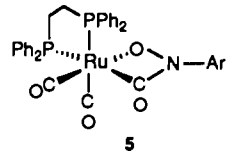
and monomer.[32] No substantial evidence supporting the presence of 2^+ in solutions of $\{[Ru(dppe)(CO)_3]_2\}^{2+}$ was obtained. The expected increase in metal–metal bond strength in going from the Mn to the Ru system apparently allows the dimer to form despite the larger size of the chelating ligand and the unfavorable electrostatic forces.

While the lifetime of 2^+ is short, it is competitively trapped by using organonitroso compounds, Ph_3CH, or Bu_3SnH. The question as to why 2^+ does not abstract halogens from CH_2Cl_2 or Bu_3SnCl remains unclear. Considering the ease of halogen abstraction by **1a** (eq 3), it would seem unlikely that thermodynamics alone could explain the inability of 2^+ to abstract a halogen. Perhaps halogen atom abstraction is kinetically slower than hydrogen atom abstraction to such an extent that the former cannot compete with dimerization. Among the halogen donors CH_2Cl_2 has been shown to be the least reactive toward chlorine abstraction using transition metal-centered radicals.[8,33]

Relation to the Catalysis of Nitroaromatic Carbonylation. The neutral complexes **1** and **2** are known catalysts for the carbonylation of nitroaromatics in alcohols to give carbamates (eq 6).

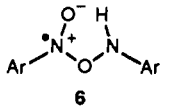
$$ArNO_2 + 3CO + CH_3OH \rightarrow 2CO_2 + ArNHC(O)OCH_3 \quad (6)$$

Among these phosphine-substituted complexes, **2** was reported to have the fastest turnover rate.[34] In previous mechanistic studies of the catalysis of eq 6 by **2**, it was suggested that the first step involved the single electron transfer from **2** to $ArNO_2$.[16] This was followed by rapid CO_2 loss and CO addition to give the unusual, structurally characterized complex $Ru(dppe)(CO)_2[C(O)N(Ar)O]$ (**5**) as the first isolable species.[17] Weak EPR signals were observed



5

following the mixing of either the nitroaromatic or the corresponding nitrosoaromatic with **2** in the catalytic solutions at room temperature and atmospheric pressure of CO.[16] For *p*-chloronitrosobenzene, the signal appeared at $g = 2.013$ with two hyperfine couplings observable of 11.4 and 3.2 G. The larger value could be assigned unambiguously to the ^{14}N coupling because of the 1:1:1 intensity pattern. The smaller coupling was originally assigned to coupling to the ortho hydrogens, and the structure of the active species **6** was proposed to result from the nitrosoarene



6

trapping of the protonated (from the methanol) radical anion of the nitrosoarene itself. Previous studies of the reactivity of nitrosoarene radical anions in basic media provided the basis for this suggestion.[29] The similarity of the spectral data reported here to those data from the previous study allow us to suggest that the spin-trapped radical cation $\{Ru(dppe)(CO)_3[N(O)Ar]\}^+$ is an alternative structure of the EPR-active species. Whatever the nature of the EPR-active species, it should noted that it probably forms only when the nascent radical pair (eq 1) separate and escape from the solvent cage.

Although the ruthenium radical cation does not appear to be involved in the rate-determining step of the catalysis, the single electron transfer event provides the mechanism by which the substrate interacts with the catalyst. The studies described in this paper provide a background of characterization and reactivity data that can be correlated directly with the studies involving the working catalyst.

Conclusions

The zerovalent ruthenium complexes $Ru(PR_3)_2(CO)_3$, where R = Ph, Cy, *p*-Tol, and Bz, and $Ru(dppe)(CO)_3$ have been found to undergo one-electron chemical and electrochemical oxidations giving the corresponding radical cations $[Ru(PR_3)_2(CO)_3]^+$ and $[Ru(dppe)(CO)_3]^+$. The stabilities of the radical cations depend on the nature of the phosphine ligand, and all are always less stable than the analogous iron complexes. The infrared and EPR spectra are consistent with a five-coordinate, low-spin d^7 complex but are unable to differentiate between a square-pyramidal and trigonal-bipyramidal structure. The radicals are able to abstract halogen atoms from organic halides and tri-*n*-butyltin chloride and hydrogen atoms from triphenylmethane and tri-*n*-butyltin hydride. The radicals can be trapped by using tetrachloro-*o*-quinone and organonitroso compounds. Evidence for radical dimerization was found only with the complex containing the chelating ligand, $Ru(dppe)(CO)_3$.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-8714326). We thank John Bullock for obtaining the cyclic voltammogram of $Fe(PPh_3)_2(CO)_3$.

(32) Tyler, D. R.; Goldman, A. S. *J. Organomet. Chem.* **1986**, *311*, 349.
(33) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388.
(34) Grate, J. H.; Hamm, D. H.; Valentine, D. H. U.S. Patent 4,603,216, 1986.

Contribution from Sterling Chemistry Laboratory, Yale University, 225 Prospect Street, New Haven, Connecticut 06511

Dihydrogen Complexes in Catalysis: Isotope Exchange Reactions

Ana C. Albeniz,* D. Michael Heinekey, and Robert H. Crabtree

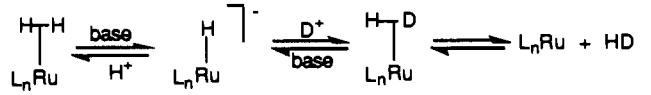
Received March 15, 1991

Dihydrogen complexes $[CpRu(CO)(PR_3)(\eta^2\text{-}H_2)]X$ (R = Ph (**1**), Cy (**2**); X = BF_4^-, $CF_3SO_3^-$), $[Ru(dppe)_2H(\eta^2\text{-}H_2)]BF_4$ (**3**), and $[Ir(bq)(PPh_3)_2H(\eta^2\text{-}H_2)]SbF_6$ (**5**) were tested as catalysts for H/D exchange between ROH and D_2. Complex **5** is the most efficient, while **3** is moderately active and **1** and **2** are essentially inactive. Maximum activity arises when an M–H group is cis to a coordination site capable of binding both H_2 and ROH. The relevance of these results to the mechanism of H/D exchange in hydrogenase is also discussed.

Introduction

Molecular hydrogen complexes[1-10] are of current interest largely in connection with the difficult structural and spectroscopic problems they pose. Less attention has been given to their unusual reactivity patterns. They are often kinetically more efficient

Scheme I



* To whom correspondence should be addressed at: Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain.

Table I. H^+/D_2 Exchange Activity for Complexes 1–4

complex	ROH[a]	turnovers/min
$[CpRu(CO)(PPh_3)(\eta^2\text{-}H_2)](CF_3SO_3)$ (1)	*t*-BuOH	0.1
$[CpRu(CO)(PCy_3)(\eta^2\text{-}H_2)](CF_3SO_3)$ (2)	*t*-BuOH	0.1
$[Ru(dppe)_2H(\eta^2\text{-}H_2)]BF_4$ (3)	*t*-BuOH	2
$[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ (4)	*t*-BuOH	27
4	EtOH	16
4	Cy_3COH	12
4	MeOH	7.5
4	CF_3CH_2OH	2.5
$RhCl(PPh_3)_3$	*t*-BuOH	0

[a] Complex:ROH = 1:100 in CH_2Cl_2 as solvent.

Bronsted acids[3d,4,7c] than their classical counterparts, which have terminal M–H bonds only. They can also undergo rapid and reversible dissociation of H_2.[3,4b,7b,c,9] These two properties suggest that H_2 complexes might be good catalysts for H/D exchange between a protic solvent and D_2, because catalytic activity requires that the D_2 enters the coordination sphere and then exchanges. Hydrogenases carry out this H/D exchange reaction, and we proposed[11] the η^2-H_2 structure for hydrogen binding in hydrogenase.

All three types of hydrogenase, [Ni, Fe, S], [Ni, Fe, Se], and [Fe, S] contain transition-metal ions that are believed to be the H_2 binding site, but the oxidation states and exact coordination environments involved remain unclear. In the Ni-containing hydrogenase the Ni is believed to be the site of H_2 binding.[12] Hydrogenases catalyze H^+/D_2 exchange, although this is not the physiological role of these enzymes.[13]

We have reported a Ni complex that catalyzes H^+/D_2 exchange but were unable to detect any intermediate hydrides, largely because of the paramagnetism of the metal.[11b] There are few H^+/D_2 exchange catalysts involving metals other than Ni, for example Olive's Pd–salen[14] and the Os and Ru porphyrins of Collman et al.,[15] where a mechanism based on the deprotonation of a coordinated H_2 has been proposed (Scheme I).

We were interested in knowing whether H_2 complexes are in general good catalysts for H^+/D_2 exchange and have now studied a number of Ru and Ir systems in which the presence of a coordinated H_2 can be firmly established.

Table II. Substrate Properties and Activity for the Ir System[a]

ROH	K_{eq}[b]	pK_a[c]	turnovers/min
MeOH	4.55	15.5	7.5
EtOH	3	15.9	16
t-BuOH	0.64	19	27
CF_3CH_2OH	0.31	12.4	2.5
Cy_3COH	0		12

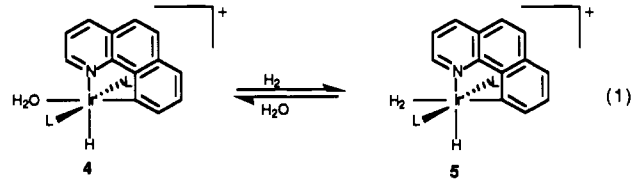
[a] $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ (4) as catalyst. [b] $K_{eq} = [Ir\text{-}OHR]P_{H_2}/[Ir\text{-}(H_2)][ROH]$ for eq 2 at 25 °C; estimated error ±15% (see Experimental Section for details). [c] Reference 16a.

Results

We chose complexes in which an H_2 is known to be present, either alone or cis or trans to a terminal M–H group, to see if any structure/activity relationship can be discerned. The simple dihydrogen complexes $[CpRu(CO)(PR_3)(\eta^2\text{-}H_2)]X$ (R = Ph (1), Cy (2); X = BF_4^-, $CF_3SO_3^-$) can be synthesized by the method of Chinn and Heinekey[4c] by addition of an acid (HBF_4 or CF_3SO_3H) to a dichloromethane solution of the neutral hydride $[CpRu(CO)(PR_3)H]$. The isolated complexes lose H_2 rather easily, and so to test for H^+/D_2 exchange the neutral hydride was dissolved in CH_2Cl_2 and a noncoordinating alcohol, such as ^{t}BuOH, was added in a molar ratio of complex to ROH of 1 to 100. The dihydrogen complex was generated "in situ" by addition of CF_3SO_3H (0.8 equiv) in a D_2 atmosphere. Only 0.8 equiv was used so that an excess of acid is avoided. D_2 was then bubbled through the mixture for 5 min, and the appearance of any –OD signal was monitored by ^{2}D NMR spectroscopy.

In other cases where the H_2 complex is more stable, they can be isolated and their activity determined directly. This was the method used for *trans*-$[Ru(dppe)_2H(\eta^2\text{-}H_2)]BF_4$ (3), formed by protonation of the neutral dihydride $[Ru(dppe)_2H_2]$ with HBF_4.[3a] The results obtained for these Ru complexes are collected in Table I.

Table I also contains the data for $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ (4, bq = 7,8-benzoquinolinato),[7c] which is known to bind H_2 to give the dihydrogen complex $[Ir(bq)(PPh_3)_2H(\eta^2\text{-}H_2)]SbF_6$ (5).[7a,c] H_2O has to be carefully excluded in the synthesis of 5, since H_2 is readily lost and the complex reverts to the aqua derivative (eq 1). In this case the M–H and M–(H_2) groups are cis.



4 5 (1)

As can be seen from Table I, 4 is by far the most efficient catalyst for H^+/D_2 exchange and so this system was studied in detail. Significantly, very different activity is observed when different alcohols are used as the protic substrates.

The reason could be that either the alcohols have to bind to the metal or the more basic alcohols more efficiently deprotonate the H_2 ligand. Mixtures of ROH and the dihydrogen complex 5 in CD_2Cl_2 were analyzed by ^{1}H NMR spectroscopy. For all the alcohols tested, except the extremely bulky Cy_3COH, a new hydride signal appeared around δ –16 corresponding to a newly formed iridium complex with bound ROH (6, eq 2). The equilibrium constants for eq 2 are shown in Table II (see Experimental Section for details).

Table II also includes the pK_a values for the alcohols, which we use in the discussion.[16] The pK_b values for ROH, although

(1) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.
(2) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.
(3) (a) Morris, R. H.; Sawyer, J. F.; Shiraalian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (b) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (c) Capellani, E. P.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Steele, M. R. *Inorg. Chem.* **1989**, *28*, 4437. (d) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875.
(4) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (b) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824. (c) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.
(5) Siedle, A. R. *Inorg. Chem.* **1988**, *27*, 1593.
(6) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506. (b) *Ibid.* **1987**, 1675.
(7) (a) Crabtree, R. H.; Lavin, M. *Chem. Commun.* **1985**, 794. (b) *Ibid.* **1985**, 1661. (c) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (d) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 124. (e) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.
(8) (a) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27. (b) Church, S. P.; Grevels, F.-W.; Herrman, H.; Scheffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30. (c) Sweaney, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374. (d) Sweaney, R. L.; Moroz, A. *J. Am. Chem. Soc.* **1989**, *111*, 3577.
(9) (a) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (b) Bianchini, C.; Pérez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279.
(10) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261.
(11) (a) Crabtree, R. H. *Inorg. Chim. Acta* **1986**, *125*, L7. (b) Zimmer, M.; Schulte, G.; Luo, X.-L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 193.
(12) Cammack, R.; Fernandez, V. M.; Schneider, K. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH: Weinheim, Germany, 1988; Chapter 8, p 167.
(13) (a) Van der Zwaan, J. W.; Albracht, S. P. J.; Fontijn, R. D.; Slater, E. C. *FEBS Lett.* **1985**, *179*, 271. (b) Lespinat, P. A.; Berlier, Y.; Fauque, G.; Czechowski, M.; Dimon, B.; Le Gall, J. *Biochimie* **1986**, *68*, 55.
(14) Henrici-Olive, G.; Olive, S. J. *J. Mol. Catal.* **1976**, 121.
(15) Collman, J. P.; Wagenknecht, P. S.; Hembre, R. T.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 1294.

$$[Ir(bq)(PPh_3)_2H(\eta^2\text{-}H_2)]SbF_6 + ROH = \underset{5}{} \quad [Ir(bq)(PPh_3)_2H(ROH)]SbF_6 + H_2 \quad (2)$$
$$\underset{6}{}$$

more relevant to the present situation, are less reliable and not known for all the alcohols studied.[16] The order of acid–base character of the alcohols follows that expected from inductive electron release by the R group.

Discussion

Ruthenium Systems. The dihydrogen ligand in the first system we tested, $[CpRu(CO)(PPh_3)(\eta^2\text{-}H_2)]X$ (**1**) ($X = BF_4^-, CF_3SO_3^-$), has proved to be quite acidic.[4c] Like many such complexes, it can be easily deprotonated by NEt_3 and other weak bases.[4a,c] This implies that H^+/D_2 exchange might be possible through a pathway similar to the one depicted in Scheme I. Catalyst stability was a concern, however, because $[CpRu(CO)(PPh_3)(\eta^2\text{-}H_2)]X$ is stable only at low temperature. Even in the presence of a base as weak as ether, it decomposes at room temperature to give free H_2 and bridging-hydride dimers of the type $\{[CpRu(CO)(PPh_3)]_2(\mu\text{-}H)\}X$.[4c] If catalysis is to be seen at room temperature, the presence of H_2 or D_2 must protect the catalyst from decomposition.

Experimentally no H/D exchange was observed at −10 °C and only trace activity occurred at room temperature (0.1 turnovers/min). The color change of the solution in the latter case clearly indicated that catalyst decomposition had taken place, and so H_2 does not protect the catalyst from decomposition.

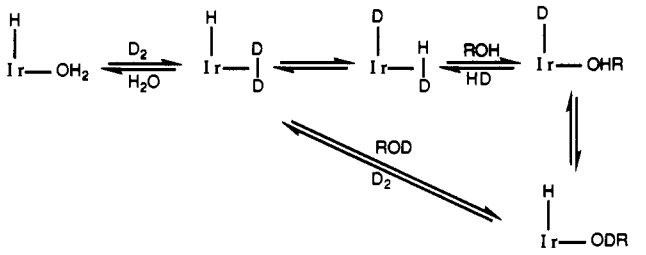
In this case the instability of the catalyst seems to prevent successful exchange. To try to avoid the formation of dimers, we moved to a derivative with a bulkier phosphine, $[CpRu(CO)(PCy_3)(\eta^2\text{-}H_2)]X$ (**2**).[4c] **2** is stable in solution at 298 K for several hours; slow decomposition ($X = CF_3SO_3^-$) leads to the appearance of a new Cp signal at δ 5.19. This is most probably due to H_2 loss and coordination of the counteranion because no new resonances are seen in the hydride region. Bubbling D_2 through a CD_2Cl_2 solution of **2** for 2 min did not lead to a noticeable decrease in the intensity of the H_2 resonance or disappearance of the small δ 5.19 Cp signal of the partially decomposed sample; H_2 loss seems to be irreversible in this system, and so **2** turned out to be no better as a catalyst for D_2/H^+ exchange than its PPh_3 analogue.

We next moved to the complex *trans*-$[Ru(dppe)_2H(\eta^2\text{-}H_2)]BF_4$ (**3**) of Morris et al.[3a] This complex easily undergoes reversible H_2 loss at room temperature without apparent dimerization or deactivation. Intramolecular exchange of the hydrogens in the $\eta^2\text{-}H_2$ moiety with the terminal hydride does occur, but the process is known to be more difficult than in the Fe or Os analogues, and $\Delta G^{\ddagger}$(Ru) is known to be greater than 15 kcal/mol.[3b] **3** is somewhat active for D_2/H^+ exchange: 2 turnovers/min were observed at room temperature with *t*-BuOH as the protic substrate (Table I). The presence of a terminal Ru–H in **3** allows a new exchange mechanism to operate, by which D_2 deuterates the terminal hydride position and this in turn subsequently exchanges with coordinated ROH. This will be discussed in detail below (mechanism A, Scheme II). The more efficient this exchange, the more active the catalyst would be, provided reversible H_2 loss is possible to ensure H_2–D_2 scambling. To test this mechanism in detail, we turned to a related iridium complex that is more convenient to study.

Iridium Complex. In 1985 we briefly noted that $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ (**4**, bq = 7,8-benzoquinolinato)[7c] undergoes exchange with D_2 to give the D_2O complex, and we have now studied its catalytic activity for H/D exchange between D_2 and ROH. $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ reacts with H_2 to form the dihydrogen complex $[Ir(bq)(PPh_3)_2H(\eta^2\text{-}H_2)]SbF_6$ (**5**),[7a,c] which is easily deprotonated and which undergoes rapid and reversible H_2 loss. The terminal hydride and the dihydrogen ligand are mutually cis, and rapid exchange results in a single averaged hydride resonance being observed by ^1H NMR spectroscopy at room temperature. Moreover, equilibration of the protons in the *cis*-$H(H_2O)$ moiety is observed for complex **4**.[7a,c]

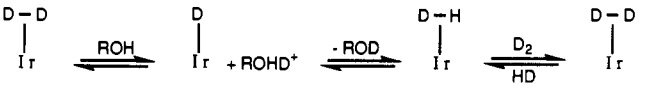
Scheme II

Mechanism A



Scheme III

Mechanism B



Complex **4** turned out to be a more efficient catalyst for D_2/H^+ exchange than the Ru systems: bubbling D_2 through a mixture of **4** and *t*-BuOH in CH_2Cl_2 gave 27 turnovers/min. It was observed that the activity of the catalyst depends on the protic substrate used and the activity increased in the order CF_3CH_2OH < MeOH < Cy_3COH < EtOH < *t*-BuOH (Table I). This activity trend does not correlate well either with the coordination ability or with the acidic properties of the alcohols tested (Table II).

It seems that at least two different mechanisms can operate in this process. In mechanism A of Scheme II, the $\eta^2\text{-}D_2$ ligand first exchanges with a terminal hydride and HD is then displaced by ROH, which then exchanges with the terminal D. Each step proposed in Scheme II has been observed independently in prior work.[7a,c] In mechanism B of Scheme III, direct deprotonation of the $\eta^2\text{-}D_2$ ligand by the alcohol is followed by reprotonation of the hydride and loss of HD.

In mechanism A, H_2 and ROH compete for the same coordination site and for efficient catalysis their binding ability should be comparable. The equilibrium constants for eq 2 were therefore measured for the different alcohol substrates (Table II). The use of an alcohol that is a better ligand tends to block the access of H_2 to the metal and therefore reduces the catalytic activity of the complex. This effect is shown by the very different catalytic activities observed for MeOH and EtOH, whose acid–base properties are similar but not their ability to bind Ir (Table II). MeOH is a better ligand than EtOH, and so fewer turnovers are seen when MeOH is used as a substrate.

Mechanism B requires an alcohol basic enough to deprotonate the H_2 ligand. This pathway accounts for the large difference in activity detected for *t*-BuOH and CF_3CH_2OH: both are equally poor ligands for Ir in this system, but they have very different acidic properties (Table II), the more acidic CF_3CH_2OH being the worse substrate. Cy_3COH ($K_{eq} = 0$) does not appear to coordinate at all to iridium, yet is an active substrate, suggesting that a pure mechanism B may well operate in this case. In the case of the bulky alcohols, it is also possible that the D_2 first exchanges with water through mechanism A and that the alcohol deprotonates the coordinated water.[17]

As a control, we verified that Wilkinson's catalyst, known to form a classical dihydride on reaction with H_2, does not catalyze H^+/D_2 exchange under these conditions.

Conclusions

Several dihydrogen complexes of Ru and Ir have been tested for catalytic activity in D_2/H^+ exchange. Maximum activity is

(16) (a) Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223. (b) Arnett, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260. (c) Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983.

(17) The exchange between $[Ir(bq)(PPh_3)_2D(D_2O)]SbF_6$ and Cy_3COH was tested. A mixture of the complex and Cy_3COH in CH_2Cl_2 under Ar was analyzed by ^2D NMR spectroscopy. Deuteration of the alcohol was observed. Even if it could not be detected spectroscopically, a small amount of free D_2O could account for the observed exchange.

found when an M-H moiety and a cis-coordination site available to D_2 and ROH are both present. Two mechanisms are discussed. In mechanism A, M-D_2 exchanges with the cis M-H site, and binding of ROH is followed by exchange with the cis M-D. In this case M-D acts as an intermediate deuterium reservoir in the process.

An alternative pathway (mechanism B) is based on deprotonation of the η^2-D_2 ligand by ROH acting as a base. The data show that mechanism A is certainly important for the coordinating alcohols, but mechanism B cannot be excluded. Conversely, for the noncoordinating alcohol, mechanism B operates.

In the case of hydrogenase, the Ni-C EPR signal has been shown to be associated with a nickel hydride.[18] The H/D exchange activity of the enzyme could therefore result from the presence of a site cis to this hydride at which H_2 and perhaps also H_2O can bind.

Experimental Section

^{2}D NMR spectra were recorded on a Bruker WM 500 spectrometer; chemical shifts were measured by using C_6D_6 as a reference. ^{1}H NMR spectra were recorded on a Bruker WM 250 instrument; chemical shifts were measured with reference to the residual solvent resonances.

Reagents were purchased from Aldrich Chemical Co. CH_2Cl_2, C_6D_6, and $CDCl_3$ were dried over CaH_2 and stored under Ar; the alcohols were distilled before use from CaH_2 (MeOH, CF_3CH_2OH) or Mg (EtOH, *t*-BuOH) under Ar.

The dihydrogen complexes were prepared according to published procedures.[3a,c,4c,7c]

H^+/D_2 Exchange Reactions. $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ (**4**, 6 mg, 5.3×10^{-3} mmol) was dissolved in CH_2Cl_2 (0.5 mL) in an NMR tube. *t*-BuOH (50 μL, 0.53 mmol) was added to the solution and 25 μL of a C_6D_6 solution in CH_2Cl_2, 0.167 M, as a standard. D_2 was bubbled through a solution for 2 min (5 cm^3/min flow), and the sample was immediately placed into the NMR probe. The amount of deuterated alcohol formed was calculated by measuring the integration ratio of the ^{2}D signal at δ 1.2 against the standard C_6D_6 (δ 7.15). Complete relaxation was ensured by using a pulse delay of at least five T_1's.

The H^+/D_2 exchange experiments using MeOH, EtOH, CF_3CH_2OH, and Cy_3COH as protic substrates and the experiments with complexes **1**-**3** as catalysts were carried out in the same way.

Reactions of $[Ir(bq)(PPh_3)_2H(\eta^2\text{-}H_2)]SbF_6$ (5) with Alcohols. Reaction with EtOH. A 0.01 M solution of $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$ (42.5 mg, 0.037 mmol) in CD_2Cl_2 (3.5 mL) was prepared in a Schlenk flask. CaH_2 (ca. 20 mg) was added to the solution, and H_2 was introduced in the flask; the mixture was let to stand for 30 min. A 0.5-mL volume of the supernatant solution was transfered to an NMR tube under a H_2 atmosphere. EtOH (6.2 μL, 0.106 mmol) was added to the solution, and a ^{1}H NMR spectrum (250 MHz, 298 K) was recorded. Distinct signals for the new EtOH complex **6** [δ 9.28 (b, 1 H, aromatic), -16.19 (t, $^2J_{H-P}$ = 15.8 Hz, Ir-H)] and for the dihydrogen complex **5** [δ 8.87 (b, 1 H, aromatic), -7.1 (vb, Ir-[H_3])] were observed.

The experiments using MeOH, *t*-BuOH, CF_3CH_2OH, and Cy_3COH as alcohols were carried out in the same way. ^{1}H NMR of the alcohol complexes (250 MHz, 298 K, δ): MeOH, 9.10 (b, 1 H), -16.09 (t, $^2J_{H-P}$ = 15 Hz); *t*-BuOH, -16.08; CF_3CH_2OH, -16.0.

The equilibrium constants were determined by integration of the distinct signals corresponding to **5** (δ 8.87) and the new Ir-ROH complex (aromatic or hydride signal). A pulse delay of at least five T_1's was used to ensure complete relaxation. Alcohol concentrations were determined by NMR integration of the aliphatic ROH signals in each case.

Acknowledgment. We thank the Spanish Ministry of Education and the Fulbright Commission (A.C.A.) and the NSF and NIH for funding.

Registry No. **1**, 135257-57-7; **2**, 135257-58-8; **3**, 97950-57-7; **4**, 98938-36-4; **5**, 102493-45-8; **6**, 135283-76-0; $[Ir(bq)(PPh_3)_2D(D_2O)]SbF_6$, 135310-51-9; $RhCl(PPh_3)_3$, 74735-07-2; *t*-BuOH, 75-65-0; EtOH, 64-17-5; Cy_3COH, 17687-74-0; MeOH, 67-56-1; CF_3CH_2OH, 75-89-8; hydrogenase, 9027-05-8; H_2, 1333-74-0.

(18) Moura, J. J. G.; Teixeira, M.; Moura, I.; LeGall, J. In *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Ed.; VCH: Weinheim, Germany, 1988; Chapter 9, p 191.

Contribution from the Laboratoire de Chimie des Métaux de Transition, URA-CNRS 419, Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

Synthesis and X-ray Structures of Two Unprecedented Heteropolymetalates $[As_3M_3O_{15}]^{3-}$ (M = Mo, W) and $[As_6CoMo_6O_{30}]^{4-}$. First Examples of Linear Triarsenate(III) and Cyclic Triarsenate(III)

J. Martin-Frère, Y. Jeannin,* F. Robert, and J. Vaissermann

Received March 7, 1991

Two new heteropolymetalates $[As_3M_3O_{15}]^{3-}$ (M = Mo, W) and $[As_6CoMo_6O_{30}]^{4-}$ have been prepared and their structures solved. **1**: $Na_3[As_3Mo_3O_{15}]\cdot 10H_2O$, monoclinic, space group $P2_1/a$, a = 19.160 (1) Å, b = 15.000 (5) Å, c = 8.241 (1) Å, β = 92.26 (1)°, and Z = 4. The structure is made of a Mo_3O_{13} group stabilized by an unprecedented linear $As_3O_7^{5-}$ triarsenate(III). **2**: $Na_3[As_3W_3O_{15}]\cdot 10H_2O$ is isostructural to **1**. **3**: $[Co(H_2O)_6]K_2[As_6CoMo_6O_{30}]$, cubic, space group $Pa3$, a = 14.890 (1) Å, and Z = 4. It was obtained by reaction of Co^{2+} with $[As_3Mo_3O_{15}]^{3-}$. The structure derives from the Anderson type; the central octahedron is filled up by cobalt, and it is capped on both sides by an unprecedented $As_3O_6^{3-}$ *cyclo*-triarsenate(III).

Heteropolymolybdates and heteropolytungstates were isolated for the first time in the second half of the nineteenth century.[1] Several authors became interested in that chemistry and described several species with the only help of chemical analysis. Particularly, several heteropolymolybdates and heteropolytungstates containing low Mo/As(III) and W/As(III) ratios were described by Gibbs[2] and by Ephraim and Feidel.[3] In this series the richest compound in arsenic corresponds to the composition M/As = 1 in atoms. Treated by a solution of a divalent Z cation (Z = Mn^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}), arsenomolybdates were found, and Gibbs gave them the formula $6MoO_3$, $3As_2O_3$, $2ZO,6H_2O$. The identification of those compounds was only based upon chemical analysis. This family has never been reinvestigated so that their structure remained unknown.

During the course of a general study of arsenic(III)-containing heteropolymetalates, we revisited the work of Gibbs and we have investigated by X-ray diffraction the structures of an arsenatomolybdate and of an arsenatotungstate in which the atom metal/As ratio is equal to 1. Those compounds exhibit an isolated M_3O_{13} group; it is actually stabilized by a linear triarsenate(III), itself observed for the first time. As a matter of fact, a metaarsenite was crystallographically described by Menary,[4] but it is

(1) Marignac, C. *C. R. Acad. Sci.* **1862**, *55*, 888. Marignac, C. *Ann. Chem.* **1862**, *25*, 362.
(2) Gibbs, W. *Am. Chem. J.* **1885**, *7*, 313.
(3) Ephraim, F.; Feidel, H. *Z. Anorg. Chem.* **1910**, *66*, 51.
(4) Menary, J. W. *Acta Crystallogr.* **1958**, *11*, 742.

0020-1669/91/1330-3635$02.50/0