Kinetic and Mechanistic Investigation of the Sequential Hydrogenation of Phenylacetylene Catalyzed by $OsHCl(CO)(PR_3)_2$ [PR_3 = PMe-*t*-Bu_2 and P-*i*-Pr_3]

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Abstract: The reactivities of the hydrido carbonyl complexes $OsHCl(CO)(PR_3)_2$ (PR_3 = PMe-*t*-Bu_2 (**1**), P-*i*-Pr_3 (**2**)) toward hydrogen, alkynes, and oxygen have been studied. The solutions of **1** and **2** are rapidly decolorized upon contact with H_2 under ambient conditions; the decolorized solution of **2** shows in benzene-d_6 a ^1H NMR spectrum that is consistent with the formation of the dihydrogen compound $OsHCl(\eta^2\text{-}H_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (**3**). The reactivity of **1** and **2** toward alkynes depends on the type of alkyne used. The title complexes react with acetylene, propyne, and phenylacetylene by insertion to give the five-coordinate vinylosmium compounds $Os(CH{=}CHR)Cl(CO)(PR_3)_2$ (**7** and **8**); the same starting materials in the presence of *t*-BuC≡CH and PhC≡CPh are completely inert. Treatment of **2** with $MeO_2CC{\equiv}CCO_2Me$ leads to the compound $Os[C(=CHCO_2Me)C(OMe)=O]Cl(CO)(P\text{-}i\text{-}Pr_3)_2$; the *trans*- and *cis*-alkyne hydrido intermediates have been observed. The hydridoosmium(II) complexes **1** and **2** also react with O_2 to form the dioxygen adducts $OsHCl(\eta^2\text{-}O_2)(CO)(PR_3)_2$ (**11** and **12**). The complexes **1** and **2** catalyze the sequential hydrogenation of phenylacetylene in 2-propanol solution at 60 °C. Selectivities close to 100% are achieved for the hydrogenation of the alkyne to the alkene. The kinetic investigation of this reaction provides evidence that indicates that the formation of styryl derivatives is the step that determines the selectivity for the hydrogenation to the alkene.

Homogeneous hydrogenation by transition-metal complexes has played a key role in the fundamental understanding of catalytic reactions and has proved to be of great utility in practical applications.[1] Important recent developments have focused on the kinetic and mechanistic aspects,[2] as well as on theoretical investigations[3] of this important class of reaction. Also, a number of interesting publications have appeared, dealing with closely related topics such as the insertion of olefins into M-H bonds,[4] oxidative addition-reductive elimination reactions,[5] and the mechanisms of hydrogen activation.[1,6] A further major contribution to the field is the recent discovery of dihydrogen complexes,[7] which provides a deeper insight into the oxidative addition of molecular hydrogen to transition metals.

Despite the wealth of information available concerning the catalytic chemistry of ruthenium compounds,[1a-e,2a,b,8] the potential of osmium complexes for homogeneous catalytic transformations has hitherto been little exploited. Activation of molecular hydrogen by osmium complexes has long been established,[9] but the resulting hydrides have usually been found or assumed to be too stable for catalytic applications. The once generalized view that 5d metals form too stable bonds with molecules typically involved in catalytic cycles and, therefore, are not of any practical use has proved to be invalid, for instance, in the case of iridium complexes.[10] A similar situation could be anticipated for osmium, if the ligands and the reaction conditions are appropriately selected.

Examples of homogeneous catalysis by osmium compounds up to now have been essentially restricted to carbonyl clusters.[11] Apart from some brief early reports on the ability of mononuclear osmium complexes to reduce olefins,[12] efficient homogeneous catalysis by hydrido-phosphine derivatives of osmium has only recently been recognized in our laboratories.[8,13,14]

Continuing our work in this field, we now report the first example of a kinetic and mechanistic investigation of the hydrogenation of an alkyne and of a reaction catalyzed by a mononuclear osmium complex, namely, the hydrogenation of phenylacetylene and styrene by use of $OsHCl(CO)(PR_3)_2$ (**1**, R_3 = Me-*t*-Bu_2; **2**, R = *i*-Pr) as catalyst precursors. We also present evidence for the formation of dihydrogen adducts of **1** and **2**.

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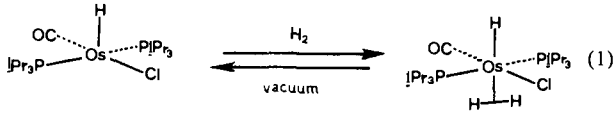
Although dihydrogen complexes of a variety of metals have now been identified,[7] as far as we know only a few examples have been reported to date in osmium chemistry.[7a,e,f] Finally, the characterization of related dioxygen derivatives of **1** and **2** and their behavior in connection with the proposed catalytic cycles is also reported, which supplements recent studies reported by some of us on the coordination chemistry of osmium complexes.[15]

Results and Discussion

1. Reactivity of 1 and 2. The five-coordinate osmium(II) complexes **1** and **2** react with ligands L such as CO, PMe_3, and $P(OMe)_3$ to produce the corresponding octahedral compounds $OsHCl(CO)(L)(PR_3)_2$ in excellent yields.[15a,16] We now find that the hydrido carbonyl compounds **1** and **2** also react with hydrogen (see eq 1). Solutions of **1** and **2** are rapidly decolorized upon

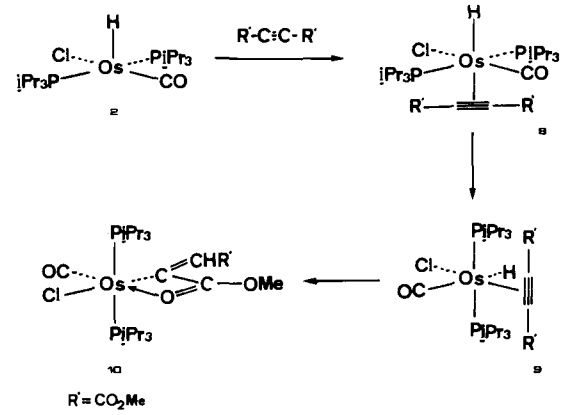


(1)

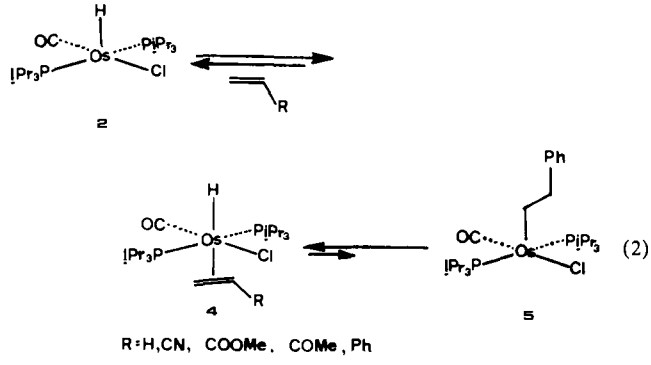
2 3

contact with H_2 under ambient conditions; volumetric measurements indicate that ca. 1 mol of H_2/mol of Os is absorbed. The ^1H NMR spectrum of **2** in benzene-d_6 also shows marked changes when the solution is exposed to hydrogen. The Os–H triplet at −31.9 ppm characteristic of **2** disappears, and a new pattern is observed, consisting of a triplet at −7.9 (J_{H-P} = 18.6 Hz, T_1 = 886 ms) plus a broad singlet at −1.3 ppm (T_1 = 18 ms). The phosphine protons appear as a multiplet at 2.55 ppm plus a doublet of virtual triplets at 1.27 ppm (N = 13.6 Hz, J_{HH} = 7.6 Hz). A strong ν_{CO} absorption at 1913 cm^{-1} is also characteristic of the new species. All these changes are totally reversed under vacuum at room temperature. The solutions are highly unstable, which has precluded isolation of the product. Nevertheless, the chemical shift and the broadness of the signal at −1.3 ppm, together with the absence of coupling to the phosphines and T_1 data, are in good agreement with data previously reported for dihydrogen complexes.[7]

Scheme I



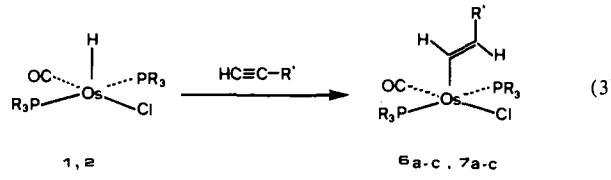
Olefins with electron-withdrawing substituents such as CN, COMe, and CO_2Me bind to **2** to produce the hexacoordinate compounds **4**. In the case of unactivated alkenes, e.g., ethylene, coordination is weak, and the 18-electron species are only stable in the presence of excess olefin.[15a] The reaction of **2** with styrene is less clear. The ^1H NMR spectrum of **2** in benzene-d_6 shows some changes when the solution is treated with styrene. The triplet at −31.9 ppm disappears, and a new broad signal at −27.9 ppm is observed; under this conditions, the styrene signals are broad. However, **2** is recovered unchanged after the solution is treated with methanol. The addition of styrene to a solution of $OsDCl(CO)(P\text{-}i\text{-}Pr_3)_2$ in benzene-d_6 shows a phenomena of D–H exchanged between Os–D and styrene. Thus, in the ^1H NMR spectrum after 20 min at room temperature appears the signal at −27.9 ppm, whereas the intensity of the styrene signals at 6.61 ppm decreases. These observations can be rationalized in terms of a rapid equilibrium between **2**, **4**, and **5**, according to eq 2.



(2)

R=H,CN, COOMe, COMe, Ph

The reactivity of **1** and **2** toward alkynes depends on the type of alkyne used. Whereas the hydrido carbonyl complexes react with acetylene, propyne, and phenylacetylene by insertion to give the five-coordinate vinylosmium compounds **6** and **7** almost quantitatively (eq 3), the same starting materials in the presence



(3)

of *t*-BuC≡CH and PhC≡CPh are completely inert. We assume that in both cases steric effects are mainly responsible for this behavior. Complexes **6** and **7** form red to deep violet solids which are relatively stable in air and have been characterized by elemental analysis and mass spectrometry.[17] The ^1H NMR data, in particular the large H–H coupling constant of 13–14 Hz for the two vinyl protons in **6b**, **6c**, **7b**, and **7c** (for exact values, see

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(17) The synthesis of **7a** and **7c** has already been described; see ref 15b.

the Experimental Section) leave no doubt that in all cases the *E* isomer is formed. For **7c**, the trans position of the metal and the phenyl group at the C=C bond has already been confirmed by X-ray analysis.[15b]

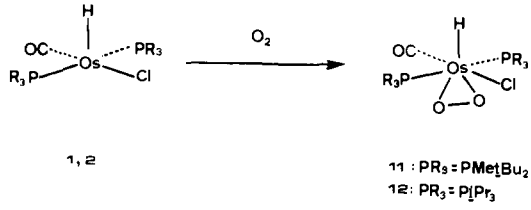
In contrast to PhC≡CPh, the corresponding acetylene derivative R′C≡CR′ with R′ = CO_2Me reacts with **2** to give a 1:1 adduct, **8**, for which, according to the spectroscopic data, the structure shown in Scheme I is proposed. The trans configuration of the $HOsC_2R'_2$ fragment is mainly supported by the significant change in the chemical shift of the Os–H signal which appears ca. 28 ppm downfield compared with **2**. A similar δ value for Os–H has been found for the compound $OsHCl(CO)_2(P\text{-}i\text{-}Pr_3)_2$ containing a CO ligand trans to hydride.[15a]

Whereas complex **8** as a solid is stable under nitrogen for days, in solution a smooth rearrangement occurs. In chloroform at room temperature, the colorless solution of **8** turns yellow, and after 30 min the ^1H NMR spectrum shows, besides the hydride resonance of the starting material, a second triplet at −3.40 ppm ($J_{H\text{-}P}$ = 28.0 Hz). In addition, the signal of the methyl protons of the ester groups becomes broad. The formation of a new compound is also indicated by the ^{31}P NMR spectrum of the chloroform solution that shows two singlets at 22.87 (for **8**) and 24.63 ppm. We assume that these changes are due to an isomerization process which leads to the cis isomer **9**.

The alkyne hydrido complex **9**, however, is also labile and subsequently reacts to give the vinylosmium compound **10**. In the ^1H NMR spectrum of the chloroform solution, the hydride resonances of **8** and **9** disappear and a new signal at 6.20 ppm is observed, which is very similar in chemical shift to the signal of the β-H proton of the vinyl ligand in **7c** (δ = 6.02 (dt), $J_{P\text{-}H}$ = 2.0, $J_{H\text{-}H}$ = 14.0 Hz).[15b] Furthermore, the broad absorption of the ester protons sharpens to give two singlets at 3.77 and 3.84 ppm, which indicates that the two CO_2Me groups are no more equivalent. The proposal that one of the ester units coordinates to the osmium via the C=O oxygen is strongly supported by the IR spectrum which shows two C=O stretching frequencies at 1700 and 1560 cm^{-1} (cf. **8**: ν(CO) = 1700 cm^{-1}). Compound **10** forms a deep yellow microcrystalline solid which is moderately stable in air and easily soluble in most organic solvents.

Scheme I summarizes the results obtained for the reaction of **2** with $C_2(CO_2Me)_2$. It should be mentioned that an analogue of **10** having an exocyclic CH_2 instead of a $CHCO_2Me$ group has recently been isolated in our laboratory and structurally characterized by X-ray analysis.[16,18] The preparation of the ruthenium compound $Ru[C(=CH\text{-}CH=CHCO_2Me)C(OMe)=O](C\equiv CCO_2Me)(CO)(PPh_3)_2$ comparable in structure to **10** from $RuHCl(CO)(PPh_3)_3$ and $C_2(CO_2Me)_2$ has been reported by Santos et al., but in this case, no alkyne hydrido intermediates have been observed.[19]

The hydridoosmium (II) complexes **1** and **2** also react with O_2 to form the stable dioxygen adducts **11** and **12**, respectively (see eq 4). They have first been observed as the main products in



1, 2

11 : PR_3 = PMetBu$_2$
12: PR_3 = PiPr$_3$

(4)

the decomposition of the dihydrogen compounds $OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2$ in the presence of oxygen but are more conveniently prepared by direct interaction of **1** and **2** with O_2. The IR spectra (Nujol) of **11** and **12** show absorption bands ν(O–O) at 862 (**11**) and 837 (**12**) cm^{-1}, suggesting the possibility of a η^2-peroxo coordination mode.[20]

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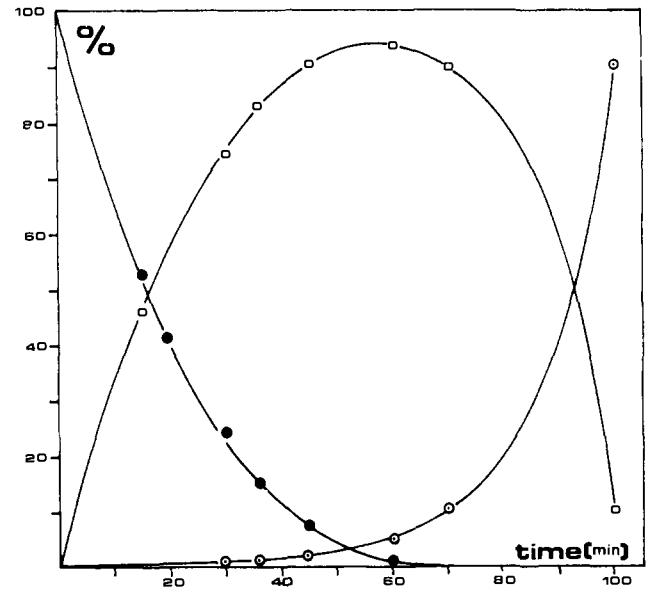
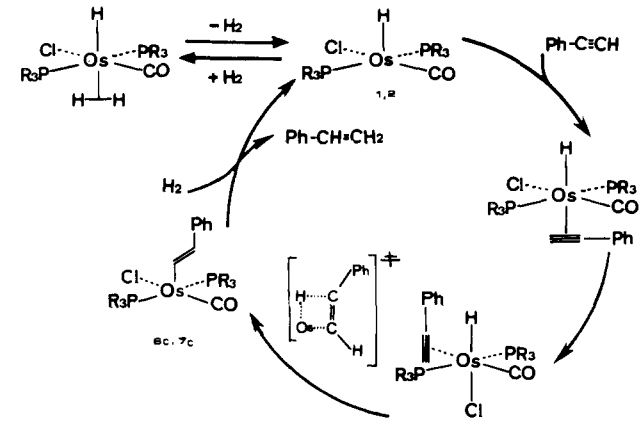


Figure 1. Hydrogenation of phenylacetylene catalyzed by OsHCl-$(CO)(P\text{-}i\text{-}Pr_3)_2$ in 2-propanol at 60 °C (1 atm of H_2; 2.5×10^{-3} M $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$, 0.25 M HC≡CPh). (●) Phenylacetylene, (□) styrene, (⊙) ethylbenzene.

Scheme II. Catalytic Cycle for the Hydrogenation of Phenylacetylene to Styrene



A further reaction of interest in connection with our catalytic investigations is that of the air-stable vinyl derivatives **6c** and **7c** with H_2 to produce styrene, ethylbenzene, and the dihydrogen complexes $OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2$, often contaminated with **11** and **12**, respectively. This hydrogenation reaction together with the formation of the vinyl compounds **6c** and **7c** (eq 3) constitutes a catalytic cycle for the reduction of phenylacetylene to styrene (see Scheme II) whose kinetics and mechanism form the subject of the second part of the paper.

2. Hydrogenation Catalysis. As expected from the coordination chemistry described above, **1** and **2** efficiently catalyze the sequential hydrogenation of phenylacetylene in 2-propanol solution. At 60 °C and atmospheric pressure, selectivities close to 100% are achieved for the hydrogenation of the alkyne to the alkene, as illustrated in Figure 1. Reduction of the double bond only begins to take place when most of the alkyne has been consumed. In the absence of the alkyne, however, styrene is hydrogenated to ethylbenzene at faster rates than those observed in the reduction of the acetylenic triple bond. No reduction of the organic substrates was observed in 2-propanol under Ar, showing that hydrogen transfer from the solvent does not represent an important

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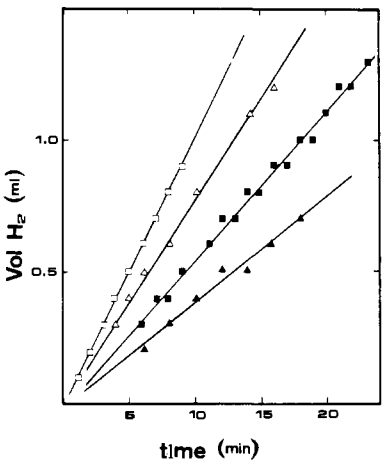


Figure 2. H_2 gas uptake plots for the OsHCl(CO)(PMe-*t*-Bu_2)$_2$-catalyzed hydrogenation of phenylacetylene to styrene in 2-propanol at 60 °C (1 atm of H_2; 4.5 × 10^{-3} M OsHCl(CO)(PMe-*t*-Bu_2)$_2$). [HC≡CPh]: (▲) 0.13 M; (■) 0.20 M; (△) 0.27 M; (□) 0.32 M.

Table I. Kinetic Data for the Hydrogenation of Phenylacetylene to Styrene Catalyzed by **1**

T, K	$P(H_2)$, atm	10^3[Os], M	[PhCCH], M	$10^7(-dV/dt)$, L s^{-1}	10^3k_{obs}, s^{-1} atm^{-1}	10^3k_s, M^{-1} s^{-1} atm^{-1}
333	1.00	2.5	0.28	7.3	1.34	4.8
	1.00	3.0	0.26	8.8	1.33	5.1
	1.00	3.7	0.26	13.0	1.59	6.1
	1.00	4.5	0.27	12.5	1.26	4.7
	1.00	4.5	0.13	6.3	0.64	4.9
	1.00	4.5	0.20	9.2	0.93	4.6
	1.00	4.5	0.32	16.7	1.68	5.3
	0.44	4.5	0.32	5.2	1.20	3.8
	0.64	4.5	0.32	7.2	1.15	3.6
	0.84	4.5	0.32	11.7	1.42	4.4
	1.21	4.5	0.32	15.1	1.28	4.0
313	1.00	4.5	0.32	4.8	0.52	1.6
323	1.00	4.5	0.32	8.3	0.87	2.7
329	1.00	4.5	0.32	11.3	1.16	3.6

mechanistic pathway in the catalysis.

Kinetics of the Hydrogenation of Phenylacetylene to Styrene. Initial hydrogenation rates were obtained from gas uptake experiments at 60 °C, as exemplified in Figure 2 for complex **1**.

A simple rate law for a catalytic hydrogenation reaction is

$$-d[\text{substrate}]/dt = -d[H_2]/dt = k_5[\text{substrate}]^m[\text{cat}]^n[H_2]^q \quad (5)$$

For the C≡C to C=C bond reduction, working at constant temperature and large excess of substrate, this rate law is further simplified to

$$-d[\text{substrate}]/dt = -d[H_2]/dt = k_{obs}[\text{cat}]^n(P(H_2))^q \quad (6)$$

The reactions were followed by measuring the hydrogen consumption as a function of time. The volume of H_2 corrected to 1 atm was converted to a pseudo-zero-order rate constant k_{obs} by using eq 7, where $-dV/dt$ is the initial rate measured from gas

$$-(dV/dt)/RTV_{sol} = k_{obs}[\text{cat}]^n(P(H_2))^q \quad (7)$$

uptake experiments, R is the molar gas constant, T is the temperature (K), and V_{sol} is the total volume of the reacting solution.

In order to determine the rate dependence on the various reaction components, hydrogenation runs were performed at different catalyst (**1**) and substrate concentrations and at different hydrogen pressures (Table I). Plots of log $(-dV/dt)$ versus log [Os] and log $(-dV/dt)$ versus log $P(H_2)$ yield straight lines of slope 1.01 and 1.22, respectively, showing that the reduction of phenylacetylene is first order in catalyst concentration and hydrogen pressure. The values of k_{obs} collected in Table I were thus obtained from eq 7 for $n = 1$ and $q = 1$. Plots of log $(-dV/dt)$ versus log [PhCCH] yield a straight line of slope 1.05, demonstrating that

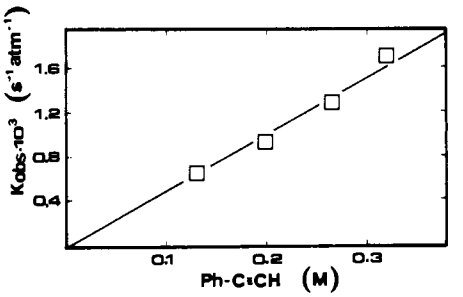


Figure 3. Rate constant for the hydrogenation of phenylacetylene to styrene catalyzed by OsHCl(CO)(PMe-*t*-Bu_2)$_2$ in 2-propanol at 60 °C (1 atm of H_2; 4.5 × 10^{-3} M OsHCl(CO)(PMe-*t*-Bu_2)$_2$).

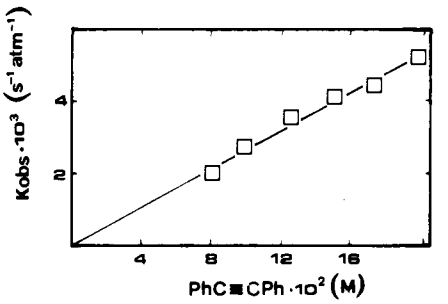


Figure 4. Rate constant for the hydrogenation of phenylacetylene to styrene catalyzed by OsHCl(CO)(P-*i*-Pr_3)$_2$ in 2-propanol at 60 °C (1 atm of H_2; 1.2 × 10^{-3} M OsHCl(CO)(P-*i*-Pr_3)$_2$).

Table II. Kinetic Data for the Hydrogenation of Phenylacetylene to Styrene Catalyzed by **2**[a,b]

T, K	10^3[Os], M	[PhCCH], M	$10^7(-dV/dt)$, L s^{-1}	10^4k_{obs}, s^{-1} atm^{-1}	10^2k_8, M^{-1} s^{-1} atm^{-1}
335	1.2	0.08	52.5	20.4	25.2
	1.2	0.10	71.3	27.8	28.0
	1.2	0.13	90.0	35.3	28.0
	1.2	0.15	106.6	41.1	27.2
	1.2	0.17	114.8	44.2	25.3
	1.2	0.20	134.1	52.2	26.2
334	0.7	0.13	40.8	26.3	20.6
	1.2	0.13	75.1	29.7	22.8
	1.8	0.13	103.0	26.6	20.5
	2.3	0.13	198.3	40.2	30.9
338	1.2	0.08	68.0	26.2	32.3
340	1.2	0.08	73.0	27.9	34.5
344	1.2	0.08	83.3	31.5	38.8

[a] In *i*-PrOH under 1 atm of H_2. [b] The complex **2** was generated in situ by reaction of **7c** with H_2.

the reaction is first order also in substrate concentration (i.e., $m = 1$ in eq 5). The catalytic rate law therefore is

$$d[\text{styrene}]/dt = -d[\text{PhCCH}]/dt = k_8[\text{PhCCH}][\text{cat}]P(H_2) \quad (8)$$

and

$$k_{obs} = k_8[\text{PhCCH}] \quad (9)$$

A plot of k_{obs} versus [PhCCH] (Figure 3) yields values for k_8 at 60 °C of (5.1 ± 0.2) × 10^{-3} M^{-1} s^{-1} atm^{-1} for **1**. Following a kinetic analysis analogous for **2**, the data collected in Table II and Figure 4 lead to a value for k_8 at 60 °C of (23.5 ± 1.3) × 10^{-2} M^{-1} s^{-1} atm^{-1}.

The NMR spectrum of the catalytic solutions shows that the vinyl intermediates are the main species. This suggests that the rate of formation of styrene is determined by the rate of reaction of vinyl compounds with hydrogen. Therefore, the following set of reactions must be consistent with the catalytic cycle:

$$\text{Os–H} + \text{PhCCH} \underset{}{\overset{k_f}{\rightleftharpoons}} \text{Os–vinyl} \quad \text{(fast)} \quad (10)$$

$$\text{Os–vinyl} + H_2 \xrightarrow{k_{11}} \text{Os–H} + \text{styrene} \quad \text{(slow)} \quad (11)$$

The rate of formation of styrene follows the kinetic law

$$d[\text{styrene}]/dt = k_{11}[\text{Os-vinyl}]P(H_2) \quad (12)$$

Since [Os-vinyl] = k_f[Os-H][PhCCH], then

$$d[\text{styrene}]/dt = k_{11}k_f[\text{Os-H}][\text{PhCCH}]P(H_2) \quad (13)$$

The inspection of eq 13 shows that the rate of the catalytic reaction is directly proportional to [**1**], [PhCCH], and $P(H_2)$, which agrees well with experimental data (see eq 8).

The dioxygen adducts **11** and **12** are also good catalyst precursors, but an induction period is observed, after which the hydrogenation behavior is essentially identical with that of the parent hydrides **1** and **2**; this induction period is most likely related to the slow displacement of dioxygen by phenylacetylene.

Kinetics of the Hydrogenation of Styrene. In the absence of phenylacetylene, compounds **1** and **2** catalyze the hydrogenation of styrene to ethylbenzene at rates of about 1 order of magnitude faster than those observed for C≡C bond reduction. The reaction profile is essentially the same if the catalytic runs are performed with solutions of the monohydrides **1** and **2** pretreated with styrene or hydrogen, respectively, for 30 min at room temperature. The most accurate kinetic data were obtained for complex **1**, and consequently the discussion that follows is based on these results.

Typical gas uptake measurements are shown in Figure 5. Following a kinetic analysis analogous to that described above for phenylacetylene, at atmospheric pressure, we deduce from the data collected in Table III and Figure 6 that the rate law for the reduction of C=C bonds is

$$-d[\text{styrene}]/dt = k_{14}[\text{styrene}][\text{cat}] \quad (14)$$

with a value of k_{14} of (9.9 ± 0.6) × 10^{-2} M^{-1} s^{-1} at 23 °C.

3. Hydrogenation Mechanisms. Scheme II illustrates the catalytic cycle for the selective hydrogenation of phenylacetylene to styrene. The reaction of the monohydride or the dihydrogen with the alkyne is rapid and leads to stable 16-electron vinyl complexes. The elementary steps involved in the formation of the styryl derivatives **6c** and **7c** are too rapid to be observed by spectroscopic methods. However, it has been shown by NMR spectroscopy that acetylenedicarboxylic methyl ester coordinates to **2** trans to the hydride at room temperature; then rearrangement to the cis isomer takes place, followed by insertion to yield the corresponding vinyl species. It is reasonable to assume that the same sequence of events is operative in the formation of the styryl compounds **6c** and **7c**. The slow step of this catalytic cycle is the reaction of these five-coordinate complexes with hydrogen to yield the olefin and regenerate the monohydrides in equilibrium with the dihydrogen complexes. Although more intimate details of this cycle remain to be elucidated, the reaction of the vinyl compounds with hydrogen is likely to involve a series of elementary steps. One plausible sequence would be the oxidative addition of H_2—perhaps via a dihydrogenvinylosmium intermediate—to yield the 18-electron Os(IV) species $OsH_2(CH{=}CHPh)(Cl)(CO)(PR_3)_2$, followed by reductive elimination of styrene.

The hydrogenation of styrene to ethylbenzene is less clear-cut from a mechanistic point of view. In light of the coordination chemistry presented above, the mechanism shown in Scheme II may also be operative for this reduction, but another possible route could be the initial coordination of H_2.

The high selectivity observed for the hydrogenation of phenylacetylene to styrene merits further comment. The independent study of the reduction of C≡C and C=C bonds indicates that the latter is kinetically favored and thus the origin of this selectivity cannot be kinetic. Under catalytic conditions, the vinyl compounds are the main species; these vinyl complexes represent a thermodynamic sink that causes virtually all the osmium present in solution to be tied up in this form, and consequently the kinetically unfavorable pathway becomes essentially the only one available in the presence of alkyne. We believe that it is this **thermodynamic** difference, qualitatively illustrated in Scheme III, that may be at the origin of the high selectivity in the hydrogenation of the C≡C bond.

4. Concluding Remarks. In spite of the wealth of information available concerning the homogeneous hydrogenation of alkenes,[1] remarkably few details have been previously reported for alkynes, even though many catalysts have been tested and found to be effective in this reaction.[1d] Highly selective hydrogenation to the corresponding alkene has been observed for ruthenium,[1d] osmium,[13] and rhodium[21,22] catalysts. In all cases, the origin of the selectivity has been ascribed to stronger coordination of the alkyne to the metal center with respect to binding of the olefin. Also, alkyne hydrogenation usually proceeds at slower rates than alkene reduction, and this has generally been explained by the greater difficulty of a coordinated alkyne to undergo insertion into a M–H bond. Schrock and Osborn[21] established catalytic cycles involving both cationic dihydrides and neutral monohydrides for the rho-

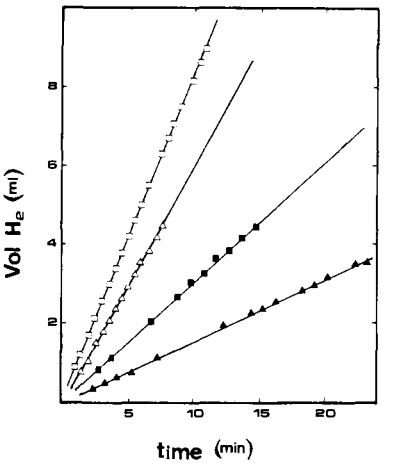


Figure 5. H_2 gas uptake plots for the $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$-catalyzed hydrogenation of styrene to ethylbenzene in 2-propanol at 23 °C (1 atm of H_2; 2.5 × 10^{-3} M $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$). [Styrene]: (▲) 0.07 M; (■) 0.13 M; (△) 0.20 M; (□) 0.30 M.

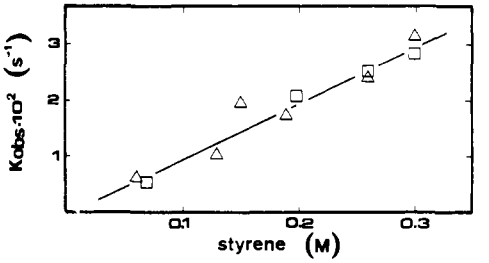


Figure 6. Rate constant for the hydrogenation of styrene to ethylbenzene catalyzed by $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ in 2-propanol at 23 °C (1 atm of H_2; (□) 2.5 × 10^{-3} M; (△) 1.3 × 10^{-3} M $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$).

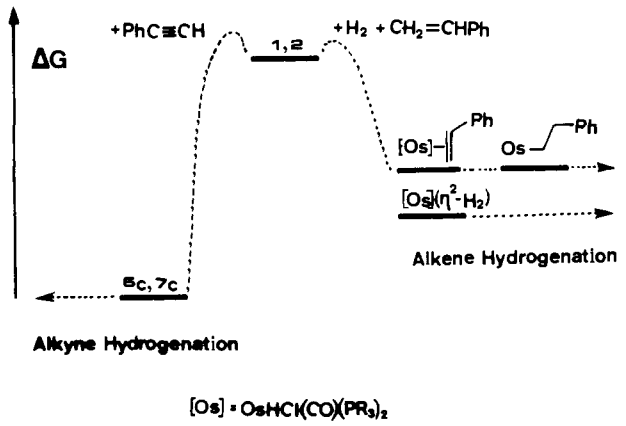
Table III. Kinetic Data for the Hydrogenation of Styrene to Ethylbenzene Catalyzed by **1**[a]

T, K	10^3[Os], M	[styrene], M	$10^6(-dV/dt)$, L s^{-1}	10^2k_{obs}, s^{-1}	10^2k_{14}, M^{-1} s^{-1}
296	2.5	0.26	12.1	2.48	9.5
	1.3	0.26	5.9	2.40	9.2
	0.7	0.26	1.8	1.28	4.9
	1.3	0.30	7.7	3.12	10.4
	1.3	0.20	4.3	1.75	8.8
	1.3	0.15	4.6	1.89	12.6
	1.3	0.13	2.5	1.01	7.8
	1.3	0.06	1.5	0.61	10.1
	2.5	0.30	13.7	2.82	9.4
	2.5	0.20	10.1	2.08	10.4
	2.5	0.13	5.0	1.04	8.0
	2.5	0.07	2.6	0.53	7.5
304	1.3	0.06	2.9	1.14	19.0
309	1.3	0.06	4.5	1.77	29.5
319	1.3	0.06	9.9	3.74	62.4

[a] In *i*-PrOH under 1 atm of H_2.

(21) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143.
(22) Usón, R.; Oro, L. A.; Sariego, R.; Valderrama, M.; Rebullida, C. *J. Organomet. Chem.* **1980**, *197*, 87.

Scheme III. Qualitative Diagram of Free Energy for the Hydrogenation of Phenylacetylene Catalyzed by the Complexes $OsHCl(CO)(PR_3)_2$ (PR_3 = PMe-*t*-Bu_2, P-*i*-Pr_3)



dium-catalyzed hydrogenation of hexynes; interestingly, the monohydrides were found to be considerably more active than the dihydrides. In the latter case, rapid sequential transfer of the two hydrides with retention of the geometry about the double bond was invoked in order to explain the exclusive formation of the product arising from a cis addition.

In this paper we have provided evidence indicating that for the monohydrides **1** and **2** it is not the difference in the coordinating power of the substrates that is important in determining selectivities for the hydrogenation **to the alkene** but the tendency of the alkyne to undergo insertion to yield the vinyl intermediate.

In the light of these results, it is clear that further work needs to be done in order to fully understand the general kinetic and mechanistic aspects of alkyne hydrogenation by metal hydrides, which have so far remained at the level of speculative extrapolations of our knowledge of alkene reactions.

Experimental Section

General Considerations. All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under nitrogen prior to use. Phenylacetylene (Merck) was purified by distillation and styrene (Merck) by passage through an alumina column.

Physical Measurements. NMR spectra were recorded on a Varian EM 360, a Bruker Crysospec WM 400 (^{1}H), and a Bruker WH-90 FT (^{31}P). Chemical shifts are expressed in parts per million upfield from $Si(CH_3)_4$ (^{1}H) and 85% H_3PO_4 (^{31}P). The T_1 experiments were 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 457 and mass spectra with a Varian MAT CH7 instrument (70 eV). C, H analyses were carried out with a Perkin–Elmer 240 C microanalyzer.

The catalytic reactions were followed by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256). The analysis of the products of the catalytic reactions was carried out on a Perkin-Elmer 3920 B gas chromatograph with an FFAP on Chromosorb GHP 80/100-mesh (3.6- × $^1/_8$-in.) column at 100 °C. The chromatograph was connected to a Perkin-Elmer M2 calculation integrator.

Starting Materials. The complexes $OsHCl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (**1**), $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**2**), and $Os(CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (**7c**) were prepared by published methods.[15a,b] The complex $OsDCl(CO)(P\text{-}i\text{-}Pr_3)_2$ was obtained by reaction of $OsCl_3{\cdot}H_2O$ with P-*i*-Pr_3 in methanol-d_4.

Preparation of $OsHCl(\eta^2\text{-}H_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (3). **3** was prepared in situ as follows: In a NMR tube and at room temperature, 20.3 mg (0.035 mmol) of **2** was dissolved in 1 mL of benzene-d_6, and H_2 was bubbled through the solution for 5 min during which the color of the solution changed from red to colorless. ^{1}H NMR (benzene-d_6, 20 °C): δ −7.90 (t, $J_{P\text{-}H}$ = 18.6 Hz, 1 H, OsH, T_1 = 886 ms), −1.30 (br, 2 H, $Os(H_2)$, T_1 = 18 ms), 1.27 (dvt, N = 13.6 Hz, $J_{H\text{-}H}$ = 7.6 Hz, 36 H, PCHCH_3), 2.55 (m, 6 H, PCHCH$_3$).

Preparation of $Os(CH{=}CH_2)Cl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (6a). Acetylene was bubbled through a solution of **1** (142.2 mg, 0.25 mmol) in 10 mL of benzene for 5 min at room temperature. The solution was concentrated in vacuo to ca. 0.5 mL, and 10 mL of methanol was added. A red precipitate was formed, which was filtered off, washed with methanol, and dried in vacuo; yield 141 mg (94%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.30 (vt, N = 13.0 Hz, 18 H, PCCH_3), 1.36 (vt, N = 13.0 Hz, 18 H, PCCH_3), 1.50 (vt, N = 6.5 Hz, 6 H, PCH_3), 3.96 (ddt, $J_{H\alpha\text{-}H\beta_2}$ = 14.0, $J_{H\beta_1\text{-}H\beta_2}$ = 1.0, $J_{P\text{-}H\beta_2}$ = 2.0 Hz, 1 H, $CH_\alpha{=}CH_{\beta_1}H_{\beta_2}$), 4.80 (ddt, $J_{H\alpha\text{-}H\beta_1}$ = 7.0, $J_{H\beta_2\text{-}H\beta_1}$ = 1.0, $J_{P\text{-}H\beta_1}$ = 1.5 Hz, 1 H, $CH_\alpha{=}CH_{\beta_1}H_{\beta_2}$), 7.60 (ddt, $J_{H\beta_2\text{-}H\alpha}$ = 14.0, $J_{H\beta_1\text{-}H\alpha}$ = 7.0, $J_{P\text{-}H\alpha}$ = 1.0 Hz, 1 H, $CH_\alpha{=}CH_{\beta_1}H_{\beta_2}$). ^{31}P NMR ($CDCl_3$, 25 °C): δ 5.63 (s). IR (CH_2Cl_2, 25 °C): ν(CO) 1900 (s) cm^{-1}. Anal. Calcd for $C_{21}H_{45}ClOOsP_2$: C, 41.95; H, 7.55, M_r, 601.18. Found: C, 41.57; H, 7.74; M_r, 602 (MS).

Preparation of $Os(CH{=}CHCH_3)Cl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (6b). Methylacetylene was bubbled through a solution of **1** (110.0 mg, 0.19 mmol) in 5 mL of benzene for 1 min. The resulting solution was stirred during 10 min under methylacetylene at room temperature. The solvent was removed and the solid residue treated with 5 mL of hexane. After the solution was cooled to −78 °C, a red precipitate was formed, which was filtered off and dried in vacuo; yield 95 mg (81%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.16 (vt, N = 12.0 Hz, 18 H, PCCH_3), 1.23 (vt, N = 12.0 Hz, 18 H, PCCH_3), 1.43 (vt, N = 6.0 Hz, 6 H, PCH_3), 1.80 (ddt, $J_{H\beta\text{-}H}$ = 5.0, $J_{H\alpha\text{-}H}$ = 1.0, $J_{P\text{-}H}$ = 2.0 Hz, 3 H, $CH_\alpha{=}CH_\beta CH_3$), 4.13 (dtq, $J_{H\alpha\text{-}H\beta}$ = 13.0, $J_{H\text{-}H\beta}$ = 1.0, $J_{P\text{-}H\beta}$ = 2.0 Hz, 1 H, $CH_\alpha{=}CH_\beta CH_3$), 6.30 (dtq, $J_{H\beta\text{-}H\alpha}$ = 13.0, $J_{H\text{-}H\alpha}$ = 5.0, $J_{P\text{-}H\alpha}$ 2.0 Hz, 1 H, $CH_\alpha{=}CH_\beta CH_3$). ^{31}P NMR ($CDCl_3$ 25 °C): δ 17.60 (s). IR (CH_2Cl_2, 25 °C): ν(CO) 1905 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{47}ClOOsP_2$: C, 42.95; H, 7.70. Found: C, 42.42; H, 7.90.

Preparation of $Os(CH{=}CHPh)Cl(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (6c). A suspension of **1** (115.0 mg, 0.20 mmol) in 5 mL of hexane was treated with phenylacetylene (22.1 μL, 0.22 mmol) and stirred for 30 min at room temperature. The dark-blue precipitate was filtered off, repeatedly washed with hexane, and dried in vacuo; yield 120 mg (89%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.20 (vt, N = 12.0 Hz, 18 H, PCCH_3), 1.36 (vt, N = 12.0 Hz, 18 H, PCCH_3), 1.50 (vt, N = 6.0 Hz, 6 H, PCH_3), 5.40 (dt, $J_{H\alpha\text{-}H\beta}$ = 13.5, $J_{P\text{-}H\beta}$ = 1.5 Hz, 1 H, $CH_\alpha{=}CH_\beta Ph$), 7.18 (m, 5 H, $CH_\alpha{=}CH_\beta Ph$), 8.20 (dt, $J_{H\beta\text{-}H\alpha}$ = 13.5, $J_{P\text{-}H\alpha}$ = 1.5 Hz, 1 H, $CH_\alpha{=}CH_\beta Ph$). ^{31}P NMR ($CDCl_3$, 25 °C): δ 19.15 (s). IR (CH_2Cl_2, 25 °C): ν(CO) 1905 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{49}ClOOsP_2$: C, 47.86; H, 7.29. Found: C, 48.15; H, 7.46.

Preparation of $Os(CH{=}CHMe)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (7b). **7b** was prepared analogously as described for **6b**, starting with **2** (82.9 mg, 0.15 mmol) and methylacetylene: dark-red crystals; yield 80 mg (90%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.27 (dvt, N = 12.5 Hz, $J_{H\text{-}H}$ = 6.5 Hz, 36 H, PCHCH_3), 2.93 (m, 6 H, PCHCH$_3$), 1.67 (ddt, $J_{H\beta\text{-}H}$ = 3.0, $J_{H\alpha\text{-}H}$ = 1.0, $J_{P\text{-}H}$ = 1.5 Hz, 3 H, $CH_\alpha{=}CH_\beta CH_3$), 4.30 (dtq, $J_{H\alpha\text{-}H\beta}$ = 13.0, $J_{H\text{-}H\beta}$ = 1.5, $J_{P\text{-}H\beta}$ = 1.0 Hz, 1 H, $CH_\alpha{=}CH_\beta CH_3$), 6.30 (dtq, $J_{H\beta\text{-}H\alpha}$ = 13.0, $J_{H\text{-}H\alpha}$ = 3.0, $J_{P\text{-}H\alpha}$ 1.5 Hz, 1 H, $CH_\alpha{=}CH_\beta CH_3$). ^{31}P NMR ($CDCl_3$, 25 °C): δ 17.23 (s). IR (CH_2Cl_2, 25 °C): ν(CO) 1895 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{47}ClOOsP_2$: C, 42.95; H, 7.70; M_r, 615.21. Found: C, 42.69; H, 7.80; M_r, 616 (MS).

Reaction of $OsHCl(\eta^2\text{-}H_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ with HC_2Ph: Preparation of $Os(CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (7c). To a NMR tube containing a benzene-d_6 solution of $OsHCl(\eta^2\text{-}H_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (0.035 mmol in 1 mL) was added phenylacetylene (40 μL, 0.35 mmol). The reaction was followed by ^{1}H NMR analysis. ^{1}H NMR: δ 1.27 (dvt, N = 14.0 Hz, $J_{H\text{-}H}$ = 7.0 Hz, 18 H, PCHCH_3), 1.28 (dvt, N = 14.0 Hz, $J_{H\text{-}H}$ = 7.0 Hz, 18 H, PCHCH_3), 2.87 (m, 6 H, PCHCH$_3$), 6.02 (dt, $J_{H\alpha\text{-}H\beta}$ = 14.0, $J_{P\text{-}H\beta}$ = 2.0 Hz, 1 H, $CH_\alpha{=}CH_\beta Ph$), 7.12 (m, 5 H, $CH_\alpha{=}CH_\beta Ph$), 8.66 (d, $J_{H\beta\text{-}H\alpha}$ ≈ 14.0 Hz, 1 H, $CH_\alpha{=}CH_\beta Ph$).

Preparation of *trans*-$OsHCl(CO)(\eta^2\text{-}C_2(CO_2Me)_2)(P\text{-}i\text{-}Pr_3)_2$ (8). A solution of **2** (105.0 mg, 0.18 mmol) in 10 mL of benzene was treated with $C_2(CO_2Me)_2$ (22.0 μL, 0.18 mmol). The resulting solution was stirred for 5 min at room temperature and concentrated in vacuo to ca. 0.5 mL. After slow addition of hexane (5 mL), a white precipitate was formed, which was filtered off, repeatedly washed with hexane, and dried in vacuo; yield 102 mg (79%). ^{1}H NMR ($CDCl_3$, 25 °C): δ −2.80 (t, $J_{P\text{-}H}$ = 28.0 Hz, 1 H, OsH), 1.30 (dvt, N = 13.0 Hz, $J_{H\text{-}H}$ = 6.2 Hz, 18 H, PCHCH_3), 1.37 (dvt, N = 13.0 Hz, $J_{H\text{-}H}$ = 6.2 Hz, 18 H, PCHCH_3), 2.87 (m, 6 H, PCHCH$_3$), 3.77 (s, 6 H, OCH_3). ^{31}P NMR ($CDCl_3$, 25 °C): δ 22.87 (s). IR (CH_2Cl_2, 25 °C): ν(CO) 1950 (Os–CO), 1700 (MeOCO); ν(Os–H) 2100; ν(C≡C) 1840 cm^{-1}. Anal. Calcd for $C_{25}H_{49}ClO_5OsP_2$: C, 41.86; H, 6.89. Found: C, 41.84; H, 6.89.

Preparation of $Os[C(=CHCO_2Me)C(OMe)=O]Cl(CO)(P\text{-}i\text{-}Pr_3)_2$ (10). A solution of **8** (72.0 mg, 0.10 mmol) in 5 mL of chloroform was stirred for 48 h at room temperature, under argon. The solvent was evaporated under reduced pressure to ca. 0.5 mL. Slow addition of hexane led to the precipitation of a yellow solid, which was filtered off, washed with hexane, and dried in vacuo. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.30 (dvt, N = 13.0 Hz, $J_{H\text{-}H}$ = 6.2 Hz, 18 H, PCHCH_3), 1.43 (dvt, N = 13.0 Hz, $J_{H\text{-}H}$ = 6.2 Hz, 18 H, PCHCH_3), 2.73 (m, 6 H, PCHCH$_3$), 3.77 (s, 3 H, C=CH(CO$_2Me$)), 3.84 (s, 3 H, C(OMe)=OOs), 6.20 (br, 1 H, =CH(CO$_2$Me)). ^{31}P NMR ($CDCl_3$, 25 °C): δ 12.0 (s). IR (CH_2Cl_2, 25 °C): ν(CO) 1905 (Os–CO), 1700 (=CHCOOMe), 1560

(C(OMe)=OOs) cm^{-1}. Anal. Calcd for $C_{25}H_{49}ClO_5OsP_2$: C, 41.86; H, 6.89. Found: C, 41.60; H, 7.08.

Preparaton of $OsHCl(\eta^2\text{-}O_2)(CO)(PMe\text{-}t\text{-}Bu_2)_2$ (11). Bubbling of O_2 through a suspension of **1** (100.0 mg, 0.18 mmol) in 10 mL of hexane led to solution of the complex and to precipitation of a white solid, which was filtered off, washed with hexane, and dried in vacuo; yield 98 mg (93%). ^1H NMR ($CDCl_3$, 25 °C): δ -3.20 (t, J_{P-H} = 32.0 Hz, 1 H, OsH), 1.50 (vt, N = 14.6 Hz, 18 H, $PCCH_3$), 1.60 (vt, N = 14.6 Hz, 18 H, $PCCH_3$), 1.90 (vt, N = 8.4 Hz, 6 H, PCH_3). ^{31}P NMR ($CDCl_3$, 25 °C): δ 24.87 (s). IR (Nujol): ν(CO) 1955, ν(O-O) 862 cm^{-1}. Anal. Calcd for $C_{19}H_{43}ClO_3OsP_2$: C, 37.59; H, 7.14. Found: C, 37.42; H, 7.53.

Preparation of $OsHCl(\eta^2\text{-}O_2)(CO)(P\text{-}i\text{-}Pr_3)_2$ (12). **12** was prepared by the same procedure as **11** but starting with **2** (100.0 mg, 0.18 mmol): white crystals; yield 98 mg (93%). ^1H NMR ($CDCl_3$, 25 °C): δ -2.40 (t, J_{P-H} = 30.0 Hz, 1 H, OsH), 1.42 (dvt, J_{H-H} = 6.0 Hz, N = 14.0 Hz, 36 H, $PCHCH_3$), 2.90 (m, 6 H, $PCHCH_3$). ^{31}P NMR ($CDCl_3$, 25 °C: δ 25.50 (s). IR (Nujol): ν(Os-H) 2095 (w), ν(CO) 1947 (vs), ν(O-O) 837 cm^{-1}. Anal. Calcd for $C_{19}H_{43}ClO_3OsP_2$: C, 37.59; H, 7.14. Found: C, 37.63; H, 7.62.

Catalytic Reactions. A degassed solution of the catalyst in 2-propanol (4 mL) was syringed through a silicone septum into a 25-mL flask attached to a gas buret, which was in turn connected to a Schlenck manifold. The system was evacuated and refilled with hydrogen three times, and the flask was then inmersed in a constant-temperature bath. The substrate, dissolved in deaerated 2-propanol (4 mL) was subsequently introduced through the septum and the mixture was vigorously shaken during the run. For the experiments involving pretreatment, the catalyst solution was shaken under hydrogen for 30 min at the reaction temperature prior to introduction of the substrate, in one case, or shaken together with the substrate under Ar for 30 min and then evacuated and put under hydrogen. Plots of kinetic data were fitted by use of conventional linear regression programs.

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Solution and Solid-State Characterization of Europium and Gadolinium Schiff Base Complexes and Assessment of Their Potential as Contrast Agents in Magnetic Resonance Imaging

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Abstract: Two lanthanide Schiff base macrocyclic complexes, $LnHAM(OAc)_2Cl{\cdot}4H_2O$ (Ln = Eu, Gd; HAM = HexaAza-Macrocycle = $C_{22}H_{26}N_6$), have been characterized in view of the potential of the Gd complex as a magnetic resonance imaging (MRI) contrast agent. The relaxivity of $GdHAM(OAc)_2Cl$ was measured at 300 and 20 MHz and is as high as that for the gadolinium aquo ion. The number of coordinated waters, q, was measured by comparison of the luminescent lifetimes of $EuHAM(OAc)_2Cl$ in H_2O and D_2O and found to be between three and four. The complex $GdHAM(OAc)_2Cl{\cdot}4H_2O$ was characterized by single-crystal X-ray diffraction. The complex crystallizes in space group $P\bar{1}$ with Z = 2, a = 10.032 (2) Å, b = 12.765 (2) Å, c = 13.668 (3) Å, α = 69.190° (9)°, β = 72.405° (9)°, and γ = 74.07° (1)°. For 3336 independent data with $I > 3\sigma(I)$, full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms and positional parameters for 8 water hydrogens converged to unweighted and weighted R factors of 3.6% and 4.7%, respectively. The gadolinium ion is 10-coordinate with 6 nitrogen donors from the macrocycle and 4 oxygens from 2 bidentate acetate anions. The four waters and the chloride ion form a hydrogen-bonding network that includes two opposing acetate oxygens. The closest Gd--H distances for the outer-sphere water protons are 4.1 (1) and 4.2 (1) Å. The complexes are stable to decomposition in the presence of oxalate and DTPA in aqueous solution. The reduction potential of $EuHAM(OAc)_2Cl$ in aqueous solution is -0.94 V (versus Ag/AgCl) in 0.1 M KCl, which corresponds to a shift of -270 mV relative to the aquo ion. This indicates a stabilization of Eu(III) relative to Eu(II) in the macrocycle cavity by a factor of $10^{4.6}$.

Paramagnetic compounds are presently undergoing extensive evaluation as contrast agents in magnetic resonance imaging (MRI). These agents increase constrast in MRI by differentially localizing in tissues where they increase the relaxation rates of nearby water protons. Complexes of Gd(III), Fe(III), and Mn(II,III) are under intensive study because their high number of unpaired electrons (S) and long electron-spin relaxation times (T_{1e}) allow efficient relaxation of water protons.[1,2] GdDTPA[3] (DTPA = diethylenetriaminepentaacetic acid) is at present the most commonly used contrast agent because of its large magnetic moment and relatively low toxicity.[2] The high stability constant of GdDTPA reduces toxic effects of Gd(III) by lowering the concentration of free metal ion. However, one factor limiting its effectiveness as a relaxation agent is the availability of only one water coordination site in the complex.[4] The relaxivity[5] of the

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(3) GdDTPA is used here to represent a variety of complexes of Gd(III) with DTPA that may be present in aqueous solution, depending on factors such as the pH and concentration of other ligands, e.g., $Gd(DTPA)(H_2O)^{2-}$ or $Gd(HDTPA)(H_2O)^-$.

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