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Hydrogen–Deuterium Exchange of the Anionic Group 6B Transition-Metal Hydrides. Convenient, in Situ Deuterium Transfer Reagents

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Abstract: The facile exchange of hydrogen for detuerium in the anionic group 6B carbonyl hydrides $HM(CO)_4L^-$ (M = Cr, W; L = CO, $P(OMe)_3$) has been studied in THF with CH_3OD, D_2O, and CH_3CO_2D. This has provided a synthesis of the deuterides, $DM(CO)_4L^-$, as well as a convenient in situ source of deuteride reducing reagents for organic halides. A number of such reductions are described, using ^2H NMR to demonstrate both selectivity and stereospecificity for certain systems. The carbonyl region of the infrared spectra of the hydrides is not affected by deuteration of the hydrides, suggesting that the M–H or M–D vibrational modes are not coupled significantly to CO vibrations in these hydrides. The mechanism of the H/D exchange and of a related H_2 elimination reaction is discussed. It is felt that both reactions proceed via an anion-stabilized dihydride.

Introduction

The anionic group 6B transition-metal carbonyl hydrides $HM(CO)_4L^-$ (M = Cr, Mo, W and L = CO, PR_3) were first synthesized[2] by processes designed[3] to avoid the more thermodynamically stable and well-known dimeric derivatives μ-$H[M(CO)_5]_2^-$,[4] which contain the bridging hydride ligand. Structural characterizations of the monomeric[5a] and dimeric[6] hydrides have been completed, as well as studies of hydride-transfer reactions[7] and of chemistry pertinent to the water gas shift reaction,[8] and related to Fischer–Tropsch chemistry.[9]

Although the carbonyl regions of the infrared spectra of $HM(CO)_4L^-$ have been assigned,[2,3,10] the metal–hydrogen vibrations have not. For the corresponding group 8B carbonyl hydrides,[11] deuterium labeling has demonstrated coupling between the carbonyl and metal–hydrogen vibrations; however, the latter also have not as yet been identified.

In pursuing the problem of assigning M–H stretching vibrations through the synthesis and spectroscopic characterization of the group 6B deuterides $DM(CO)_4L^-$, we have discovered a facile hydrogen–deuterium exchange reaction with CH_2OD, D_2O, and CH_3CO_2D. We now wish to report on this exchange, its mechanism, and characterizations of the deuterides by infrared and ^2H NMR spectroscopies. We also report here on the use of the group 6B deuterides $DM(CO)_4L^-$ (prepared in situ by addition of CH_3OD or D_2O to solutions of the hydrides in THF) as selective and stereospecific deuterium-transfer reagents for organic halides. The ability to deuterate the hydrides in situ and to use them directly in reactions with organic molecules circumvents the synthetic problems of loss of deuterium label on glass or chromatographic surfaces.

Table I. $^1H/^2H$ NMR Spectroscopic Data[a] for $[PPN^+][HM(CO)_4L^-]$ and $[PPN^+][DM(CO)_4L^-]$ in THF Solution

anion	$\delta[M-H(D)]$	J_{P-H}[b]	J_{W-H}	J_{P-D}	J_{W-D}
$HCr(CO)_5^-$	−6.73				
$DCr(CO)_5^-$	−6.84				
$HW(CO)_5^-$	−4.10		52.5		
$DW(CO)_5^-$	−4.09				8.0
cis-$HCr(CO)_4P(OMe)_3^-$	−7.00	54			
cis-$DCr(CO)_4P(OMe)_3^-$	−6.91			8.5	
cis-$HW(CO)_4P(OMe)_3^-$	−4.35	36	54		
cis-$DW(CO)_4P(OMe)_3^-$	−4.32			5.0	8.5

[a] Spectra of the deuterides were recorded in the presence of a 2-fold mole excess of CH_3OD in order to preserve the level of enrichment. [b] All *J* values in hertz.

Hydrogen–deuterium exchange is a common reaction for d_1 alcohols or D_2O with many classes of terminal hydrides: $HRe(CO)_5$,[12] $HMn(CO)_5$,[13] $HOsCl(CO)(PR_3)_3$,[14a] $OsH_2(CO)(PR_3)_3$,[14b] and $HCo(CO)_4$,[15] as well as for dimeric bridging hydrides that are either unsaturated or sterically accessible: $H_2Re_2(CO)_8$,[16] $H_2Os_3(CO)_{10}$,[16] and $[(\mu\text{-}H)_2(Rh(PPh_3)_2)(WCp_2)]PF_6$.[17] In contrast, the bridging hydride ligands of the clusters $H_3Re_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $HRe_3(CO)_{14}$ were found to be nonexchangeable.[13,16] In order to determine if hydrogen–deuterium exchange is generally possible for terminal hydrides but not so for hindered bridging hydrides, we have extended our studies to include the dimeric systems μ-$H[M(CO)_5]_2^-$ (M = Cr, Mo, W) and, as representative of group 8B, the anionic iron complex $HFe(CO)_4^-$.

Experimental Section

All experiments were carried out under N_2 using standard Schlenk techniques or in an Ar-filled glovebox. Solvents were dried and degassed as described below and further deoxygenated with N_2 immediately prior to use. Glassware used for the syntheses of the deuterides was prewashed with D_2O or with CH_3OD. Infrared spectra were recorded in 0.1-mm CaF_2 cells on a Perkin-Elmer 283 spectrophotometer calibrated against CO and H_2O. ^1H NMR were obtained on a 90-MHz Varian EM390

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Table II. IR Spectroscopic Data[a] for Various Hydrides and Their Deuterated Analogues

	ν_{CO}, cm^{-1} [b]		
hydride/deuteride	A_1^2(vw)	E(s)	A_1^1(m)
$HCr(CO)_5^-$	2017	1883	1852
$DCr(CO)_5^-$	2017	1882	1853
$HW(CO)_5^-$	2029	1888	1856
$DW(CO)_5^-$	2030	1887	1855
	A′(m)	A′ + A″(s)	A″(m)
cis-$HCr(CO)_4P(OMe)_3^-$	1971	1854	1817
cis-$DCr(CO)_4P(OMe)_3^-$	1971	1853	1817
cis-$HW(CO)_4P(OMe)_3^-$	1982	1855	1821
cis-$DW(CO)_4P(OMe)_3^-$	1982	1853	1819
	A_1^2(vw)	E(s)	A_1^1(m)
$HFe(CO)_4^-$	2001	1880	1910
$DFe(CO)_4^-$	2005	1881	1892

[a] Spectra of the group 6B hydrides were recorded in THF solution of the PPN^+ salts in the presence of a 2-fold mole excess (2 μL) of CH_3OH (hydrides) or CH_3OD (deuterides) in order to preserve the level of enrichment of the deuterides. The iron hydride and deuteride were recorded with H_2O and D_2O, respectively. [b] Wavenumbers for CO vibrations, ±1 cm^{-1}, as calibrated against gaseous CO (above 2000 cm^{-1}) or atmospheric H_2O (below 2000 cm^{-1}).

and ^2H NMR on a Varian XL200, referenced against THF.

Materials. THF and hexane solvents were distilled under N_2 from purple Na/benzophenone. Acetonitrile was dried over CaH_2, multiply distilled from P_2O_5, and stored under N_2, over 3-Å molecular sieves. Methanol-d_1 (Aldrich, Gold Label, 99.5% enrichment) was deoxygenated with N_2 and used directly, except for experiments calling for anhydrous CH_3OD, in which case 3-Å molecular sieves (prewashed with CH_3OD and activated at 120 °C) were used. D_2O (Aldrich) was also deoxygenated with N_2, as was glacial acetic acid (Aldrich, 98% d_1). Solvents and solutions were transferred via syringe or cannula. All other materials were purchased as reagent grade or better and were used without further purification.

Exchange Experiments: Preparative. The monomeric deuterides $DM(CO)_4L^-$ (M = Cr, W; L = CO, $P(OMe)_3$) were prepared as the PPN^+ salts (PPN^+ = bis(triphenylphosphine)imminium) from the hydrides[2,3,10] by taking advantage of the facile exchange, vide infra, with methanol-d_1. The synthesis of $[PPN][DCr(CO)_5]$ is typical of all preparations. $[PPN][HCr(CO)_5]$ (0.30 g, 4.1 × 10^{-4} mol) was dissolved in ca. 20 mL of THF and treated with CH_3OD (0.10 mL, 2.4 × 10^{-3} mol) under N_2 at room temperature. The resulting orange solution was immediately filtered through Celite (prewashed with CH_3OD), and crystallization was induced by slow addition of hexane, with agitation to prevent the formation of an oil. The supernatant was withdrawn via cannulation, and the solid orange product was washed with hexane and dried in vacuo. Yields were typically 80–90% based on the starting hydride. The extent of deuteration (ca. 80% after one recrystallization in the presence of CH_3OD, as described above) could be increased by repeating the procedure, as indicated by residual hydride resonance intensities in the ^1H NMR of the labeled products. In order to prevent loss of deuterium label in subsequent storage and handling of the deuterides, it was found to be necessary to pretreat glassware, spectrophotometer cells, etc. with CH_3OD or D_2O.

Exchange Experiments: in Situ. The studies of the exchange of hydrogen in the hydrides by deuterium from the various reagents, D_2O, anhydrous CH_3OD, and CH_3CO_2D, were carried out in dry THF. Typically 1 × 10^{-4} mol of hydride were dissolved in 2–3 mL of dry THF in the glovebox. A 2-fold molar excess (8 μL for CH_3OD) of the deuterium-containing exchange reagent was added, and either ^1H NMR, ^2H NMR, or IR spectra were obtained. The exchange was complete within the time of obtaining the spectra, as shown by the presence of the fully developed deuteride signal in the ^2H NMR (Table I), decrease of the hydride signal in the ^1H NMR, and/or shifts in the ν_{CO} absorptions in the infrared spectra (Table II), notable only for $[PPN][DFe(CO)_4]$. The small amounts of CH_3OH, H_2O, H_2O, etc. that were necessarily present in these experiments did not significantly alter the spectra (chemical shifts or infrared frequencies) or interfer with deuterium-transfer reactions, as checked by control experiments with the pure deuterides in the absence of these reagents. The in situ deuterium-transfer experiments were performed by using solutions of the deuterides prepared from the hydrides in this same way. A 3-fold mole excess of the organic substrate RX was then added, and the reduction was allowed to take place at 45 °C for 1–3 h. The alkane product was identified by both ^2H NMR and by gas chromatographic analysis on a Perkin-Elmer Sigma 2 instrument.

Decomposition Experiments. The decomposition of the monomeric hydride $[PPN][HW(CO)_5]$ by protic solvents, or in the presence of protic reagents in various solvents, was performed by monitoring the appearance of the product μ-$H[W(CO)_5]_2^-$ with infrared spectroscopy at 1941 cm^{-1}. A qualitative order of reactivity was established on the basis of the relative rate of appearance of the hydride-bridged dimer. These experiments were performed at 26.0 ± 0.1 °C, using 0.03 mmol of the starting hydride in 15 mL of THF, with a 100-fold mol excess of the reagents HBF_4, CH_3CO_2H, PhOH, H_2O, or CH_3OH.

Results and Discussion

The anionic group 6B metal carbonyl deuterides $DM(CO)_4L^-$ (M = Cr, W; L = CO, $P(OMe)_3$) can be prepared from the corresponding hydrides by taking advantage of the facile exchange shown in eq 1. As described in the Experimental Section, the

$$HM(CO)_4L^- + CH_3OD \xrightleftharpoons{THF} DM(CO)_4L^- + CH_3OH \qquad (1)$$

deuterides can be isolated and, if further enrichment is desired, the procedure repeated. These preparations typically employ an excess of the CH_3OD exchange reagent, and the methanol-d_1 does not need to be dried in any special way, because the exchange can also be accomplished with D_2O. The exchange is rapid and appears to be quite general for this class of monomeric hydrides. In subsequent handling of the deuterides, the label was readily lost if care was not taken to pretreat glassware, spectrophotometer cells, etc. with CH_3OD or D_2O. Under the synthetic conditions noted above, no complications due to the decomposition shown in eq 2 were noted. The relative rates of reactions 1 and 2 will be discussed below.

$$2HM(CO)_4L^- \xrightarrow{H^+} \mu\text{-}H[M(CO)_4L]_2^- + {}^1/_2H_2 \qquad (2)$$

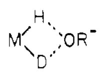
The exchange was also studied on a smaller scale by ^1H (5-mm tube) or ^2H (10-mm tube) NMR spectroscopy. These in situ experiments employed 1.0 × 10^{-4} mol of starting hydride (as the PPN^+ salts), a 2-fold molar excess of deuterium reagent, and dry THF solvent. Solutions of the hydrides were treated at room temperature with the exchange reagent, and the NMR spectra were quickly taken. All of the monomeric group 6B hydrides studied here exchanged quickly ($t_{1/2} < 1$ min) with CH_3OD (anhydrous), D_2O, and CH_3CO_2D, as shown by the loss of intensity in the hydride resonance (^1H NMR) or the appearance of the deuteride resonance (^2H NMR) at nearly the same chemical shift (Table I).

A comparison is presented in Table II of the infrared spectroscopic data for the deuterides and hydrides of interest here. It is especially interesting that for both the group 6B hydrides $HM(CO)_5^-$ and *cis*-$HM(CO)_4PR_3^-$ CO vibrational modes are not significantly coupled to M–H/D modes, as shown by small or nonexistent shifts in ν_{CO} upon deuteration. This was also observed for the neutral carbonyl hydrides (deuterides) $HMn(CO)_5$ and $HRe(CO)_5$, where the M–H and M–D stretching frequencies were found to be removed from the carbonyl region of the infrared spectrum.[12b,13] For example, ν_{MH} is reported to be 1775 (M = Mn) and 1882 cm^{-1} (M = Re).[12b] (Infrared and Raman studies are under way to locate the M–H/D modes and to understand why these modes are not coupled to CO modes in the anions $HM(CO)_4L^-$.) In contrast, the CO modes in the anions $HM(CO)_4^-$ (M = Fe, Ru, Os) were found to be coupled to M–H/D modes, although the M–H/D stretching frequencies were not observed.[11]

We have also studied the possibility of exchange of hydrogen for deuterium in the anion $HFe(CO)_4^-$ using anhydrous CH_3OD, D_2O, and CH_3CO_2D. The iron hydride does not exchange with dry CH_3OD. It does exchange slowly ($t_{1/2} > 1$ h) with D_2O (10-fold excess) and readily with CH_3CO_2D, as shown by shifts[11] in the IR spectrum (Table II) and by ^2H NMR.

The results reported here, together with those mentioned in the Introduction suggest as a general trend the facile exchange of terminal hydride ligands, both in hydrides considered to be acidic (such as $HMn(CO)_5$) and those considered to be hydridic (the anionic hydrides of this study). Reports of the lack of exchange of bridging hydride ligands in clusters were extended in this work, using the anionic dimers μ-H[M(CO)$_5$]$_2^-$, M = Cr, W. The latter did not exchange over prolonged periods in THF with either CH_3OD or D_2O. The more basic bridging hydride in [(μ_2-H)(μ_2-(Ph)$_2$PCH$_2$CH$_2$P(Ph)$_2$)Mo$_2$(CO)$_8^-$][18] also did not exchange with CH_3OD or D_2O. There are exceptions to the general rule of nonexchange for bridging hydride ligands. These are the μ_2-bridging dihydrides such as $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ where the hydride ligands are less crowded by CO ligands than is true of other μ_2-hydride bridges in nonexchanging clusters and where the metal centers are electronically unsaturated.[13,16] Another obvious exception would be hydride-bridged dimers which are capable of dissociation to a monomeric hydride.

It is especially impressive that the ability of the hydrides to exchange with d_1 alcohols and D_2O (see Introduction) covers a range of acidities and a variety of anionic, neutral, and cationic hydride complexes. The mechanism that we favor for this exchange process in the group 6B anionic hydrides involves the associative and reversible formation of the anion-stabilized dihydride I, where OR$^-$ = CH_3O^-, OD$^-$, or $CH_3CO_2^-$. A precedent for this structure can be found in the known borohydride complexes (μ-H)$_2$BH$_2$M(CO)$_4^-$ (M = Cr, Mo),[5] although the coordination number of the metal in (μ-H)$_2$BH$_2$M(CO)$_4^-$ is probably one less than that proposed here.



I

If the anion-stabilized dihydride structure above is an important intermediate or transition state in H/D exchange, then, as the base strength of OR$^-$ is diminished or its leaving ability is enhanced, H_2 (actually, HD) elimination may become competitive with H/D exchange. This would give the pentacoordinate species [M(CO)$_4$L], which are known to react with the hydrides HM(CO)$_4$L$^-$ to form dimeric, hydride-bridged products,[2,3] as in eq 2. We have in fact observed this reaction for the anionic group 6B hydrides in exchange experiments employing larger excesses of the deuterium reagents CH_3OD, D_2O, or CH_3CO_2D. The initial and rapid exchange to form the deuterides is followed by a subsequent and slower decomposition to the deuteride-bridged dimers μ-D[M(CO)$_4$L]$_2^-$, as monitored via ^{2}H NMR.

In this connection we have studied the relative rates of decomposition of the hydride HW(CO)$_5^-$ in THF by various acids (see Experimental Section). The relative order of reactivity was found to be $HBF_4 > CH_3CO_2H > PhOH > H_2O > CH_3OH$, paralleling the increasing aqueous pK_a for these acids. These experiments differ from the in situ exchange experiments described above in that a 100-fold excess of the acids were employed. For HBF_4 and CH_3CO_2H, vigorous evolution of hydrogen was observed upon addition of the acid. The decomposition by CH_3OH and by PhOH was also studied in the more polar solvent acetonitrile, and the rate of production of μ-H[W(CO)$_5$]$_2^-$ was found to be 3–4 times faster than in the less polar THF solvent. This is consistent with the localized negative charge in the above-proposed anion-stabilized dihydride; when the anion OR$^-$ is stabilized by the more polar solvent, H_2 elimination becomes faster.

Although we favor this simple anion-stabilized dihydride intermediate or transition state for both H/D exchange of and H_2 elimination from the anionic group 6B hydrides, other mechanisms must be considered: (1) The reaction may involve protonation at the hydride ligand in a more or less linear fashion: M–H$^-$···D–OMe. It is hard to imagine in this case, however, how H/D exchange could be so competitive with H_2 elimination if an incipient dihydride were not intimately associated with the anion OR$^-$. (2) The reactions could proceed by simple dissociation of a proton from the hydride, assisted by hydrogen bonding to available basic sites in the medium (eq 3). This model involves

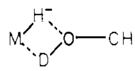
$$MH \rightleftharpoons M^- + H^+ \qquad (3)$$

loss of the hydride ligand as H$^+$ without much M–D bond formation in the transition state. Although this is an attractive possibility for the neutral and the more acidic[19] hydrides such as HCo(CO)$_4$ and HMn(CO)$_5$, the similar reaction, eq 4, for the

$$HM(CO)_4L^- \rightleftharpoons H^+ + M(CO)_4L^{2-} \qquad (4)$$

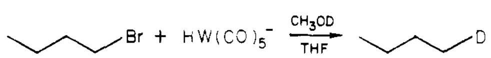
hydridic group 6B anions is not so reasonable. Furthermore, we would expect that more basic hydrides, such as those in which L = P(OMe)$_3$ as opposed to CO, would be less inclined to undergo H/D exchange by a route involving deprotonation. In fact, substitution of CO by P(OMe)$_3$ accelerates the rate of H/D exchange (vide infra).

It is appropriate to consider the continuum of possibilities involving CH_3OD association with the M–H group ranging from zero to complete M–D bond formation or zero to complete M–H bond cleavage. The two possibilities are distinguishable in that one case (II, M–H bond cleavage via hydrogen bonding of an acidic hydride ligand to methanol) does not involve a dihydride, while the other case (I, formation of a M–D bond via protonation by CH_3OD at the metal) does involve a dihydride, stabilized by CH_3O^-. We have been able to substantiate the latter case (formation of an anion-stabilized dihydride) with the following competition experiment. A solution containing equal molar amounts of the two hydrides HCr(CO)$_5^-$ and *cis*-HCr(CO)$_4$P(OMe)$_3^-$ was treated with 1 equiv of anhydrous CH_3OD. The first formed deuteride was *cis*-DCr(CO)$_4$P(OMe)$_3^-$, indicating faster exchange for the phosphite-substituted hydride. Thus the rate of H/D exchange is faster for the hydride complex in which CO has been replaced by the stronger σ-electron donor P(OMe)$_3$. Such increased electron density should retard loss of the hydride ligand as H$^+$ (structure II) but should enhance protonation at the metal to give a dihydride (structure I). Careful rate and equilibrium studies of H/D exchange are presently underway in order to determine if there is a kinetic isotope effect.



II

Finally, we wish to report on a very convenient use of the group 6B anionic deuterides (generated in situ by exchange with the hydrides with CH_3OD) as deuterium-transfer reagents for the reduction of organic halides. We have found that it is possible to react the hydrides in THF, in the presence of CH_3OD or D_2O, with a variety of organic halides to give, in some cases, stereospecific incorporation of deuterium. All reductions that are normally possible with the hydrides[7] can be performed in the presence of CH_3OD or D_2O to give deuterides. The deuterium-labeled products can be identified conveniently with ^{2}H NMR and GC analysis. Reactions 5–9 are representative.



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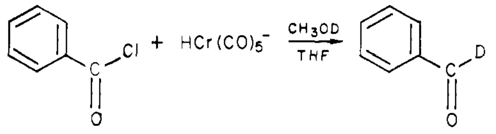

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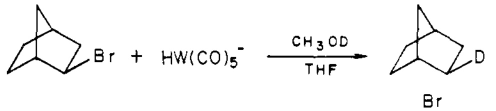

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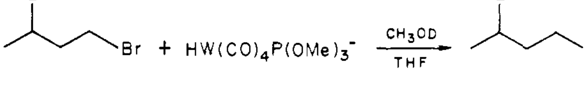

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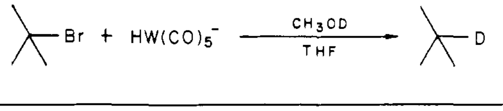

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Reaction 7 demonstrates the stereospecific nature of these reductions using $DW(CO)_5^-$; only the exo isomer (δ 1.49) is formed. Reaction 8 demonstrates the selectivity of these reductions; as noted elsewhere,[7] primary halides are reduced more readily than are secondary halides.

Summary

The anionic group 6B carbonyl hydrides undergo a facile exchange of deuterium for hydrogen with the reagents CH_3OD, D_2O, and CH_3CO_2D. This affords a convenient synthesis or in situ source of the deuterides. Labeling the hydrides with deuterium in this way does not cause changes in the CO region of the infrared spectra of the hydrides, suggesting that the CO and M–H/D stretching vibrations are not coupled in these complexes.

The ability to undergo H/D exchange has been shown to be general for a large variety of terminal hydrides. In contrast, the bridging hydride ligand does not generally exchange with CH_3OD or D_2O, with the exceptions noted in the Discussion. When a large excess of exchange reagent is used, hydrogen elimination (leading to dimer formation) becomes observable, although in all cases H/D exchange occurs more readily. The decomposition by acids of the monomeric hydrides via hydrogen elimination is faster in the order: $HBF_4 > CH_3CO_2H > PhOH > H_2O > CH_3OH$. A common anion-stabilized dihydride intermediate or transition state is proposed both for H/D exchange and for the slower H_2 elimination processes.

The facile exchange of the hydrides with CH_3OD or with D_2O affords a convenient in situ source of the deuterides $DM(CO)_4L^-$ for either spectroscopic studies or for deuterium transfer (sometimes selectively and/or stereospecifically) to organic halides.

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Registry No. $HCr(CO)_5^-$, 18716-81-9; *cis*-$HCr(CO)_4P(OMe)_3^-$, 89210-44-6; $HW(CO)_5^-$, 77227-36-2; *cis*-$HW(CO)_4P(OMe)_3^-$, 82963-27-7; $DCr(CO)_5^-$, 90900-59-7; *cis*-$DCr(CO)_4P(OMe)_3^-$, 90900-60-0; $DW(CO)_5^-$, 89210-45-7; *cis*-$DW(CO)_4P(OMe)_3^-$, 90900-61-1; $HFe(CO)_4^-$, 18716-80-8; CH_3OH, 67-56-1; CH_3CO_2H, 64-19-7; H_2, 1333-74-0.

Molecular Environment Effects in Redox Chemistry. Electrochemistry of Ether-Linked Basket-Handle and Amide-Linked Basket-Handle and Picket-Fence Iron Porphyrins

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Abstract: The presence of basket-handle chains or a picket-fence structure exerts a pronounced influence on the redox and coordination chemistry of iron porphyrins. The electrochemical behavior of four different ether-linked basket-handle, three different amide-linked basket-handle, and one amide-linked picket-fence iron porphyrins was investigated in comparison with 5,10,15,20-tetra-*o*-anisylporphyrin in the first series and 5,10,15,20-tetraphenylporphyrin in the second. Large effects of the superstructures appear in the thermodynamics of the three successive $Fe^{III} \rightarrow Fe^{II} \rightarrow Fe^{I} \rightarrow Fe^{I\cdot}$ reduction steps and the Cl^-/DMF substitution reaction at Fe^{II}. The kinetics of the latter reaction also varies significantly in the series. All four reactions are thermodynamically unfavored by the ether-linked chains while the amide-linked structures produce completely opposite effects. Changes as large as 4–5 orders of magnitude result. Steric hindrance to solvation of the negatively charged complexes appears as the predominant effect of the ether-linked structures. Steric interactions between the chains and the axial ligands also manifest themselves in the thermodynamics of the $[Fe^{II}DMF]/[Fe^{I}]^-$ electron-transfer reaction as well as the Cl^-/DMF substitution process at Fe^{II}. These effects also exist in the amide-linked series. They are, however, largely overcompensated by a specific effect of the NHCO groups involving hydrogen bonding and/or dipole–charge interactions resulting in a strong stabilization of the negatively charged species. In both series, steric interactions between the chains and the axial ligands appear to be responsible for the large variations in the ligand exchange and electron-transfer reactions when passing from flexible to more rigid chains.

In an effort to mimic and understand the dioxygen transport and activation properties of hemoproteins, several types of superstructured iron porphyrins have been synthesized and characterized during the last 10 years. These "picket-fence",[2] "capped",[3] "cyclophane",[4] "pocket",[5] "crowned",[6] "strapped",[7] and "basket-handle"[8] iron porphyrins were originally devised to protect

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