

## Mechanisms of group transfer in anionic transition metal hydrides and alkyls

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**Abstract** – Studies of intermolecular hydride transfer from coordinatively saturated  $\text{HM}(\text{CO})_4\text{L}^-$  ( $\text{M} = \text{Cr}, \text{W}; \text{L} = \text{CO}, \text{PR}_3$ ) conclude the M-H functional group to be isolated and the gp 6 metal center to be inaccessible to entering substrates. In contrast the analogous  $\text{HFe}(\text{CO})_3\text{L}^-$  show a metal-based, rather than hydride-based, nucleophilicity. Hydride transfer reactions of  $\text{HW}(\text{CO})_5^-$  are compared with the methyl analogues in  $\text{MeW}(\text{CO})_5^-$ . The latter are considerably more sluggish in reactions with various organic substrates (RX,  $\text{RC}(\text{O})\text{Cl}$ ,  $\text{RC}(\text{O})\text{H}$ ) and display characteristics of  $\text{Me}\cdot$  radical intermediates.

Studies of soluble transition metal complexes containing the hydride ligand have guided applications of the metal-hydrogen functional group to inorganic and organic synthesis. As importantly, knowledge gained from understanding well-characterized structural/chemical relationships may be extrapolated to heterogeneous systems of hydrogen, dissociatively adsorbed on a catalytically active metal surface, which are less amenable to chemical and spectroscopic monitoring. Our own research has focused on anionic transition metal hydrides,<sup>1</sup> primarily of derivatives of gp 6 and gp 8 metal carbonyls, such as I and II.

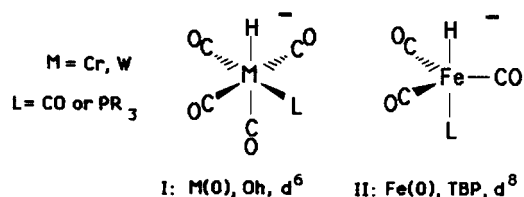
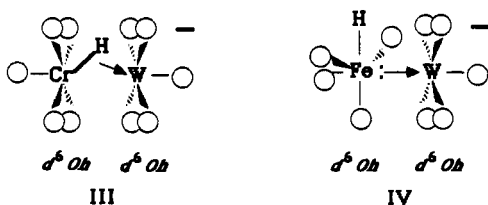


Table 1. Mulliken Atomic Charges From Fenske-Hall Molecular Orbital Calculations.

H	-.432	-.239	-.210
M	+.375	-.176	-.248
$\text{C}_{\text{ox}}$	-.160	+.022	(P, +.545)
$\text{O}_{\text{ox}}$	-.126	-.230	
$\text{C}_{\text{eq}}$	-.061	+.055	-.023
$\text{O}_{\text{eq}}$	-.104	-.181	-.237

In gp 6 settings the metal hydrogen bond is viewed as an isolated functional group in that the metal is not accessible to entering substrates. That is, the supporting ligands are not labile and the metal is in a preferred  $d^6$ , Oh setting, and indisposed towards oxidative addition. Thus the site of reactivity is hydride ligand based rather than metal centered. In contrast, the  $\text{HFe}(\text{CO})_3\text{L}^-$  anions<sup>2</sup> are expected to display a metal based nucleophilicity in that the  $d^8$ , TBP anions are prone to oxidative addition, generating an Oh,  $d^6$ , Fe(II) center. Charge distributions were calculated for representative anions by the Fenske-Hall approach and results are given in Table I. Note the charge distribution differs for the two types of

anions and also that the substitution of a  $\text{PR}_3$  ligand for CO results in more electron density on the metal for the TBP gp 8 complexes. This calculated charge distribution is supported by site selective ion-pair studies. In low polarity solvents such as  $\text{Et}_2\text{O}$  or THF, the alkali cations  $\text{Na}^+$  or  $\text{Li}^+$  were found to form tight ion pairs with  $\text{HFe}(\text{CO})_3\text{L}^-$  at carbonyl oxygen or Fe sites,<sup>3</sup> whereas with the  $\text{HW}(\text{CO})_4\text{L}^-$  anions there is evidence for contact ion pairing at the hydride as well as CO oxygen sites.<sup>4</sup> An even clearer indication of electron distribution is the interaction of our hydride anions with transition metal Lewis acids. The  $\text{HM}(\text{CO})_5^-$  anion readily displaces THF from photochemically generated  $\text{THF}\cdot\text{M}(\text{CO})_5$  yielding the mixed metal hydride dimers of structural form III whereas the products of  $\text{HFe}(\text{CO})_4^-$  or of  $\text{MeFe}(\text{CO})_4^-$  and  $\text{THF}\cdot\text{M}(\text{CO})_5$  are of form IV.<sup>5</sup>



Charge distribution differences are expected to manifest themselves in the mechanism(s) chosen by a particular metal hydride in its reaction with a particular substrate. The mechanistic possibilities of gp 6 anionic TM hydrides are expected to be limited to

- 1)  $\text{S}_{\text{N}}2$ , hydride site reactivity,
- 2) hydrogen atom transfer from the anion
- 3) electron transfer followed by hydrogen atom transfer from the neutral radical.

Both 2) and 3) involve radical intermediates. Indications that more than one mechanism might be operative have come from our work<sup>6</sup> and earlier work of Bergman,<sup>7</sup> using as mechanistic probes the reactions of alkyl halides. The rates of reaction of *n*-BuBr with the anionic hydrides follow a second order kinetic rate expression, first order in metal hydride and first order in alkyl bromide. Table II shows that the rate of reduction of *n*-BuBr have an opposite dependence on metal hydride as compared to *t*-BuBr.<sup>6</sup>

Table II. Reaction of  $\text{PPN}^+\text{HM}^-$  with  $\text{RX}$ : Dependence on  $\text{PPN}^+\text{HM}^-$ .

M	RATE = $k_2[\text{HM}^-][\text{RX}]$		
	$k_2 \times 10^3 \text{ sec}^{-1}\text{M}^{-1}$		
	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	<i>s</i> -C <sub>4</sub> H <sub>9</sub> Br	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Br
Cr(CO) <sub>5</sub>	1.79(±0.05)	1.65(±0.28)	3.17(±0.08)
W(CO) <sub>5</sub>	3.31(±0.13)	1.79(±0.05)	2.81(±0.16)
Cr(CO) <sub>4</sub> P(OCH <sub>3</sub> ) <sub>3</sub>	30	1.89(±0.06)	0.81(±0.05)
W(CO) <sub>4</sub> P(OCH <sub>3</sub> ) <sub>3</sub>	50	4.24(±0.18)	0.21(±0.01)

There is hardly any change in  $k_2$  values for  $\text{HCr}(\text{CO})_5^-$  with increasing degree of branching of the RBr. With the  $\text{P}(\text{OMe})_3$  substituted hydrides however a decrease in rate constant parallels the increase in branching until with the 3° alkyl bromides the reactivity of the  $\text{P}(\text{OMe})_3$  substituted hydride is actually less than that of the all-CO hydrides,  $\text{HM}(\text{CO})_5^-$ .

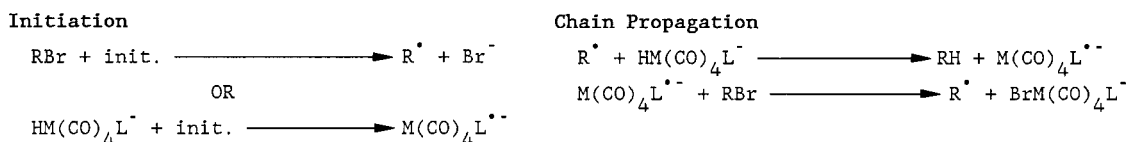
This difference in rate constants is substantiated by product distributions in competition reactions. Thus when a 1:1 mixture of primary- and tertiary- BuBr was reacted with one equivalent of metal hydride, the  $\text{HCr}(\text{CO})_5^-$  showed selectivity for the tertiary center,  $\text{HW}(\text{CO})_5^-$  showed some selectivity for the primary halide and there was 100% selectivity for *n*-BuBr in the case of the  $\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3^-$ .

The reduction of organic halides that are precursors to radicals which are subject to rapid skeletal rearrangements is a well known landmark reaction for the physical organic chemist. The cyclopropyl carbonyl radical for example undergoes a rapid ring-opening reaction yielding the linear alkenyl radical.<sup>8</sup> If the rate of ring opening is faster than the rate of H• abstraction by the cyclized radical, the presence of linear product is clear indication of the presence of a radical path. For example, with  $R_3SnH$ , all of the product is from the rearranged radical, and reductions by  $R_3SnH$  are accepted as following chain mechanisms. Bergman has found for  $CpV(CO)_3H^-$ , a substantial amount of rearranged product but nevertheless a large amount of cyclized (product) also resulted.<sup>7</sup> For the gp 6 anionic hydrides the different distribution depends on the presence or absence of  $P(OMe)_3$  substituent.<sup>6</sup> With no other information we might conclude the cyclopropyl-carbonyl radical is formed but in the case of  $HW(CO)_4P(OMe)_3^-$  either there are fewer radicals formed (i.e., an  $S_N2$  path is preferred) or the cyclopropyl-carbonyl radical abstracts H• from some H• source faster than it rearranges. This is the usual problem with these radical probes.

In an attempt to circumvent the problems inherent with skeletal rearrangement radical probes, the reactions of group 6 metal hydrides,  $PPN^+HM(CO)_4L^-$  ( $M = Cr, L = CO; M = W, L = CO, P(OMe)_3$ ), with two mechanistic probes, 6-bromo-1-hexene and 4-bromo-3,3-dimethyl-1-butene, in THF at 25°C were studied.<sup>9</sup> Neopentyl-like probe was reduced (presumably) exclusively by a radical chain process, and the second-order rate constants ( $k_H$ ) for hydrogen atom abstraction from  $HM(CO)_4L^-$  by the intermediate radical, 2,2-dimethyl-3-butenyl, were determined. The 1-hexenyl bromide unhindered probe was reduced by both an  $S_N2$  pathway and a radical chain process. The second-order rate constants for hydrogen atom abstraction from  $HM(CO)_4L^-$  by 5-hexenyl were estimated, and the percentages of reduction of 1-hexenyl-bromide by the  $S_N2$  pathway and the radical chain process were calculated. The percentage of reduction by the  $S_N2$  pathway increased in the order  $HCr(CO)_5^-$  (90%) <  $HW(CO)_5^-$  (99%) <  $HW(CO)_4P(OMe)_3^-$  (100%).

The mechanism expressed below is the typical radical chain mechanism proposed for the reductions of alkyl tin hydrides, and also by Bergman, et al., for reductions of  $RX$  by  $CpV(CO)_3H^-$ .<sup>7</sup> What our work adds to the latter is evidence that the observed unrearranged products arise both from direct trapping of  $R\cdot$  and from hydride displacement of  $Br^-$  from the original  $RBr$  substrate. We have further substantiated that the substrate to be reduced can

### Scheme



elicit substantially different reaction behavior from metal hydrides. For example, whereas  $HCr(CO)_5^-$  selects  $S_N2$  displacement over the radical chain pathway in a rate ratio of 9:1 for 1°-alkyl bromides, it should not be concluded that the  $S_N2$  path will predominate with other electrophiles. With 3°-alkyl bromides and  $HCr(CO)_5^-$  the radical chain velocity must be many times greater than that for either reduction pathway of 1°-alkyl bromides. Substrates with more positive carbon centers, as in the carbonyl carbon of acyl halides, generate hydride transfer character whereas less electrophilic carbon centers (as in  $RI$  and some  $RBr$ ) are better matched for 1-electron process -- also readily accommodated by the anionic hydrides. It is therefore reasonable that intermediate situations exist wherein similar barriers provide access to contemporaneous paths, i. e., exclusive reaction paths are not mandated.

Neutral complexes of early transition metal hydrides have also been observed to react as nucleophilic hydride transfer reagents. Labinger and Komadina<sup>10</sup> compared various neutral transition metal hydrides according to their ability to reduce the ketones  $CH_3C(O)CH_3$  and  $CF_3C(O)CH_3$ . For example,  $CpMo(CO)_3H$  was unreactive with both ketones;  $Cp_2MoH_2$  reacted with

the more electrophilic  $\text{CF}_3\text{C}(\text{O})\text{CH}_3$  over the course of one day but not at all with  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ ;  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  reduced acetone slowly and  $\text{CF}_3\text{C}(\text{O})\text{CH}_3$  upon time of mixing; and  $\text{Cp}_2\text{ZrH}_2$  reacted instantaneously even with  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ .<sup>10</sup> That work is part of the basis for describing the early transition metal hydrides as having "hydridic" character, whereas the later transition metal hydrides, particularly those rich in carbonyls and prone to yield very stable anions upon deprotonation, behave as acids in many of their reactions.

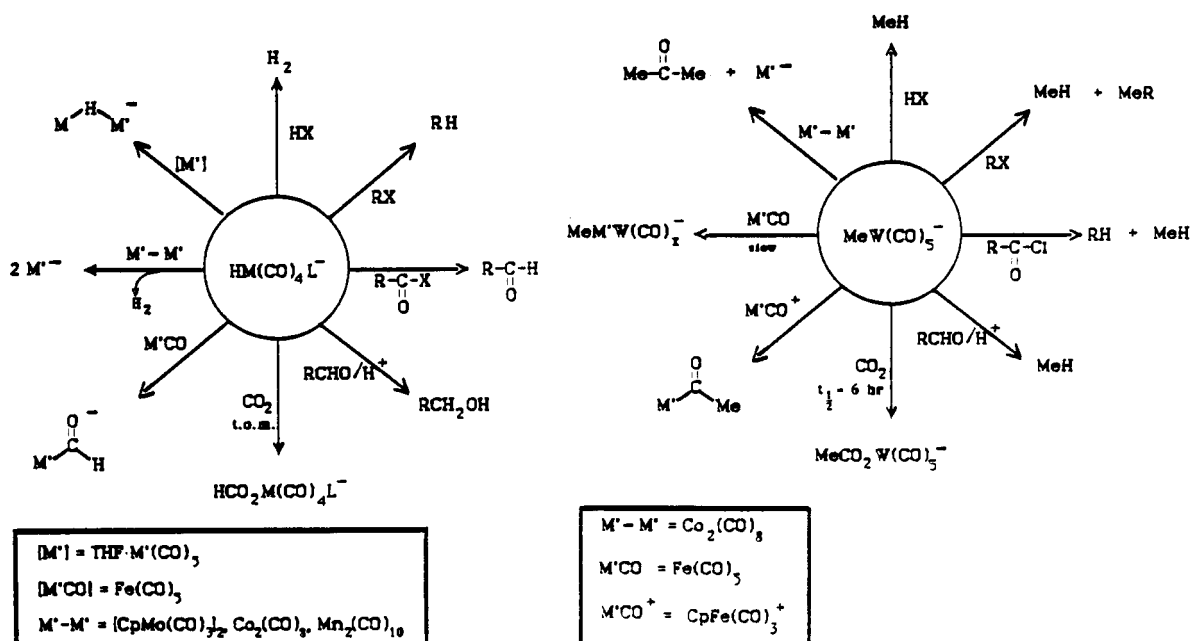
In order to provide a more definite comparison of neutral nucleophilic hydride,  $(\eta\text{-C}_5\text{H}_5)_2\text{Nb}(\text{H})\text{CO}$  with the anionic group 6 hydrides we have undertaken kinetic and radical probe studies of organic halide reductions.<sup>11</sup> As might have been expected,  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  reduced *n*-BuBr, much more slowly (one to two orders of magnitude) than the analogous reactions with anionic hydrides. In contrast, reduction of *t*-BuBr by  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  proceeded approximately three times more rapidly than reduction of *n*-BuBr by the niobium hydride and was similar in rates to the anionic hydrides for reactions with RX. Reductions of 6-bromohexene (yielding rearranged products), as well as phenylacetyl chloride (yielding decarbonylated products) provided evidence for radical intermediates.

The gp 6 metal carbonyls provide a unique opportunity to compare the reactivity of a metal hydride functional group and metal alkyl or-aryl functional group. Using the CO ligand as a spectroscopic handle the appropriate IR stretching frequencies

	$\nu(\text{CO}) \text{ cm}^{-1}$ (as $\text{PPN}^+$ salts in THF)		
$\text{MeW}(\text{CO})_5^-$	2028 w	1883 s	1834 m
$\text{HW}(\text{CO})_5^-$	2029 w	1888 s	1856 m

indicate a very similar electronic distribution in the two anions. Cyclic voltammetry show that irreversible oxidation occurs with greater ease for the  $\text{MeW}(\text{CO})_5^-$  ( $E_p = +.391 \text{ v}$ ) as compared to  $\text{HW}(\text{CO})_5^-$  ( $E_p = +.447 \text{ v}$ ).<sup>12</sup> Certainly the nucleophilic site of reactivity is much more accessible in the hydride as compared to the  $\text{MeW}(\text{CO})_5^-$ .

Comparisons of reactivity for the two functionalities are shown below in the "reactivity wheels." Reactions with electrophiles such as  $\text{CO}_2$  indicate the sluggish nature of the methyl-tungsten as compared to the hydridotungsten complex. The hydride from  $\text{HW}(\text{CO})_5^-$  also



transferred to a metal-activated carbon monoxide with much greater ease than is a methyl group from  $\text{MeW}(\text{CO})_5^-$ . Whereas the  $\text{HW}(\text{CO})_5^-$  will reduce the metal-metal bond of typical metal carbonyl dimers, the  $\text{MeW}(\text{CO})_5^-$  is reactive at R.T. with only the weakest of these dimers,  $\text{Co}_2(\text{CO})_8$ .<sup>13</sup> Whereas the anionic hydride can form aggregates with coordinatively unsaturated, 16-electron metal centers, (structure II) such bridges cannot be formed with the  $\text{W-CH}_3^-$  functionality.

The inaccessibility of a site of nucleophilicity in  $\text{MeW}(\text{CO})_5^-$  apparently "turns on" reaction paths not observed for  $\text{HW}(\text{CO})_5^-$ . For example, some Me-R coupling products are observed for reaction of the methyl anion with RX and decarbonylation occurs in reductions of acylchlorides.<sup>13</sup> Since the rate of this decarbonylation ( $t_{1/2} = 150$  min. for  $\text{PhC}(\text{O})\text{Cl} \rightarrow \text{PhH}$ ) is faster than the measured gas phase decarbonylation of the  $\text{PhC}(\text{O})\cdot$  radical,<sup>14</sup> it appears that the metal enhances the loss of CO from  $\text{PhC}(\text{O})\text{Cl}$  and other  $\text{RC}(\text{O})\text{X}$ . The role of late transition metals in such reactions has been established to involve straight forward oxidative addition, deinsertion of CO from  $\text{RC}(\text{O})\text{M}$  and reductive elimination of  $\text{RH}$ .<sup>15</sup> Such a pathway is much less likely for the gp 6, zerovalent metal. In contrast gp 14 metal hydrides have been shown to promote decarbonylations by radical pathways.<sup>16</sup> There is little information or precedent available for oxidative addition or deinsertion reactions of transition metal based radical anions, the likely intermediates in these reactions. Hence at the present time, the role of the gp 6 transition metal is not understood.

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