 (2) Å). There are only two other structurally characterized osmium complexes containing triisopropylphosphine: the pseudooctahedral osmium(II) cation $[(C_6H_6)(P^iPr_3)\overline{OsCH{=}C(I)C(OMe){=}O}]^{+}$[14] and the dihydridoosmium(IV) derivative **7a**.[8] Whereas the Os–P bond lengths observed in **5a** compare well with that in the cationic species (2.383 (3) Å), they are significantly longer than those found in **7a** (2.304 (3) and 2.289 (3) Å), where the metal center exhibits a higher oxidation state.

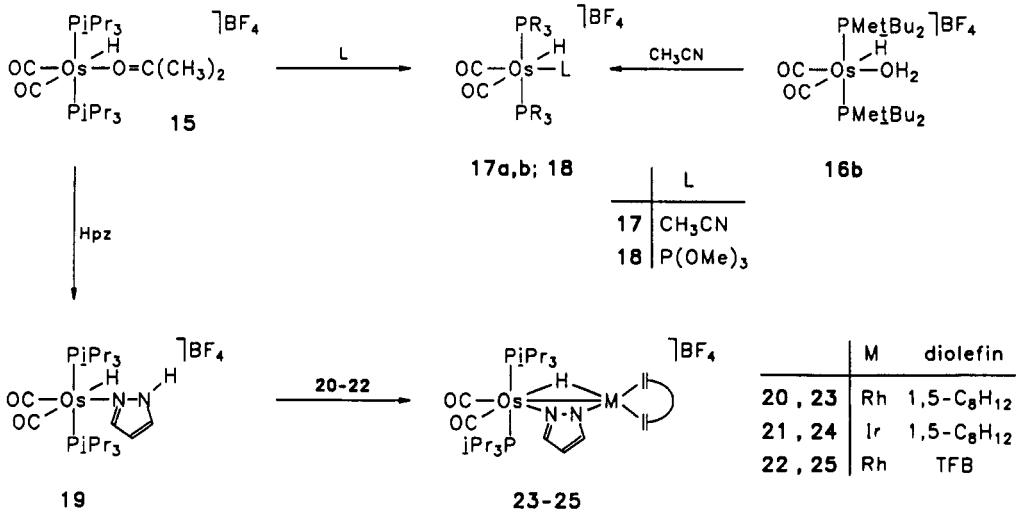
In spite of the disorder that involves one carbonyl ligand, both Os–CO distances are rather similar (1.901 (8) and 1.879 (14) Å) and are clearly in the range expected for terminal carbonyl groups bound to osmium (1.880–1.927 Å).[15] To the best of our knowledge, there is no previous report in the literature dealing with the X-ray structural analysis of a methylosmium(II) complex. The existence of disorder between the $CH_3$ ligand and its trans carbonyl group unfortunately makes the discussion of the Os–$CH_3$ bond length (2.198 (17) Å) somewhat difficult as the error associated with this figure is increased. However, the distance found in **5a** seems to be longer than that observed in the structurally related complex $[OsH(CS_2Me)(CO)_2(PPh_3)_2]$ (2.137 (5) Å), where an Os–C bond is also trans to a carbonyl ligand.[16]

The hydride ligand was found using the La Placa and Ibers method[17] and refined at a Os–H bond length of 1.63 (6) Å. This distance is in the range (1.64–1.68 Å) determined by neutron diffraction in $[OsH_6(P^iPr_2Ph)_2]$[10a] and $[OsH_4(PMe_2Ph)_3]$[18] despite the markedly different metal oxidation state. The Os–H value in **5a** also lies within the range of osmium–hydride distances found by a number of X-ray studies, e.g. 1.64 (6) Å in $[OsH(CS_2Me)(CO)_2(PPh_3)_2]$,[16] where a similar H–Os–CO arrangement is present.

**3. Reactions of Complexes 5a,b with Electrophiles.** The investigations aimed to elucidate the reactivity of the hydrido methyl derivatives **5a,b** are summarized in Scheme III. Whereas both compounds react with iodine to give

(13) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295.
(14) Werner, H.; Weinand, R.; Otto, H. *J. Organomet. Chem.* **1986**, *307*, 49.
(15) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.
(16) Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273.
(17) La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511.
(18) Hardt, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

**Scheme IV**




(a: $PR_3 = PiPr_3$; b: $PR_3 = PMetBu_2$)

**Table III. Crystallographic Data for 5a**

| | |
|---|---|
| formula | $C_{21}H_{46}O_2OsP_2$ |
| MW | 582.74 |
| cryst size, mm | 0.20 × 0.30 × 0.50 |
| cryst system | monoclinic |
| space group | $P2_1/c$ |
| $a$, Å | 8.704 (2) |
| $b$, Å | 27.591 (5) |
| $c$, Å | 11.703 (3) |
| $\beta$, deg | 111.54 (2) |
| $V$, Å$^3$ | 2614 (1) |
| $Z$ | 4 |
| $D$(calcd), g cm$^{-3}$ | 1.48 |
| $\lambda$(Mo K$\alpha$ radiation), Å; technique | 0.710 69; bisecting geometry |
| monochromator | graphite oriented |
| $\mu$, cm$^{-1}$ | 50.16 |
| scan type | $\omega/2\theta$ |
| $2\theta$ range, deg | 3–55 |
| no. of data collcd | 6506 |
| no. of unique data | 5583 |
| no. of unique obsd data | 3864, $F_o > 6\sigma(F_o)$ |
| no. of params refined | 251 |
| $R$ | 0.028 |
| $R_w$[a] | 0.029 |
| max, min abs corr | 1.163–0.812 |

[a] $w = 1.0746/[\sigma^2(F_o) + 0.00053F_o^2]$.

almost quantitatively the diiodides **9a,b**, the reaction of **5a** with a 5-fold exess of phenylacetylene does not lead to the formation of the bis(alkynyl) complex $[Os(C{\equiv}CPh)_2(CO)_2(P^iPr_3)_2]$. It gives instead the alkynyl hydrido compound **10** in 71% yield. Similarly, on treatment of **5a** or **5b** with HCl, $CH_3CO_2H$, and $CF_3CO_2H$, the monohydrides **11**, **12**, and **13a,b** are obtained. The chloro hydrido complex was already known and had been prepared on addition of CO to the stable five-coordinate species $[OsHCl(CO)(P^iPr_3)_2]$.[19]

The reaction of **5a** with excess trifluoracetic acid under reflux conditions gives the bis(trifluoroacetate) **14** in 58% yield. This white crystalline compound as well as the above mentioned monohydrides have been fully characterized by elemental analysis and IR as well as NMR spectroscopic data.

The protonation of **5a** with an ether solution of $HBF_4$ in presence of acetone leads to quantitative formation of the cationic hydrido complex **15**. If water instead of acetone is used as a Lewis base, the aqua hydrido compounds **16a,b** are obtained also in excellent yields. The $BF_4$ salts **15** and **16a,b** form colorless crystals which are only slightly air-sensitive and quite stable in nitromethane or chloroform solution. In the $^1H$ NMR spectra, the hydride signals of the $[OsH(L)(CO)_2(PR_3)_2]^+$ cations (L = acetone, $H_2O$) are found at $\delta$ −1.3 and −3.2, that is, at lower field compared with the uncharged hydrido complexes **10–13**. (For more details of the IR and NMR spectra, see the Experimental Section.)

**4. Ligand Substitution Reactions of Complex 15.** The acetone ligand in **15** can be readily displaced by acetonitrile, trimethyl phosphite, or pyrazole (Hpz) to yield the cationic complexes **17–19** (see Scheme IV). The substitution is certainly facilitated by the weakness of the Os–acetone bond.

The pyrazole ligand in **19** contains an acidic NH group which is capable of reacting with the methoxy-bridged dimers $[M(\mu\text{-OMe})(COD)]_2$ (**20**, M = Rh; **21**, M = Ir; COD = cycloocta-1,5-diene) and $[Rh(\mu\text{-OMe})(TFB)]_2$ (**22**, TFB = tetrafluorobenzobarrelene)[20] to give the heterobinuclear complexes **23–25**. In acetone solution under reflux, **23** and **25** were obtained as yellow solids in nearly quantitative yields. In contrast, under the same conditions complex **24** was isolated in ca. 50% yield together with the starting materials **19** and **21**, respectively. The presence of a bridging hydride ligand in **23** and **25** is substantiated by the $^1H$ NMR spectra that show in the high-field region a doublet-of-triplets owing to Rh–H and P–H coupling. The $^1H$ NMR spectrum of **24** contains in the hydride region a triplet at $\delta$ −11.1 with a P–H coupling constant of 9.1 Hz. As the rhodium or iridium center in these heterobimetallic compounds is coordinatively unsaturated, a dative Os→M bond can be proposed. Related binuclear complexes have recently been described by Cowie et al.[21]

The acetone ligand in **15** can also be displaced by alkenes and alkynes. Treatment of **15** with methyl vinyl ketone in 1,2-dichloroethane leads, after 12 h under reflux, to a pale yellow solution from which on addition of ether a white solid is isolated. According to the elemental analysis, the composition corresponds to a 1:1 adduct of the frag-

(19) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.

(20) Uson, R.; Oro, L. A.; Cabeza, J. *Inorg. Synth.* **1985**, *23*, 126.

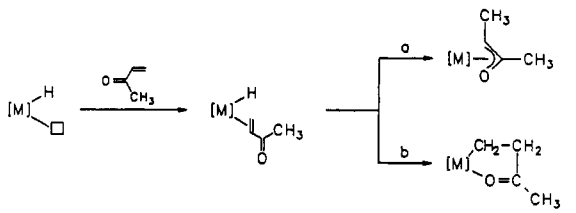
(21) (a) Antonelli, D. M.; Cowie, M. *Organometallics* **1990**, *9*, 1818. (b) Hilts, R. H.; Franchuk, R. A.; Cowie, M. *Ibid.* **1991**, *10*, 304.

Table IV. $^{31}P\{^1H\}$ NMR Spectral Data for the Reaction of 15 with Methyl Propiolate as a Function of Time ($T$ = 22 ± 1 °C)

| | δ, ppm | | | | | intensity ratio | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| time | 15 | 30 | 28 | 31 | 29 | 15 | 30 | 28 | 31 | 29 |
| 45 min | 37.0 | 36.6 | 17.9 | | | 7 | 5 | 1 | 0 | 0 |
| 4 h | 37.0 | 36.6 | 17.9 | 13.1 | | 1 | 0.5 | 1 | 0.3 | 0 |
| 23 h | 37.0 | 36.6 | 17.9 | 13.1 | | 0.5 | 0.006 | 1 | 0.4 | 0 |
| 3 days | 37.0 | 36.6 | 17.9 | 13.1 | 18.5 | 0.4 | 0.006 | 1 | 0.4 | 0.6 |
| 6 days[a] | 37.0 | 36.6 | 17.9 | 13.1 | 18.5 | 0.4 | 0.006 | 1 | 0.4 | 0.06 |

[a] After the mixture is warmed, which is obtained after 6 days at room temperature, to 60 °C for 20 h, its composition is similar to that formed by direct reaction of 15 with methyl propiolate in 1,2-dichloroethane after 50 h under reflux conditions (28:29 = 5:1).

Scheme V



ment $[OsH(CO)_2(P^iPr_3)_2]BF_4$ and methyl vinyl ketone. Similar products are obtained on treatment of 15 with methyl 2-butiolate and methyl propiolate. The $^1H$ NMR spectra of these compounds do not contain a signal in the hydride region, which suggests that an insertion of the unsaturated substrate into the Os–H bond of 15 has taken place.

In principal, two types of products can be obtained by insertion of methyl vinyl ketone into a M–H bond (Scheme V). The insertion following pathway a which is in agreement with the Markovnikov rule would lead to an oxaallyl complex whereas a five-membered metallacycle (see pathway b) would be the result of an anti-Markovnikov type of insertion. There are several reports in the literature that in certain reactions of iron,[22] ruthenium,[23] cobalt,[24] and rhodium compounds[25] (oxaallyl)metal intermediates are formed; more recently, stable (oxaallyl)-molybdenum and -tungsten complexes have been isolated.[26]

The displacement of the acetone ligand in 15 by methyl vinyl ketone and the subsequent insertion of the unsaturated ketone into the Os–H bond gives compound 26 (see Scheme VI). According to the IR and $^1H$ NMR spectra, there is no doubt that an anti-Markovnikov type of insertion has taken place. The IR spectrum shows together with the Os(C≡O) bands at 2010 and 1940 $cm^{-1}$ a C=O stretching frequency at 1620 $cm^{-1}$ corresponding to a coordinated ketonic C=O group. (For comparison, see refs 14 and 27a.) In the $^1H$ NMR spectrum, besides the signals of the phosphine protons three absorptions are observed at δ 3.49, 2.56, and 1.96 which are assigned to the $OsCH_2$, $OsCH_2CH_2$, and $OCH_3$ protons of the metallacycle.

The IR and $^1H$ NMR spectra of the solid obtained from 15 and methyl 2-butiolate indicate that in contrast to 26 the cationic complex 27 contains a four-membered ring with an exocyclic C=C double bond. The $^1H$ NMR spectrum contains resonances at δ 6.84, 4.0, and 2.10 which are assigned to the $=CHCH_3$, $OCH_3$, and $=CHCH_3$ hydrogen atoms. The geminal nature of the =CH and $=CCH_3$ protons is strongly supported by the H–H coupling constant of 7.0 Hz, which is a typical value for a $=CHCH_3$ arrangement.

Complex 27 is the result of the regioselective migration of the hydride ligand from the metal to the $C\equiv CCH_3$ carbon of the carboxylate. This selectivity, however, is not observed for the insertion of the C≡C triple bond of methyl propiolate into the Os–H bond of 15. Thus, the $^{31}P\{^1H\}$ NMR spectrum of the compound obtained from 15 and $HC\equiv CCO_2Me$ shows tow singlets at δ 18.3 and 17.7 with an intensity ratio of approximately 5:1, which are assigned to the isomers 28 and 29, respectively (see Scheme VI). Characteristic signals in the $^1H$ NMR spectra are those at δ 7.56, 6.47 ($=CH_2$), and 4.03 ($OCH_3$) for 28 and at δ 10.6 (OsCH=CH), 6.9 (OsCH), and 4.07 ($OCH_3$) for 29. Attempts to separate the two isomers by fractional crystallization or column chromatography remained unsuccessful.

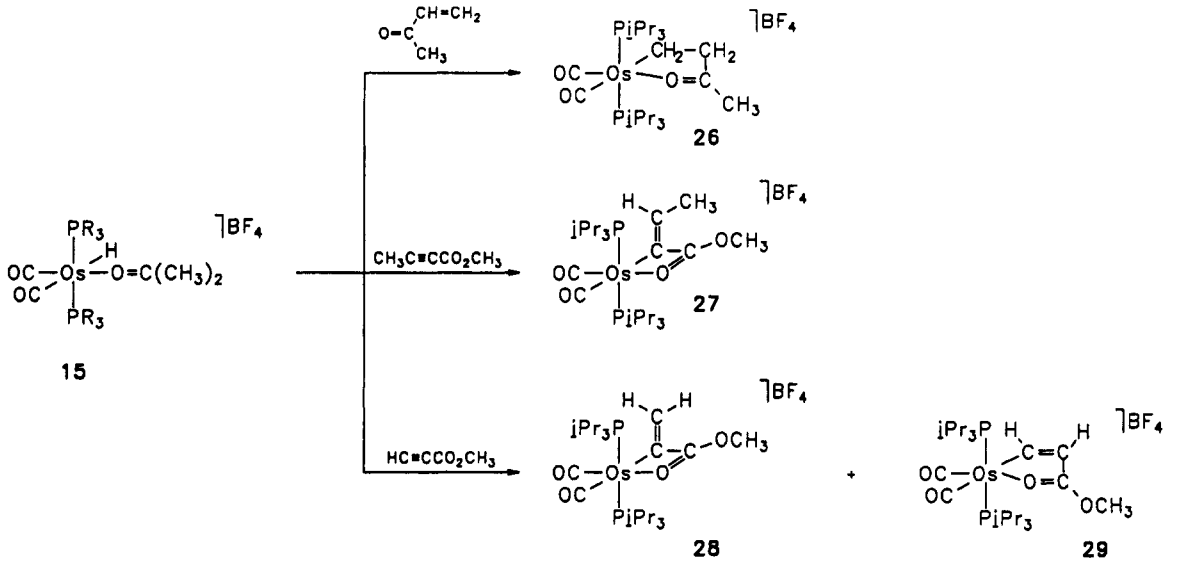
The formation of 28 and 29 merits further comment. The insertion of $HC\equiv CCO_2Me$ into the Os–H bond of 15 must involve the initial displacement of the acetone ligand by the alkyne to give an alkyne hydrido intermediate 30, followed by the migration of the hydride from the metal to the CH or $CCO_2Me$ carbons of the carboxylate. Path a and path b shown in Scheme VII correspond to the Markovnikov and anti-Markovnikov type of insertion, respectively. The Markovnikov insertion leads directly to 28 whereas the alternative route (anti-Markovnikov) first gives compound 31 that is subsequently isomerized to 29. Although the mechanism for the isomerization is not completely established, precedents for this process are known.[27]

In order to obtain more information about the mechanism of the insertion of $HC\equiv CCO_2Me$ into the Os–H bond, a spectroscopic study of the reaction was undertaken. Table IV lists the $^{31}P\{^1H\}$ NMR spectroscopic data of the reaction mixture at room temperature as a function of time. The signals at δ 37.0, 18.5, and 17.9 correspond to compounds 15, 29, and 28 as is shown by comparison with pure samples. The other signals at δ 36.6 and 13.1 are assigned to 30 and 31 on the basis of the considerations which are mentioned above and by comparison with the $^1H$ NMR spectra of the reaction mixture in $CDCl_3$. These spectra contain the resonances of $HC\equiv CCO_2Me$ and of 15, 28, and 29 together with signals at δ 3.78 (s; $CO_2CH_3$), –3.73 (t; $J$(PH) = 20.5 Hz; OsH), and 3.70 (s; $CO_2CH_3$) that can be assigned to 30 and 31, respectively. After warming of the reaction mixture obtained after 6 days to 60 °C for 20 h, its composition was similar to that formed by direct reaction of 15 with $HC\equiv CCO_2Me$ in 1,2-dichloroethane after 50 h under reflux conditions.

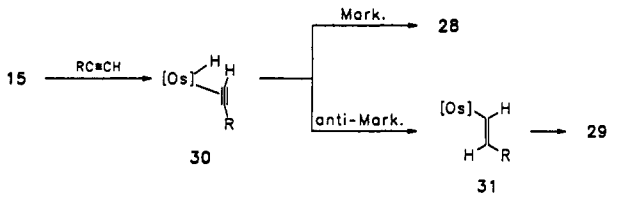
Regarding the intensity ratio shown in Table IV, it can be inferred that (1) the insertion of the alkyne into the Os–H bond is faster than the displacement of the acetone ligand by the substrate, (2) the Markovnikov type of insertion is more favored than the anti-Markovnikov type,

(22) Alper, H.; Keung, E. C. H. *J. Org. Chem.* **1972**, *37*, 2566.
(23) (a) Prince, R. H.; Raspin, K. A. *J. Chem. Soc. A* **1969**, 612. (b) Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887. (c) Dedieu, M.; Pascal, Y. L. *J. Mol. Catal.* **1980**, *9*, 71.
(24) Goetz, R. W.; Orchin, M. *J. Am. Chem. Soc.* **1963**, *85*, 2782.
(25) Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958.
(26) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.
(27) (a) Werner, H.; Meyer, U.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1989**, *122*, 2097. (b) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

**Scheme VI**



**Scheme VII**



(R = $CO_2CH_3$; [Os] = $[Os(CO)_2(PiPr_3)_2]BF_4$)

and (3) the isomerization reaction from **31** to **29** is facilitated by increasing the temperature.

## Conclusion

The present study was initiated by the unexpected finding that the conversion of cyclohexanone to cyclohexanol by hydrogen transfer from ROH with **2a** or **2b** as catalyst does not proceed if 2-propanol is replaced by methanol, ethanol, or 2-methoxyethanol as the hydrogen source. (Some details of the catalytic experiments are described in the Experimental Section.) Whereas the reaction of **2a,b** with methanol under reflux affords the dihydrides **4a,b**, under the same conditions the starting materials react with ethanol and 2-methoxyethanol to give the novel alkylhydridoosmium(II) complexes **5a,b** and **6a,b** in good yields. In accordance with previous work,[9] we assume that the formation of **5a,b** and **6a,b** occurs by controlled fragmentation of the primary alcohol $RCH_2OH$ (R = $CH_3$, $MeOCH_2$) into an alkyl group R, CO, H, and dihydrogen, which is liberated. We note that there are reports in the literature[6,19,28,29] that hydrido as well as carbonyl hydrido complexes can be obtained on treatment of halogenometal compounds with primary or secondary alcohols, but as far as we know, there was only one example recently described which established a fragmentation process similar to that leading to **5a,b** and **6a,b**, respectively.[9]

The conclusive result of the investigations concerned to the reactivity of the hydrido methylosmium complexes **5a,b** is that proton attack preferentially leads to cleavage of the Os–$CH_3$ and not of the Os–H bond. This finding is fully in agreement with previous assumptions[30] that in compounds of the **5d** transition metals M–H bonds are in general more stable (thermodynamically) than their M–C counterparts. The stronger M–H bond causes a higher activation energy for the irreversible $H_2$ elimination compared with the $CH_4$ elimination, and thus the observed cleavage of the M–C bond in **5a,b** seems to be kinetic in nature.

The studies aimed to elucidate the reactivity of complex **15** illustrate that the acetone ligand is only weakly bound and can be easily displaced by various Lewis bases without changing the stereochemistry of the $[Os(CO)_2(P^iPr_3)_2]$ unit. Unsaturated substrates such as methyl vinyl ketone or $CO_2Me$-substituted alkynes do not only coordinate but also insert into the Os–H bond to give four- and five-membered metallacycles. Subsequent reactions of these compounds with the emphasis of using them for the formation of new C–C bonds are presently being studied in our laboratories.

## 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. The starting materials $[OsHCl(CO)(P^iPr_3)_2]$ (**1a**),[9] $[OsH(\eta^2\text{-}BH_4)(CO)(PR_3)_2]$ (**2a,b**),[6] $[OsH_2Cl_2(PR_3)_2]$ (**7a,b**),[8] and $[M(\mu\text{-}OMe)(diolefin)]_2$ (**20–22**)[20] were prepared by published methods.

**Physical Measurements.** IR spectra were recorded on Perkin-Elmer 783 and 1420 infrared spectrophotometers, and NMR spectra on JEOL FX 90 Q, Bruker AC 200, and Varian 200 XL instruments. The spectroscopic study for the hydrogen-transfer reactions was performed by recording the $^{31}P\{^1H\}$ NMR spectra of the solutions. The spectra showed, depending on the alcohol used, signals at $\delta$ 41.7 for methanol, $\delta$ 24.2 for ethanol, $\delta$ 25.4 for 2-methoxyethanol, and $\delta$ 49.0 for 2-propanol, assigned to the complexes **4a**, **5a**, **6a**, and **3a**, respectively, by comparison with pure samples. The spectroscopic study of the reaction of complex **15** with methyl propiolate was followed at room temperature by measuring the $^{31}P\{^1H\}$ NMR spectrum as a function of time. The reaction mixture was prepared in an NMR tube reproducing the stoichiometric conditions (see preparation of **28** and **29**). Samples were capped under argon and then immersed into 1-cm-diameter tubes containing $CDCl_3$ (85% $H_3PO_4$). The hydrogen-transfer reactions were followed by measuring the

(28) Early examples: (a) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 1262. (b) Vaska, L. *Ibid.* **1964**, *86*, 1943. (c) Chatt, J.; Shaw, B. L.; Field, A. E. *J. Chem. Soc.* **1964**, 3466.

(29) Gill, D. F.; Shaw, B. L. *Inorg. Chim. Acta* **1979**, *32*, 19 and references cited therein.

(30) (a) Calado, J. C. G.; Dias, A. R.; Salem, M. S.; Marthinho Simoes, J. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1174. (b) Yoneda, G.; Blake, D. M. *Inorg. Chem.* **1981**, *20*, 67 and references therein.

conversion to cyclohexanol as a function of time with an FFAP on Chromosorb GHP 80/100 mesh column at 100 °C on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector.

**Preparation of *cis,cis,trans*-$[OsH_2(CO)_2(PR_3)_2]$ (4a,b). Method a.** A solution of **2a,b** (150 mg, 0.27 mmol) in 20 mL of methanol was heated for 6 h under reflux. After being cooled to room temperature, the solution was concentrated to ca. 4–5 mL in vacuo and stored at −78 °C. A colorless precipitate was formed, which was filtered off, washed twice with 5 mL of methanol, and dried in vacuo. Yield: 114 mg (74%) for **4a** and 107 mg (70%) for **4b**.

**Method b.** A solution of **7a,b** (130 mg, 0.22 mmol) in 10 mL of benzene was first treated with $NaBH_4$ (90 mg, 2.37 mmol) and then dropwise with 1 mL of methanol. After being stirred for 15 min at room temperature, the reaction mixture was filtered. The filtrate was concentrated to ca. 1 mL in vacuo, and then 20 mL of methanol was added. The solution was heated for 6 h under reflux and then worked up as described for method a. Yield: 76 mg (61%) for **4a** and 72 mg (57%) for **4b**. Complex **4a** was identified by comparison of the IR and $^1H$ NMR spectra with those of an authentic sample.[6]

**4b.** Anal. Calcd for $C_{20}H_{44}O_2OsP_2$: C, 42.24; H, 7.80. Found: C, 41.96; H, 7.58. IR ($C_6H_6$): $\nu$(OsH) and $\nu$(CO) 2000, 1980, 1943, 1855 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 1.61 (vt, $N$ = 6.1 Hz, $PCH_3$), 1.23 ( vt, $N$ = 12.9 Hz, $PCCH_3$), −8.83 (t, $J$(PH)) = 22.0 Hz, $OsH_2$). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 34.86 (s, t in off-resonance).

**Preparation of $[OsH(CH_3)(CO)_2(PR_3)_2]$ (5a,b). Method a.** A solution of **2a,b** (660 mg, 1.13 mmol) in 30 mL of ethanol was heated for 20 h under reflux. After being cooled to room temperature, the solution was brought to dryness in vacuo. The residue was treated with 5 mL of methanol. A colorless solid was formed, which was filtered off, repeatedly washed with methanol, and dried in vacuo. Yield: 487 mg (74%) for **5a** and 461 mg (70%) for **5b**.

**Method b.** A solution of **7a,b** (140 mg, 0.24 mmol) in 10 mL of benzene was first treated with $NaBH_4$ (100 mg, 2.63 mmol) and then dropwise with 1 mL of methanol. After being stirred for 10 min at room temperature, the solution was filtered and the filtrate was brought to dryness in vacuo. The oily residue, which owing to the $^{31}P$ NMR spectrum consists of $[OsH_6(PR_3)_2]$ (**8a,b**), was treated with 20 mL of ethanol and heated for 20 h under reflux. After being cooled to room temperature, the solution was worked up as described for method a. Yield: 81 mg (58%) for **5a** and 73 mg (52%) for **5b**.

**5a.** Anal. Calcd for $C_{21}H_{46}O_2OsP_2$: C, 43.28; H, 7.96. Found: 43.20; H, 8.14. IR (Nujol): $\nu$(OsH) 2000, $\nu$(CO) 1940, 1870 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 2.23 (m, $PCHCH_3$), 1.18 and 1.14 (both dvt, $N$ = 13.3, $J$(HH) = 6.4 Hz, $PCHCH_3$), −0.24 (dt, $J$(HH) = 2.8, $J$(PH) = 6.6 Hz, $OsCH_3$), −7.86 (tq, $J$(PH) = 22.0, $J$(HH) = 2.8 Hz, OsH). $^{13}C$ NMR (22.5 MHz, $C_6D_6$): $\delta$ 190.98 (t, $J$(PC) = 6.2 Hz, OsCO), 183.05 (t, $J$(PC) = 8.0 Hz, OsCO), 25.57 (vt, $N$ = 25.0 Hz, $PCHCH_3$), 19.15 and 19.02 (both s, $PCHCH_3$), −33.86 (t, $J$(PC) = 9.2 Hz, $OsCH_3$). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 24.2 (s, d in off-resonance).

**5b.** Anal. Calcd for $C_{21}H_{46}O_2OsP_2$: C, 43.28; H, 7.96. Found: C, 43.31; H, 8.19. IR (Nujol): $\nu$(OsH) 1995, $\nu$(CO) 1935, 1870 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 1.31 (vt, $N$ = 6.2 Hz, $PCH_3$), 1.24 and 1.22 (both vt, $N$ = 12.9 Hz, $PCCH_3$), −0.08 (dt, $J$(HH) = 2.9, $J$(PH) = 6.6 Hz, $OsCH_3$), −7.62 (tq, $J$(PH) = 22.2, $J$(HH) = 2.9 Hz, OsH). $^{13}C$ NMR (22.5 MHz, $C_6D_6$): $\delta$ 191.12 (t, $J$(PC) = 6.0 Hz, OsCO), 186.90 (t, $J$(PC) = 8.5 Hz, OsCO), 36.62 and 36.20 (both vt, $N$ = 24.0 Hz, $PCCH_3$), 30.21 and 29.26 (both s, $PCCH_3$), 5.07 (vt, $N$ = 26.8 Hz, $PCH_3$), −28.05 (t, $J$(PC) = 8.5 Hz, $OsCH_3$). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 20.9 (s, d in off-resonance).

**Preparation of $[OsH(CH_2OCH_3)(CO)_2(PR_3)_2]$ (6a,b). Method a.** Synthesis was analogously as described for **5a,b**, starting from **2a,b** (150 mg, 0.27 mmol) and 20 mL of 2-methoxyethanol. Colorless crystals formed. Yield: 116 mg (70%) for **6a** and 111 mg (67%) for **6b**.

**Method b.** Synthesis was analogously as described for **5a,b**, starting from **7a,b** (150 mg, 0.29 mmol) and 20 mL of 2-methoxyethanol. Yield: 92 mg (52%) for **6a** and 89 mg (50%) for **6b**.

**6a.** Anal. Calcd for $C_{22}H_{48}O_3OsP_2$: C, 43.12; H, 7.90. Found: C, 42.92; H, 7.77. IR ($C_6H_6$): $\nu$(OsH) 1960, $\nu$(CO) 1890, 1805 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 3.79 (dt, $J$(HH) = 1.7, $J$(PH) = 8.3 Hz, $OsCH_2$), 3.25 (s, $OCH_3$), 2.33 (m, $PCHCH_3$), 1.24 and 1.22 (both dvt, $N$ = 13.5, $J$(HH) = 6.5 Hz, $PCHCH_3$), −7.86 (tt, $J$(PH) = 22.2, $J$(HH) = 1.7 Hz, OsH). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 24.3 (s, d in off-resonance).

**6b.** Anal. Calcd for $C_{22}H_{48}O_3OsP_2$: C, 43.12; H, 7.90. Found: C, 42.62; H, 8.42. IR ($C_6H_6$): $\nu$(OsH) 1950, $\nu$(CO) 1880, 1800 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\nu$ 3.89 (dt, $J$(HH) = 1.5, $J$(PH) = 9.3 Hz, $OsCH_2$), 3.31 (s, $OCH_3$), 1.45 (vt, $N$ = 6.1 Hz, $PCH_3$), 1.26 (vt, $N$ = 12.7 Hz, $PCCH_3$, diastereotopic shift not resolved), −7.61 (tt, $J$(PH) = 21.5, $J$(HH) = 1.5 Hz, OsH). $^{13}C$ NMR (22.5 MHz, $C_6D_6$): $\nu$ 189.83 (t, $J$(PC) = 6.0 Hz, OsCO), 187.55 (t, $J$(PC) = 8.5 Hz, OsCO), 64.58 (s, $OCH_3$), 54.83 (t, $J$(PC) = 8.5 Hz, $OsCH_2$), 36.89 (vt, $N$ = 23.9 Hz, $PCCH_3$), 36.32 (vt, $N$ = 25.6 Hz, $PCCH_3$), 30.25 and 29.30 (both vt, $N$ = 4.0 Hz, $PCCH_3$), 5.22 (vt, $N$ = 25.6 Hz, $PCH_3$). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 22.3 (s, d in off-resonance).

**Preparation of $[OsI_2(CO)_2(P^iPr_3)_2]$ (9a).** A solution of **5a** (110 mg, 0.19 mmol) in 10 mL of dichloromethane was treated at room temperature with a slight excess of iodine (56 mg, 0.22 mmol). After a short time the colorless solution turned yellow and gas evolution was observed. The solution was concentrated to ca. 0.5 mL in vacuo, and 5 mL of methanol was added. A pale yellow precipitate was formed, which was filtered off, washed with methanol, and dried in vacuo. Yield: 148 mg (95%). Anal. Calcd for $C_{20}H_{42}I_2O_2OsP_2$: C, 29.28; H, 5.16. Found: C, 29.59; H, 5.21. IR (Nujol): $\nu$(CO) 2020, 1955 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 2.19 (m, $PCHCH_3$), 1.30 (dvt, $N$ = 14.0, $J$(HH) = 7.0 Hz, $PCHCH_3$). $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ −11.22 (s).

**Preparation of $[OsI_2(CO)_2(PMe^tBu_2)_2]$ (9b).** This compound was synthesized analogously as described for **9a**, starting from **5b** (100 mg, 0.17 mmol) and iodine (51 mg, 0.20 mmol). Colorless crystals formed. Yield: 120 mg (86%). Anal. Calcd for $C_{20}H_{42}I_2O_2OsP_2$: C, 29.28; H, 5.16. Found: C, 29.61; H, 4.86. IR (KBr): $\nu$(CO) 1995, 1920 $cm^{-1}$. $^1H$ NMR (90 MHz, $CDCl_3$): $\delta$ 2.19 (vt, $N$ = 6.0 Hz, $PCH_3$), 1.53 (vt, $N$ = 13.3 Hz, $PCCH_3$). $^{31}P$ NMR (36.2 MHz, $CDCl_3$): $\delta$ −10.10 (s).

**Preparation of $[OsH(C{\equiv}CPh)(CO)_2(P^iPr_3)_2]$ (10).** A solution of **5a** (150 mg, 0.26 mmol) in 10 mL of toluene was treated with phenylacetylene (142.8 $\mu$L, 1.3 mmol) and stirred for 3 d at 80 °C. After being cooled to room temperature, the solution was evaporated to dryness in vacuo. The residue was treated with 5 mL of methanol and then stored at −78 °C. A colorless precipitate was formed, which was filtered off, washed with cold methanol, and dried in vacuo. Yield: 123 mg (71%). Anal. Calcd for $C_{28}H_{48}O_2OsP_2$: C, 50.25; H, 7.23. Found: C, 49.52; H, 7.62. IR ($C_6H_6$): $\nu$(C≡C) 2095, $\nu$(OsH) 2005, $\nu$(CO) 1955, 1895 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 7.14 (m, $C_6H_5$), 2.48 (m, $PCHCH_3$), 1.23 (dvt, $N$ = 13.4, $J$(HH) = 6.6 Hz, $PCHCH_3$, diastereotopic shift not resolved), −7.64 (t, $J$(PH) = 20.9 Hz, OsH). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 25.41 (s, d in off-resonance).

**Preparation of $[OsHCl(CO)_2(P^iPr_3)_2]$ (11).** A slow stream of HCl was passed for 1 min through a solution of **5a** (100 mg, 0.17 mmol) in 10 mL of benzene. After the solution was stirred for 10 min at room temperature, the solvent was removed in vacuo, and then the residue was treated with 5 mL of methanol. A colorless precipitate was formed, which was filtered off, washed with methanol, and dried in vacuo. Yield: 91 mg (88%). Complex **11** was identified by comparison of the IR and $^1H$ NMR spectra with those of an authentic sample.[19]

**Preparation of $[OsH(O_2CCH_3)(CO)_2(P^iPr_3)_2]$ (12).** A solution of **5a** (100 mg, 0.17 mmol) in 10 mL of benzene was treated with $CH_3CO_2H$ (15 $\mu$L, 0.26 mmol) and heated for 12 h under reflux. After being cooled to room temperature, the solution was worked up as described for **11**. Colorless crystals formed. Yield: 70 mg (65%). Anal. Calcd for $C_{22}H_{46}O_4OsP_2$: C, 42.16; H, 7.40. Found: C, 41.84; H, 7.61. IR ($C_6H_6$): $\nu$(OsH) 2025, $\nu$(CO) 1950, 1905 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 2.22 (m, $PCHCH_3$), 2.18 (s, $O_2CCH_3$), 1.20 and 1.17 (both dvt, $N$ = 13.9, $J$(HH) = 6.8 Hz, $PCHCH_3$), −4.35 (t, $J$(PH) = 21.2 Hz, OsH). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 35.75 (s, d in off-resonance).

**Preparation of $[OsH(O_2CCF_3)(CO)_2(P^iPr_3)_2]$ (13a).** A solution of **5a** (90 mg, 0.15 mmol) in 10 mL of benzene was treated with $CF_3CO_2H$ (13 $\mu$L, 0.17 mmol) at room temperature. After the gas evolution was finished, the solution was stirred for 15 min and then worked up as described for **11**. Colorless crystals formed. Yield: 93 mg (91%). Anal. Calcd for $C_{22}H_{43}F_3O_4OsP_2$: C, 38.82;

H, 6.37. Found: C, 38.79; H, 6.67. IR ($C_6H_6$): $\nu$(OsH) 2015, $\nu$(CO) 1970, 1910 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 2.09 (m, PC*H*$CH_3$), 1.13 (dvt, $N$ = 13.9, $J$(HH) = 7.1 Hz, PCHC*H*$_3$, diastereotopic shift not resolved), −3.90 (t, $J$(PH) = 20.9 Hz, Os*H*). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 36.1 (s, d in off-resonance).

**Preparation of [OsH($O_2CCF_3$)(CO)$_2$(PMe$^t$Bu$_2$)$_2$] (13b).** This compound was prepared analogously as described for **13a**, starting from **5b** (90 mg, 0.15 mmol) and $CF_3CO_2H$ (13 $\mu$L, 0.17 mmol). Colorless crystals formed. Yield: 84 mg (82%). Anal. Calcd for $C_{22}H_{43}F_3O_4OsP_2$: C, 38.82; H, 6.37. Found: C, 38.40; H, 6.30. IR ($C_6H_6$): $\nu$(OsH) 2030, $\nu$(CO) 1980, 1910 $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 1.17 and 1.10 (both vt, $N$ = 12.9 Hz, PCC*H*$_3$), −4.03 (t, $J$(PH) = 20.3 Hz, Os*H*), signal of PC*H*$_3$ protons partially masked by PCC*H*$_3$ resonance. $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 32.52 (s, d in off-resonance).

**Preparation of [Os($O_2CCF_3$)$_2$(CO)$_2$(P$^i$Pr$_3$)$_2$] (14).** A solution of **5a** (135 mg, 0.23 mmol) in 10 mL of benzene was treated with excess $CF_3CO_2H$ (0.2 mL, 2.61 mmol) and heated for 3 d under reflux. After being cooled to room temperature, the solution was worked up as described for **11**. A colorless solid was isolated. Yield: 106 mg (58%). Anal. Calcd for $C_{24}H_{42}F_6O_8OsP_2$: C, 36.36; H, 5.34. Found: C, 36.26; H, 5.53. IR (KBr): $\nu$(CO) 1975, 1925, $\nu$($O_2CCF_3$) 1690 (br) $cm^{-1}$. $^1H$ NMR (90 MHz, $C_6D_6$): $\delta$ 2.18 (m, PC*H*$CH_3$), 1.07 (dvt, $N$ = 14.2, $J$(HH) = 7.1 Hz, PCHC*H*$_3$). $^{31}P$ NMR (36.2 MHz, $C_6D_6$): $\delta$ 19.9 (s).

**Preparation of [OsH(Me$_2$CO)(CO)$_2$(P$^i$Pr$_3$)$_2$]BF$_4$ (15).** A solution of **5a** (400 mg, 0.69 mmol) in 15 mL of ether was first treated with acetone (56 $\mu$L, 0.96 mmol) and then with an ether solution of $HBF_4$ (132 $\mu$L, 0.96 mmol). After the mixture was stirred for 5 min at room temperature, a white solid precipitated, which was filtered off, repeatedly washed with ether, and dried in vacuo. Yield: 442 mg (90%). Anal. Calcd for $C_{23}H_{49}BF_4O_3OsP_2$: C, 38.77; H, 6.93. Found: C, 38.76; H, 7.53. IR (Nujol): $\nu$(OsH) 2060, $\nu$(CO) 1995, 1935, $\nu$(O=CMe$_2$) 1660 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 2.46 (m, PC*H*$CH_3$), 2.18 (s, ($CH_3$)$_2$CO), 1.37 (dvt, $N$ = 13.4, $J$(HH) = 7.0 Hz, PCHC*H*$_3$, diastereotopic shift not resolved), −1.30 (t, $J$(PH) = 20.0 Hz, Os*H*). $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 36.74 (s, d in off-resonance).

**Preparation of [OsH($H_2O$)(CO)$_2$(P$^i$Pr$_3$)$_2$]BF$_4$ (16a).** A solution of **5a** (400 mg, 0.69 mmol) in 15 mL of ether was first treated with ca. 10 drops of water and then with an ether solution of $HBF_4$ (132 $\mu$L, 0.96 mmol). After the mixture was stirred for 15 min at room temperature, a white solid precipitated, which was filtered off, repeatedly washed with ether, and dried in vacuo. Yield: 408 mg (88%). Anal. Calcd for $C_{20}H_{45}BF_4O_3OsP_2$: C, 35.72; H, 6.74. Found: C, 36.05; H, 6.93. IR (Nujol): $\nu$(OH) 3391 (br), $\nu$(OsH) 2061, $\nu$(CO) 1990, 1937 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 4.20 (br, $OH_2$), 2.42 (m, PC*H*$CH_3$), 1.32 (dvt, $N$ = 14.0, $J$(HH) = 7.0 Hz, PCHC*H*$_3$, diastereotopic shift not resolved), −3.20 (t, $J$(PH) = 20.0 Hz, Os*H*). $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 36.4 (s, d in off-resonance).

**Preparation of [OsH($H_2O$)(CO)$_2$(PMe$^t$Bu$_2$)$_2$]BF$_4$ (16b).** The compound was prepared analogously as described for **16a**, starting from **5b** (400 mg, 0.69 mmol). White crystals formed. Yield: 352 mg (76%). Anal. Calcd for $C_{20}H_{45}BF_4O_3OsP_2$: C, 35.72; H, 6.74. Found: C, 35.46; H, 6.87. IR ($CH_2Cl_2$): $\nu$(OH) 3380 (br), $\nu$(OsH) 2060, $\nu$(CO) 2000, 1935 $cm^{-1}$. $^1H$ NMR (90 MHz, $CDCl_3$): $\delta$ 4.45 (br, $OH_2$), 1.46 (vt, $N$ = 6.1 Hz, PC*H*$_3$), 1.35 (vt, $N$ = 13.7 Hz, PCC*H*$_3$), −3.17 (t, $J$(PH) = 19.8 Hz, Os*H*). $^{31}P$ NMR (36.2 MHz, $CDCl_3$): $\delta$ 34.62 (s, d in off-resonance).

**Preparation of [OsH($CH_3CN$)(CO)$_2$(P$^i$Pr$_3$)$_2$]BF$_4$ (17a).** A solution of **15** (121 mg, 0.17 mmol) in 10 mL of dichloroethane was treated with a slight excess of acetonitrile (10 $\mu$L, 0.22 mmol) and stirred for 15 min at room temperature. The solution was concentrated to ca. 0.5 mL in vacuo, and then 10 mL of ether was added. A white solid precipitated, which was filtered off, repeatedly washed with ether, and dried in vacuo. Yield: 106 mg (90%). Anal. Calcd for $C_{22}H_{46}BF_4NO_2OsP_2$: C, 37.99; H, 6.67, N, 2.01. Found: C, 38.42; H, 7.36; N, 1.86. IR (Nujol): $\nu$(C≡N) 2320, $\nu$(OsH) 2060, $\nu$(CO) 1995, 1935 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 2.75 (s, NCC*H*$_3$), 2.60 (m, PC*H*$CH_3$), 1.30 (dvt, $N$ = 13.0, $J$(HH) = 7.2 Hz, PCHC*H*$_3$, diastereotopic shift not resolved), −5.88 (t, $J$(PH) = 19.0 Hz, Os*H*). $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 29.65 (s, d in off-resonance).

**Preparation of [OsH($CH_3CN$)(CO)$_2$(PMe$^t$Bu$_2$)$_2$]BF$_4$ (17b).** This compound was prepared analogously as described for **17a**, starting from **16b** (110 mg, 0.16 mmol) and acetonitrile (10 $\mu$L, 0.22 mmol). A white solid formed. Yield: 97 mg (87%). Anal. Calcd for $C_{22}H_{46}BF_4NO_2OsP_2$: C, 37.99; H, 6.67; N, 2.01. Found: C, 37.51; H, 6.87; N, 1.92. IR ($CH_2Cl_2$): $\nu$(C≡N) 2260, $\nu$(OsH) 2065, $\nu$(CO) 2000, 1945 $cm^{-1}$. $^1H$ NMR (90 MHz, $CDCl_3$): $\delta$ 2.64 (s, NCC*H*$_3$), 1.66 (vt, $N$ = 6.4 Hz, PC*H*$_3$), 1.35 (vt, $N$ = 14.2 Hz, PCC*H*$_3$), −5.69 (t, $J$(PH) = 17.8 Hz, Os*H*). $^{31}P$ NMR (36.2 MHz, $CDCl_3$): $\delta$ 25.36 (s, d in off-resonance).

**Preparation of [OsH(CO)$_2$(P(OMe)$_3$)(P$^i$Pr$_3$)$_2$]BF$_4$ (18).** This compound was prepared analogously as described for **17a**, starting from **15** (130 mg, 0.18 mmol) and trimethyl phosphite (27.3 $\mu$L, 0.22 mmol). A white solid formed. Yield: 119 mg (85%). Anal. Calcd for $C_{23}H_{52}BF_4O_5OsP_2$: C, 35.48; H, 6.73. Found: C, 35.72; H, 7.00. IR (Nujol): $\nu$(OsH) 2030, $\nu$(CO) 1990, 1925 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 3.80 (d, $J$(PH) = 11.0 Hz, POC*H*$_3$), 2.40 (m, PC*H*$CH_3$), 1.30 (dvt, $N$ = 12.6, $J$(HH) = 7.0 Hz, PCHC*H*$_3$), −8.50 [dt, $J$(PH) = 19.0 Hz (P of P$^i$Pr$_3$), $J$(PH) = 28.0 Hz (P of P(OMe)$_3$), Os*H*]. $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 19.5 (d, $J$(PP) = 31.0 Hz, *P*iPr$_3$), 86.6 (t, $J$(PP) = 31.0 Hz, *P*OCH$_3$).

**Preparation of [OsH(CO)$_2$(Hpz)(P$^i$Pr$_3$)$_2$]BF$_4$ (19).** This compound was prepared analogously as described for **17a**, starting from **15** (130 mg, 0.18 mmol) and pyrazole (Hpz; 15 mg, 0.22 mmol). A pale yellow solid formed. Yield: 111 mg (85%). Anal. Calcd for $C_{23}H_{47}BF_4N_2O_2OsP_2$: C, 38.77; H, 6.82; N, 3.87. Found: C, 38.12; H, 7.13; N, 3.93. IR (Nujol): $\nu$(NH) 3379 (br), $\nu$(OsH) 2050, $\nu$(CO) 1990, 1935 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 11.26 (br, N*H*), 7.99, 7.56 and 6.21 (all m, H$^3$, H$^5$, and H$^4$ of Hpz), 1.90 (m, PC*H*$CH_3$), 1.30 (dvt, $N$ = 14.5, $J$(HH) = 7.2 Hz, PCHC*H*$_3$), −4.80 (t, $J$(PH) = 20.0 Hz, Os*H*). $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 28.23 (s).

**Preparation of [(CO)$_2$(P$^i$Pr$_3$)$_2$Os(μ-H)(μ-pz)Rh(C$_8$H$_{12}$)]BF$_4$ (23).** A solution of **19** (80 mg, 0.11 mmol) in 10 mL of acetone was treated with **20** (29 mg, 0.06 mmol) and stirred for 15 h under reflux. After being cooled to room temperature, the solution was concentrated to ca. 1 mL in vacuo, and 10 mL of ether was added. A yellow solid precipitated, which was filtered off, washed with ether, and dried in vacuo. Yield: 92 mg (90%). Anal. Calcd for $C_{31}H_{58}BF_4N_2O_2OsP_2Rh$: C, 39.92; H, 6.27; N, 3.00. Found: C, 39.94; H, 6.15; N, 2.91. IR (Nujol): $\nu$(CO) 2010, 1960 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.2, 6.8 and 6.1 (all m, H$^3$, H$^5$, and H$^4$ of pz), 4.60 and 4.24 (both m, each 2 H, –HC=CH– of $C_8H_{12}$), 2.7 and 2.1 (both m, each 4 H, $-CH_2-$ of $C_8H_{12}$), 2.5 (m, PC*H*$CH_3$), 1.5 and 1.2 (both dvt, $N$ = 14.0, $J$(HH) = 7.0 Hz, PCHC*H*$_3$), −13.7 (dt, $J$(RhH) = 18.3, J(PH) = 11.0 Hz, Os*H*Rh). $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 18.22 (s).

**Preparation of [(CO)$_2$(P$^i$Pr$_3$)$_2$Os(μ-H)(μ-pz)Ir(C$_8$H$_{12}$)]BF$_4$ (24).** This compound was prepared analogously as described for **23**, starting from **19** (80 mg, 0.11 mmol) and **21** (39.7 mg, 0.06 mmol). A yellow solid was isolated, which owing to the IR and $^1H$ NMR spectra turned out to be a mixture of **24**, **19**, and **21** in the ratio 2:1:1. Attempts to separate the three compounds failed. Spectroscopic data for **24** are as follows. IR (Nujol): $\nu$(CO) 2029, 1970 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.2, 6.8, and 6.1 (all m, H$^3$, H$^5$ and H$^4$ of pz), 4.60 and 4.24 (both m, each 2H, –HC=CH– of $C_8H_{12}$), 2.7 and 2.1 (both m, each 4 H, $-CH_2-$ of $C_8H_{12}$), 2.5 (m, PC*H*$CH_3$), 1.5 and 1.2 (both dvt, $N$ = 14.0, $J$(HH) = 7.0 Hz, PCHC*H*$_3$), −11.1 (t, $J$(PH) = 9.1 Hz, Os*H*Ir). $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 18.32 (s).

**Preparation of [(CO)$_2$(P$^i$Pr$_3$)$_2$Os(μ-H)(μ-pz)Rh(TFB)]BF$_4$ (25).** This compound was prepared analogously as described for **23**, starting from **19** (80 mg, 0.11 mmol) and **22** (43.2 mg, 0.06 mmol). A yellow solid formed. Yield: 104 mg (90%). Anal. Calcd for $C_{35}H_{52}BF_8N_2O_2OsP_2Rh$: C, 40.01; H, 4.98; N, 2.66. Found: C, 39.88; H, 5.04; N, 2.40. IR (Nujol): $\nu$(CO) 2030, 1970 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.3, 6.8 and 6.2 (all m, H$^3$, H$^5$ and H$^4$ of pz), 5.54 (m, 2 H, CH of TFB), 4.46 and 3.97 (both m, each 2 H, =CH of TFB), 2.65 (m, PC*H*$CH_3$), 1.5 and 1.2 (both dvt, $N$ = 14.7, $J$(HH) = 7.0 Hz, PCHC*H*$_3$), −14.2 (dt, $J$(RhH) = 21.7, $J$(PH) = 10.7 Hz, Os*H*Rh). $^{31}P$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 20.96 (s).

**Preparation of {Os[$CH_2CH_2C(=O)CH_3$](CO)$_2$(P$^i$Pr$_3$)$_2$}BF$_4$ (26).** A solution of **15** (78 mg, 0.11 mmol) in 10 mL of 1,2-dichloroethane was treated with 3-buten-2-one (methyl vinyl ketone; 9.1 $\mu$L, 0.13 mmol) and stirred for 12 h under reflux. After being cooled to room temperature, the solution was filtered and the

filtrate was concentrated to ca. 1 mL in vacuo. Addition of 10 mL of ether led to the formation of a white precipitate, which was filtered off, repeatedly washed with ether, and dried in vacuo. Yield: 64 mg (80%). Anal. Calcd for $C_{24}H_{49}BF_4O_3OsP_2$: C, 39.79; H, 6.82. Found: C, 39.91; H, 7.50. IR (Nujol): $\nu$(CO) 2010, 1940, $\nu$(C=O) 1620 cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 3.49 (t, $J$(HH) = 6.9 Hz, $CH_2C(O)$), 2.56 (s, $C(O)CH_3$), 2.50 (m, $PCHCH_3$), 1.96 (tt, $J$(PH) = 10.4, $J$(HH) = 6.9 Hz, $OsCH_2$), 1.35 and 1.31 (both dvt, $N$ = 14.0, $J$(HH) = 7.2 Hz, $PCHCH_3$). $^{31}$P NMR (80.9 MHz, $CDCl_3$): $\delta$ 11.62 (s).

**Preparation of {Os[C(C(=O)OCH$_3$)=CHCH$_3$](CO)$_2$(P$^i$Pr$_3$)$_2$}BF$_4$ (27).** This compound was prepared analogously as described for **26**, starting from **15** (114 mg, 0.16 mmol) and methyl 2-butiolate (22.1 $\mu$L, 0.21 mmol). After the reaction mixture was heated for 40 h under reflux, it was worked up as described for **26**. A white solid formed. Yield: 100 mg (83%). Anal. Calcd for $C_{25}H_{49}BF_4O_4OsP_2$: C, 39.89; H, 6.56. Found: C, 40.13; H, 7.35. IR (Nujol): $\nu$(CO) 2100, 1950, $\nu$(C=O) 1530 cm$^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 6.84 (tq, $J$(PH) = 2.0, $J$(HH) = 7.0 Hz, $=CHCH_3$), 4.0 (s, $OCH_3$), 2.55 (m, $PCHCH_3$), 2.10 (dt, $J$(HH) = 7.0, $J$(PH) = 2.0 Hz, $=CHCH_3$), 1.34 and 1.25 (both dvt, $N$ = 14.3, $J$(HH) = 7.0 Hz, $PCHCH_3$). $^{31}$P NMR (80.9 MHz, $CDCl_3$): $\delta$ 16.03 (s).

**Preparation of the Isomeric Mixture of {Os[C(C(=O)OCH$_3$)=CH$_2$](CO)$_2$(P$^i$Pr$_3$)$_2$}BF$_4$ (28) and {Os[CH=CHC(=O)OCH$_3$](CO)$_2$(P$^i$Pr$_3$)$_2$}BF$_4$ (29).** These two compounds were prepared analogously as described for **26**, starting from **15** (128 mg, 0.18 mmol) and methyl propiolate (21.3 $\mu$L, 0.24 mmol). After the reaction mixture was heated for 50 h under reflux, it was worked up as described for **26**. Attempts to separate the two isomers, formed in the ratio **28**:**29** = 5:1, by fractional crystallization or chromatographic techniques failed. A white solid formed. Yield: 105 mg (78%). Anal. Calcd for $C_{24}H_{47}BF_4O_4OsP_2$: C, 39.02; H, 7.26. Found: C, 38.78; H, 6.81. IR (Nujol): $\nu$(CO) 2025, 2010, 1970, 1950 cm$^{-1}$. Data for **28** are as follows. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 7.56 (dt, $J$(PH) = 2.5, $J$(HH) = 0.8 Hz, 1 H, of $=CH_2$), 6.47 (dt, $J$(PH) = 2.5, $J$(HH) = 0.8 Hz, 1 H, of $=CH_2$), 4.03 (s, $OCH_3$), 2.6 (m, $PCHCH_3$), 1.30 (dvt, $N$ = 15.2, $J$(HH) = 7.3 Hz, $PCHCH_3$). $^{31}$P NMR (80.9 MHz, $CDCl_3$): $\delta$ 17.7 (s). Data for **29** are as follows. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 10.6 (d, $J$(HH) 9.8 Hz, $=CH$), 6.9 (dt, $J$(PH) = 1.9, $J$(HH) = 9.8 Hz, $OsCH$), 4.1 (s, $OCH_3$), 2.4 (m, $PCHCH_3$), 1.3 (dvt, $N$ = 15.2, $J$(HH) = 7.3 Hz, $PCHCH_3$). $^{31}$P NMR (80.9 MHz, $CDCl_3$): $\delta$ 18.3 (s).

**Catalytic Studies.** The hydrogen-transfer reactions were performed under argon at 60 °C, following the formation of cyclohexanol as a function of time. The reactions were carried out in a two-necked flask fitted with a condenser and a magnetic stirring bar. The second neck was capped with a Subaseal to be removed without opening the system.

In a typical procedure, to a solution of **1a** (11 mg, 0.02 mmol) in 2 mL of the alcohol was added a solution of $NaBH_4$ (3.78 mg, 0.1 mmol) in 2 mL of the alcohol. The reaction mixture was heated for 1 h at 60 °C, and a solution of 2 mmol of cyclohexanone in 4 mL of the alcohol was injected. After 4 h the conversion to cyclohexanol for the various alcohols used was 5% for methanol, 5% for ethanol, 0% for 2-methoxyethanol, and 34% for 2-propanol.

**X-ray Structure Analysis of 5a. Collection and Reduction of Data.** Crystals of **5a** suitable for X-ray study were obtained by slow cooling of a concentrated solution in ethanol. A colorless prismatic crystal was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. A summary of crystal data, intensity collection procedures, and refinement data is reported in Table III. Cell constants were obtained from the least-squares fit of the setting angles of 55 reflections in the range 20° < 2$\theta$ < 35°. The 6506 recorded reflections ($+h,-k,\pm l$) were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; a progressive intensity decay was observed (maximum value 16% at the end of data collection). Data were corrected for this decay according to standard intensities. Reflections were also corrected for absorption by using the DIFABS program.[31]

**Structure Solution and Refinement.** The structure was solved by Patterson (Os atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. At this stage, the unusual thermal parameters observed for the methyl group, C(3), and its trans carbonyl ligand (C(2) and O(2)), together with the presence of high electronic density residuals around these atoms, were indicative of a situation of ligand disorder involving both mentioned groups. A disorder model was built on the basis of the interchange of these two ligands (new atoms: C(3′), C(2′), and O(2′)), and the atoms were refined with different and complementary occupancy factors, giving rise to an improvement of the $R$ factor from 0.053 to 0.041. Further refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms of the molecule, excepting carbon atoms of the disordered ligands. Hydrogen atoms, except the hydride ligand and hydrogens of the disordered methyl group, were included in calculated positions and refined by riding on carbon atoms with a common isotropic thermal parameter. The hydride location was achieved from a detailed study of several difference Fourier maps with different cuts in $(\sin\theta)/\Lambda$.[17] The highest relation $\rho/\sigma(\rho)$ for the hydride position was observed in a Fourier map calculated with reflections with $(\sin\theta)/\Lambda < 0.40$. The coordinates obtained were included in the last cycles of refinement, with all observed data, as a normal isotropic hydrogen, with free positional parameters. The final occupancy factors for disordered atoms were 0.61 (1) for C(2), O(2), and C(3) and 0.39 (1) for primed atoms. The function minimized was $\sum(|F_o| - |F_c|)^2$ with the weight defined as $w = 1.0746/[\sigma^2(F_o) + 0.00053F_o^2]$. Atomic scattering factors, corrected for anomalous dispersion for Os and P, were taken from ref 32. Final $R$ and $R_w$ values were 0.028 and 0.029, respectively. All calculations were performed by use of the SHELX76 system of computer programs.[33]

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, atomic coordinates, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (11 pages). Ordering information is given on any current masthead page.

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(31) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
(32) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.
(33) Sheldrick, G. M. SHELX-76. *Program for Crystal Structure Determinations*; University of Cambridge: Cambridge, England, 1976.