

## The Hydride Transfer Ability of a Neutral Hydride, CP<sub>2</sub>Nb(H)CO

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Os hidretos aniônicos dos metais de transição transferem ions H<sup>-</sup> para centros eletrofílicos tais como RX, RC(O)X, RC(O)H, etc; estudos de reatividade relativa permitiram estabelecer uma ordem de reatividade geral: HW(CO)<sub>4</sub>PR<sub>3</sub><sup>-</sup> > HCr(CO)<sub>5</sub><sup>-</sup> > CpVH(CO)<sub>3</sub><sup>-</sup> > HFe(CO)<sub>4</sub><sup>-</sup>. Complexos hidretos neutros dos metais do início das séries de transição também comportam-se como reagentes transferidores de nucleófilos hidretos. Para compara-los, as reações de CP<sub>2</sub>Nb(H)CO, CP= n-C<sub>5</sub>H<sub>5</sub>, com haletos orgânicos foram estudadas. Os produtos organometálicos são os haletos de nióbio, CP<sub>2</sub>Nb(X)CO; hidrocarbonetos são obtidos. Embora o hidreto neutro não reduza n-BuBr com velocidades comparáveis às dos hidretos aniônicos dos metais do group 6, t-BuBr é reduzido com velocidade comparável. Várias sondas mecanísticas indicaram um mecanismo radicalar.

Anionic transition metal hydrides are known to transfer hydride (H<sup>-</sup>) to electrophilic carbon centers such as RX, RC(O)X, RC(O)H, etc; studies of relative reactivity have established a general reactivity order: HW(CO)<sub>4</sub>PR<sub>3</sub><sup>-</sup> > HCr(CO)<sub>5</sub><sup>-</sup> > CpVH(CO)<sub>3</sub><sup>-</sup> > HFe(CO)<sub>4</sub><sup>-</sup>. Neutral complexes of early transition metal hydrides have also been observed to react as nucleophilic hydride transfer reagents. In order to compare them reactions of CP<sub>2</sub>Nb(H)CO, CP= n-C<sub>5</sub>H<sub>5</sub>, with organic halides have been studied. The organometallic products are the niobium halides, CP<sub>2</sub>Nb(X)CO; hydrocarbons result from hydride/halide displacement. Although the neutral hydride does not reduce n-BuBr with rates as great as the group 6 anionic hydrides, t-BuBr is reduced with comparable rates. Various mechanistic probes have indicated single electron transfer or radical pathway character in reactions of CP<sub>2</sub>Nb(H)CO as compared to the anionic hydrides.

**Key words:** niobium; hydride.

### Introduction

The nucleophilic or hydride-transfer character of a transition metal hydride functional group has been noted in several studies<sup>1-5</sup> since first expressed by Labinger and Komadina more than a decade ago<sup>1</sup>. For example, reaction rates of acyl halides or n-BuBr and group 6 anionic hydrides (HM(CO)<sub>4</sub>L<sup>-</sup>; M=Cr, W; L=PR<sub>3</sub>, CO) increase in an order consistent with increasing nucleophilicity of metal hydride as a function of the metal (W > Cr) and of the ligand (L=PR<sub>3</sub> > CO). Recently Norton and coworkers ascribed the relative reactivity of neutral hydrides such as HRe(CO)<sub>5</sub>, HMn(CO)<sub>5</sub>, CpW(CO)<sub>3</sub>H, etc., towards reaction with EtRe(CO)<sub>5</sub> (or more appropriately, the metal center following migratory insertion, Re(CO)<sub>4</sub>C(O)Et) to

depend on the nucleophilicity of such hydrides<sup>5</sup>. In the earlier study of Labinger and Komadina various neutral transition metal hydrides were compared according to their ability to reduce the ketones CH<sub>3</sub>C(O)CH<sub>3</sub> and<sup>1</sup> CF<sub>3</sub>C(O)CH<sub>3</sub>. For example, CpMo(CO)<sub>3</sub>H was unreactive with both ketones; Cp<sub>2</sub>MoH<sub>2</sub> reacted with the more electrophilic CF<sub>3</sub>C(O)CH<sub>3</sub> over the course of one day but not at with CH<sub>3</sub>C(O)CH<sub>3</sub>; Cp<sub>2</sub>Nb(H)CO reduced acetone slowly and CF<sub>3</sub>C(O)CH<sub>3</sub> upon the time of mixing; and Cp<sub>2</sub>ZrH<sub>2</sub> reacted instantaneously even with<sup>1</sup> CH<sub>3</sub>C(O)CH<sub>3</sub>. 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<sup>6</sup>, behave as acids in many of

their reactions.

Certainly it is well recognized that the facility with which hydrogen is removed from a M-H bond is dependent upon the substrate, and, ultimately, the mechanism of abstraction (i.e., as  $H^+$ ,  $H$ ,  $H^-$  or via reductive elimination)<sup>3</sup>. Perhaps less well recognized, and difficult to define experimentally is the possibility of competition between the metal center vs. the hydride as a nucleophilic site. For example, the reduction of acyl chlorides by the  $Cp_2Nb(H)CO$  reagent to yield aldehydes was suggested to proceed either by metal  $S_N2$  attack on the electrophilic carbon, displacing the  $Cl^-$ , and generating the product aldehyde by reductive elimination; or, alternatively, by hydride addition to the electrophilic carbon, generating a chloro alkoxy intermediate<sup>7</sup>.

The work with group 6 anionic transition metal hydrides,  $HM(CO)_4L^-$  ( $L=CO, PR_3$ ;  $M=Cr, W$ ) has demonstrated hydride transfer ability in settings most favorable to a hydride-based reaction pathway<sup>2</sup>. That is, the metals are  $d^6$ , the geometries of the coordination complexes are octahedral, and the  $CO$  or  $PR_3$  ligands are not labile under the reaction conditions. Use of radical probe diagnostics such as the selectivity for 1<sup>st</sup> vs. 3<sup>rd</sup> alkylbromide reductions, or the reduction of alkenyl bromides whose alkenyl radicals are capable of rapid and irreversible skeletal rearrangements, have suggested the presence of simultaneously competing  $S_N2$  and radical chain pathways<sup>3</sup>. Usually  $S_N2$  mechanisms prevail, and the maximum extent to which radical chain pathway occurs takes place for  $HCr(CO)_5^-$ , and even here it accounts for only 10% of the results. More hydridic derivatives such as  $HW(CO)_5^-$  and  $cis-HW(CO)_4P(OMe)_3^-$  followed an  $S_N2$  pathway to the extent of 99% or greater. Similar probe diagnostics were used earlier by Bergaman, Kinney and Jones to delineate the mechanism of reduction by  $CpV(CO)_3H^-$ <sup>8</sup>. They concluded that the anionic vanadium hydride reacted primarily via a radical chain pathway, although the possibility of concurrent  $S_N2$ /radical chain pathways was not ruled out.

In order to provide a more definite comparison of the neutral nucleophilic hydride,  $Cp_2Nb(H)CO$  with the anionic group 6 hydrides we have undertaken kinetic and radical probe studies of organic halide reductions. That study is reported here.

## Experimental

**Methods and Materials.** An inert-atmosphere (Ar) glove box and Schlenk techniques were used for sample transfer and sample manipulations. Nitrogen was predried over an in-line column consisting of molecular sieves, calcium chloride and calcium sulfate. Tetrahydrofuran (THF), toluene and benzene were distilled under nitrogen from sodium/benzophenone ketyl. All solvents were immediately used following distillation or stored under nitrogen over the appropriate molecular sieves.  $Cp_2Nb(H)CO$  was prepared according to the literature procedure<sup>9</sup>.

**Instrumentation.** Infrared spectra were recorded on a IBM FTIR/32 or IBM FTIR/85 spectrometer. Nuclear magnetic resonance were measured on Varian spectrometers 90-MHz EM-390 and XL-200. Gas chromatographic analysis were performed on a Perkin-Elmer Sigma 2 gas chromatograph, equipped with flame ionization detector. Peak areas were determined by multiplying the widths at

half height by the peak heights or by electronics integration GC/MS were recorded on a Hewlett Packard 5890 VG 70-S spectrometer. The columns used for the detection of the hydrocarbons were picric acid ( $t=50^\circ C$ , F.R.=30), OV-17 ( $t=40^\circ C$ , F.R.=20) and Carbowax ( $t=170^\circ C$ , F.R.=30).

**Reactions of the hydrides with the organic halides:**

**General method.** Solid samples of the hydrides were weighed inside the dry box and placed in septum-capped flasks. Outside the dry box degassed THF solutions of the appropriate organic halides were added to these samples via cannula or syringe. The reaction mixture was stirred at room temperature overnight and subjected to analysis.

**Product analysis.** Organometallic products were identified by their I.R. spectra as compared to spectra of known compounds. Volatile organic products were identified by gas chromatography and GC/MS on the reaction mixtures through coinjection with authentic samples.

**Kinetic Measurements.** Inside the dry box solid samples of the hydride were placed in Schlenk tubes with a stopcock at one end and a small septum cap tightly wired to its outlet. Outside the box the solvent and the organic halides were added by syringe and the flask was immersed in a constant temperature bath. The RX concentrations were 5,10,15, 20,40,60 fold excess of the hydride. Samples were periodically withdrawn and the reaction rate was monitored by the observed decrease in intensity of the  $\nu_{CO}$  infrared absorbance of the hydride.

**Competition Reactions. Competition between linear and branched alkyl bromides for  $Cp_2Nb(H)CO$ .** A five-ml THF solution of n-butylbromide and t-butylbromide (0,238 mmol each, 3 fold excess) was added to a septum-capped flask containing 20 mg (0,0796 mmol) of  $Cp_2Nb(H)CO$ . The reaction mixture was stirred overnight at room temperature. GC analysis of the volatiles revealed the hydrocarbon distribution to be as follows: n- $C_4H_{10}$ /t- $C_4H_{10}$  = 24.7/74.0. A similar procedure was used for a mixture of s-butylbromide and t-butylbromide in ATHF. The product distribution here was n- $C_4H_{10}$ /t- $C_4H_{10}$ =14.5/85.5.

**Reaction between  $Cp_2Nb(H)CO$  and  $CO_2$ .** A 20 mg (0.0796 mmol) of  $Cp_2Nb(H)CO$  was placed under one atm of  $CO_2$  in THF, at room temperature, for 5 hours. As revealed by I.R., after this time no reaction had occurred. Under reflux conditions ( $80^\circ C$ ; 1 h) the niobium hydride decomposed.





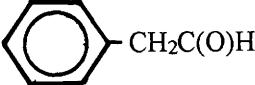
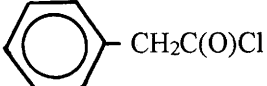
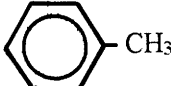
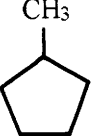


**Reaction between  $Cp_2Nb(H)CO$  and  $^{13}CO$ :** 20 mg (0.0796 mmol) of  $Cp_2Nb(H)CO$  were reacted with 1 atm of  $^{13}CO$ , in THF, at room temperature. After 3.5h the infrared spectrum showed that 23% of the starting material had exchanged CO.

**H/D Rxchange Experiments:** 30 mg (0.119 mmol) of  $Cp_2Nb(H)CO$  were dissolved in 3 ml of THF and 14,5  $\mu l$  of  $CH_3OD$  were added (0.357 mmol, 3-fold excess). The reagents were stirred at room temperature for 5 hours. The deuterium labelled product was identified by  $^2H$ NMR.  $^1H$ NMR revealed both that some of the  $^1H$  in  $Cp_2Nb(H)CO$  did not exchange and that some  $^2H$  was incorporated into the Cp ring positions. The small amount of  $CH_3OH$  that was necessarily present in these experiments did not alter either the I.R. or NMR spectra or interfere with deuterium-transfer reactions.

## Results and Discussion

For all reactions of  $Cp_2Nb(H)CO$  with RX, the metal-

**Table 1.** Organic products from the reactions of  $Cp_2Nb(H)CO$  with organic halides.

Halide	Product	Yield <sup>a</sup>
		96%
		96%
		91%
	and	
		8,8%
		63%
	and	
		37%
$s-C_4H_9Br$	$n-C_4H_{10}$	98.7%
	and	
	$t-C_4H_8$	0.74%
$t-C_4H_9Br$	$t-C_4H_{10}$	98.7%
	and	
	$i-C_4H_8$	0.92%

containing product was that of a simple H / X exchange, as described by eq. 1.1:

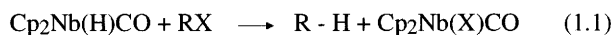


Table 1 contains a listing of organic halides used and the yield of hydrocarbon product as determined by gas chromatography. Coupling products, R-R, were not observed nor were reaction rates promoted by light. In reactions with *s*-butylbromide and *t*-butylbromide, elimination products, 1-butene and isobutene, respectively, were observed in minor amounts (<2%).

The reactions of  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  with organic halides proceed at rates convenient for monitoring by conventional  $\nu(\text{CO})$  I. R. techniques, i.e., by observing the disappearance of the  $\nu(\text{Nb}-\text{CO})$  band at  $1904 \text{ cm}^{-1}$ . They were carried out under pseudo-first-order conditions for the metal hydrides with RX generally at a 20-fold or greater excess. Following an initiation period, plots of  $\ln(A_t - A_{\infty})$  of the  $\nu(\text{CO})$  band versus time were linear. For all the kinetic runs such initiation periods were observed, in contrast to the group 6 anionic hydrides, which were kinetically well behaved over the entire reaction<sup>2</sup>. Also, in contrast to the anionic hydrides, whose kinetic rate expression was determined to be first order in each reagent, Eq. 1.2, the rate of the reaction of  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  with *n*-BuBr was independent of  $[\text{BuBr}] > 15$  fold excess, Table 2.

$$\text{rate} = k_2[\text{HM}(\text{CO})_4\text{L}][\text{RX}] \quad (1.2)$$

**Table 2.** Rates constants for the reactions of  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$ , [0.03 M] with *n*-BuBr, in THF, at 25°C.

<i>n</i> -BuBr, equiv.	$k_{\text{obs}} 10^5 \text{ s}^{-1}$
5	8,06 ( $\pm 0.69$ )
10	3.66 ( $\pm 0.41$ )
15	14.0 ( $\pm 0.70$ )
20	11.4 ( $\pm 1.21$ ) <sup>a</sup>
40	7.90 ( $\pm 0.68$ ) <sup>b</sup>
60	10.39 ( $\pm 1.17$ ) <sup>c</sup>

<sup>a</sup> Calculated at 90% confidence limit and as a mean value of three kinetic runs.

<sup>b</sup> Calculated at 80% confidence limit and as a mean value of three kinetic runs.

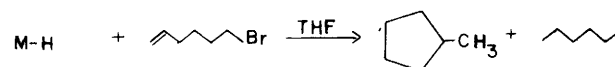
<sup>c</sup> Calculated at 80% confidence limit and as a mean value of three kinetic runs.

As Table 1 shows the reaction of  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  with  $\text{PhCH}_2\text{COCl}$  yielded some aldehyde as well as the product of decarbonylation. As the formation of toluene in these reactions is an indication that radicals are involved<sup>10</sup>, the presence of products that might arise from radical rearrangement was studied. The reaction of  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  with 6-bromohexene, Eq. 1.3, a reagent whose alkenyl radical is well-known to cyclize yielding methylcyclopentane, was studied. Both methylcyclopentane, resulting from the radical rearrangement, and 1-hexene, a product which can be formed both by a radical or  $\text{S}_{\text{N}}2$  mechanism, were observed, Eq. 1.3<sup>11</sup>.



The yield of rearranged product, methylcyclopentane, is much larger than for  $\text{CpV}(\text{CO})_3\text{H}^-$ , Table 3, an anionic hydride of the same family<sup>8</sup>, whose reactions are purportedly radical in nature.

**Table 3.** Amount of product formed<sup>a</sup> for the reactions between 6-bromohexene and  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  and anionic hydrides<sup>b</sup>.



Hydride	R.P.	U.P.
${}^{\text{a}}\text{HCr}(\text{CO})_5^-$ (0.01)	29%	71%
${}^{\text{d}}\text{HW}(\text{CO})_5\text{H}^-$ (0.01)	7%	93%
$\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3^-$ (0.01)	0%	100%
$\text{CpV}(\text{CO})_3\text{H}^-$ (0.077)	3%	97%
$\text{Cp}_2\text{Nb}(\text{H})\text{CO}$ (0.0389)	63%	37%

<sup>a</sup> G.C.yields. <sup>b</sup> Adapted from reference 4 for Gp 6 metals and ref. 8 for vanadium hydride. <sup>c</sup> Measured at  $[\text{6-bromohexene}] = 0.063 \text{ M}$ . <sup>d</sup> Measured at  $[\text{6-bromohexene}] = 0.065 \text{ M}$  in THF solution.

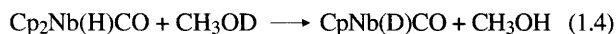
The competition reactions indicated that  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  shows selectivity for the reduction of the most hindered alkyl halide (see Experimental) This fact is consistent with the formation of the most stable free radical or carbonium ion.

The reaction rate is substantially the same in solvents like benzene or THF, and the presence of oxygen does not affect reaction rate, Table 4. In fact, it was observed that small amounts of oxygen destroyed some of the starting material, however it did not serve as a catalytic initiator. The reaction rate was observed to decrease in the presence of CO, Table 4, which could suggest that in these reactions CO loss generated a coordinatively unsaturated species, more reactive than the intact starting material. However, the niobium hydride does not lose CO very easily. For example, over a 3.5 h period, only 23% of  $^{12}\text{CO}$  in  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  exchanged with  $^{13}\text{CO}$ , a period that far exceeded our kinetic runs. Besides this, if CO was being eliminated, niobocene, a hydride containing dimer could be formed, and it was not observed in the reaction medium<sup>12</sup>. The cause of the rate decrease in the presence of CO remains undetermined.

The reaction rates for the reactions of  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  and the anionic hydrides with *n*-BuBr and *t*-BuBr were also compared, Table 5, and as can be seen, the niobium hydride

reduces *t*-BuBr almost twice as fast as CpV(CO)<sub>3</sub>H<sup>-</sup>.

Attempts to prepare the analogous deuteride, Cp<sub>2</sub>Nb(D)CO, according to Eq. 1.4, were made in order to determine whether the source of the hydride is in fact, the niobium complex.



**Table 4.** Rate constants for the reactions of Cp<sub>2</sub>Nb(H)CO, [0.00158 M], *n*-BuBr, 20 fold excess, under various conditions, in THF, at 25 °C.

Cp <sub>2</sub> Nb(H)CO + <i>n</i> -BuBr → <i>n</i> -BuBr + Cp <sub>2</sub> Nb(Br)CO		
Solvent	additive	10 <sup>5</sup> k <sub>obs</sub> s <sup>-1</sup>
THF		10.20 (± 1.00)
EtCN		3.62 (± 0.42)
C <sub>6</sub> H <sub>6</sub>		7.29 (± 1.08)
THF	<sup>a</sup> CO	4.63 (± 0.35)
THF	<sup>b</sup> O <sub>2</sub>	11.20 (± 1.50)

<sup>a</sup>1 atm of CO

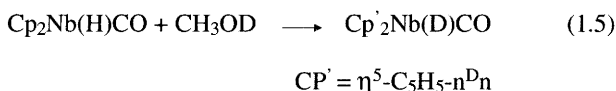
<sup>b</sup>Trace amounts added

**Table 5.** A comparison of rate constants for the reaction of anionic hydrides<sup>a</sup> and Cp<sub>2</sub>Nb(H)CO with *n*-BuBr and *t*-BuBr<sup>b</sup>.

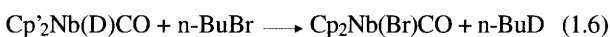
Hydride	<i>n</i> -BuBr 10 <sup>3</sup> k <sub>obs</sub> s <sup>-1</sup>	<i>t</i> -BuBr 10 <sup>3</sup> k <sub>obs</sub> s <sup>-1</sup>
cis-HW(CO) <sub>4</sub> P(OMe) <sub>3</sub> <sup>-</sup>	~50	0.21 (± 0.01)
cis-HCr(CO) <sub>4</sub> P(OMe) <sub>3</sub> <sup>-</sup>	~30	0.81 (± 0.05)
CpV(CO) <sub>3</sub> H <sup>-</sup>	2.20 (± 0.06)	0.33 (± 0.03)
HW(CO) <sub>5</sub> H <sup>-</sup>	3.31 (± 0.13)	2.81 (± 0.16)
HCr(CO) <sub>5</sub> H <sup>-</sup>	1.79 (± 0.01)	3.17 (± 0.08)
Cp <sub>2</sub> Nb(H)CO	0.0102 (± 0.01)	0.58 (± 0.03)

<sup>a</sup>Adapted from reference 2c. <sup>b</sup>Reactions were carried out at 25 °C.

<sup>1</sup>H and <sup>2</sup>HNMR spectra revealed that the majority of the deuterium was incorporated to the Cp rings, an observation made previously<sup>13,14</sup> Eq. 1.5:



Even under these circumstances the reaction described by Eq. 1.6 occurred, and some deuterium was found in the product, as determined by GC/MS, strongly suggesting that the source of the hydride is in fact the starting material.

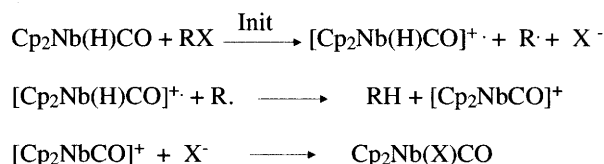


Due to the problem of Nb-D/C<sub>5</sub>H<sub>5</sub> H/D exchange, a

kinetic isotope effect could not be determined.

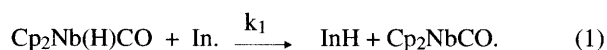
The weight of evidence, including induction periods, selectivity for 3<sup>rd</sup>-RBr and skeletal rearrangement probes, suggest that a radical mechanism is involved for the reductions of the organic halides by Cp<sub>2</sub>Nb(H)CO. The two most likely radical mechanisms are the single electron transfer and the radical chain mechanism as outlined in Schemes I and II, respectively.

#### Scheme I

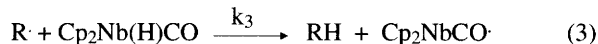
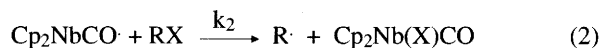


#### Scheme II

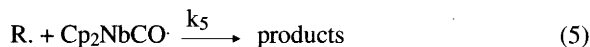
##### Initiation



##### Propagation

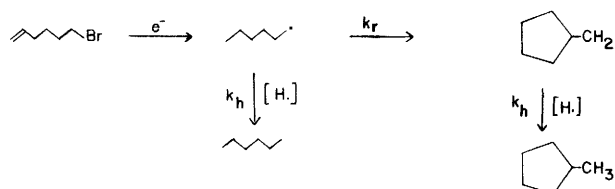


##### Termination



The single electron transfer mechanism involves the formation of the radical cationic species Cp<sub>2</sub>NbCO<sup>•+</sup>, which presumably would be stabilized by polar solvents. Instead it was observed that the reaction rate decreases by a magnitude of three, in EtCN, a solvent more polar than THF, Table 4. This fact is more suggestive of a radical chain mechanism. However, we were unable to detect any of termination step products. Nevertheless, in this mechanism, if the chain is too long, termination products are formed in small amounts, being difficult to detect them<sup>8,15</sup>. Also, for statistical reasons this mechanism is more appealing.

The mechanism through which the halide 6-bromohexene abstracts hydrogen atoms, H., can be formulated as follows:



Due to the problem of Nb-D/C<sub>5</sub>H<sub>5</sub> H/D exchange, a

The rate constant  $k_h$  is the rate at which the hydrogen atom, H, is transferred from the metal hydride to the organic halide. The  $k_r$  is the cyclization constant of the radical determined by Ingold<sup>15</sup> at  $2.5 \times 10^5 \text{ s}^{-1}$ . Hydrogen atom abstraction,  $k_h$ , can be compared for hydrides that react by the same mechanism at a particular concentration of the hydride and the organic halide. Such comparison of the  $k_h$ , found in Table 6, is in agreement with the fact that the tungsten thydride reacts with n-BuBr with just 0.3% of  $S_{H2}$  process. As expected due to increased M-H bond strengths of havier transition metals, the tungsten hydride has a smaller  $k_h$  value than the chromium hydride,  $\text{HCr}(\text{CO})_5^-$ . The latter reacts with 10% of  $S_{H2}$  process. Having this in mind we decided to compare the  $k_h$  values of  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  and  $\text{CpV}(\text{CO})_5\text{H}$ , using the  $k_r$  values reported by Ingold<sup>15</sup>, the hydrides at a concentration of 0.08 M and the organic halides at 0.002 M. The values that were obtained were  $5.24 \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$  and  $1.68 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$ , respectively. These values are also in accordance with the fact that the neutral niobium hydride has more radicl character in its reductions of the organic halides than does the anionic vanadium hydride.

**Table 6.** Hydrogen atom abstraction rate constant,  $k_h$ , for some anionic hydrides<sup>a</sup>.

Hydride	$10^6 k_h \text{ s}^{-1} \text{ M}^{-1}$
$\text{HCr}(\text{CO})_5^-$	18.4
$\text{HW}(\text{CO})_5^-$	6.4
$\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3^-$	4.6 <sup>b</sup>

<sup>a</sup>Adapted from reference 3. <sup>b</sup>Estimate. Reaction very slow.

## Conclusions

The following lines of evidence suggest that reactions of  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  with alkyl bromides involve radical intermediates:

- Substantial amounts of rearranged hydrocarbon products result from alkyl halides whose R. are prone to skeletal rearrangements;
- Selectivity for tertiary RX;
- Induction periods and less than well-behaved kinetics.

Such a propensity to react by a radical path leads to greater reactivity with sbustrates which form relatively stable radical intermediates, such as t-BuBr. In such cases, the neutral  $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$  is apparently more nucleophilic than the anionic hydrides which are more prone to hydride ( $\text{H}^-$ ) transfer reactions. Nevertheless, with substrates which react best by  $S_{N2}$  pathwasys, the nucleophilicity of the anionic hydrides predominates and demonstrates greater reactivity than the neutral niobium hydrides.

Our results do not promptlu distinguish between a chain mechanism and a single electron-transfer (non-chain) process, although much of the evidences are in favour of the former.

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