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The Nature of Alkali Cation Contact Ion Pairs with Anionic Transition-Metal Hydrides $HM(CO)_4L^-$ (M = Cr, W; L = CO, PR_3)

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Both infrared (ν(CO) region) and ^{1}H NMR results imply that in tetrahydrofuran solution the alkali cations Na^+ and Li^+ form contact ion pairs with *cis*-$HM(CO)_4PR_3^-$ (M = Cr, W; $PR_3 = P(OMe)_3$, PPh_3, PMe_3), specifically interacting at the hydride ligand or metal hydride bond density site. In contrast all the carbonyl hydrides $HFe(CO)_4^-$, $CpV(CO)_3H^-$, $HW(CO)_5^-$, and $HCr(CO)_5^-$ show a preference for contact interaction at the CO oxygen site, although the more basic metal hydride $HW(CO)_5^-$ displays some tendency for cation/tungsten hydride site interaction. The ion-pairing characteristics of the analogous anions $ClW(CO)_5^-$ and *cis*-$ClW(CO)_4P(OMe)_3^-$ were compared to the hydrides. Contact ion pairs of Na^+ or Li^+ exclusively at the chloride site were detected by ν(CO) IR spectral changes and preceded irreversible decomposition due to chloride ligand abstraction. A similar but slower alkali cation promoted decomposition of the 6B anionic hydrides was observed. The relationship between the ability of the anionic hydride carbonylates to serve as hydride donors and their tendency to interact with cations at the metal hydride site is noted.

Introduction

The disposition of the M–H bond density in transition-metal hydride complexes is subject to influences both internally from the metal and attached ligands as well as externally from reagents with which it might contact. For example, $HMn(CO)_5$ is described as a weak acid,[1] ionizing in aqueous media presumably with the assistance of substantial hydrogen bonding. With very strong acids such as $HOSO_2CF_3$[2] the hydrogen reacts as H^- yielding H_2 and $Mn(CO)_5(Tf)$ ($Tf = CF_3SO_3^-$).[2] Similarly the $Mn(CO)_5^+$ species is produced on reaction of $HMn(CO)_5$ and $AlBr_3$, producing $[Mn(CO)_5]AlBr_4$ and $Mn(CO)_5Br$.[3] Homolytic cleavage of the Mn–H bond has been convincingly demonstrated in the hydrogenation of α-methylstyrene by $HMn(CO)_5$.[4] Such substrate responsiveness or sensitivity suggests enormous complexities are to be encountered in mechanistic studies of the transition metal–hydrogen bond.

We have isolated a small portion of the M–H bond density polarization problem which is of import to studies of hydride (H^-) transfer reactions. A recent study established a relative reactivity order for various $[M]H^-$ according to their ability to reduce primary alkyl halides (yielding RH and $[M]X^-$):[5]

$$\textit{cis}\text{-}HW(CO)_4PR_3^- > \textit{cis}\text{-}HCr(CO)_4PR_3^- > HW(CO)_5^- > CpV(CO)_3H^- > HCr(CO)_5^- > HRu(CO)_4 \gg HFe(CO)_4^- \quad \text{(no reaction)}$$

The reaction follows a kinetic rate expression that is first order in each of the reactants and yields activation parameters suggestive of a large amount of order in the transition state (typical $\Delta S^{\ddagger}$ values are −30 eu).[5]

Since the negative charge in anionic metal carbonyl hydrides is substantially delocalized, as evidenced by the low ν(CO) values, a potentially reactive electrophile "sees" as basic or nucleophilic sites the carbonyl oxygen, the hydride ligand, and possibly the metal. Earlier we noted that sodium ions quite clearly and specifically interacted (formed contact ion pairs with) the carbonyl oxygen of $HFe(CO)_4^-$,[6] which is the poorest hydride/halide exchange reagent in our series above. In an attempt to discern correlations between the site of ion pairing and relative reactivities, this study has been extended to include the more reactive hydride complexes. It is also noteworthy that alkali promoters are quite general and useful in catalytic H_2/CO and H_2/N_2 reduction processes.[7,8] Fundamental studies of counterion effects on soluble model systems could prove useful in better defining their role.

Experimental Section

Inert-atmosphere (Schlenk and glovebox) techniques were used in all aspects of this work.

Solvents and Reagents. Tetrahydrofuran (THF) solvent was distilled from Na^0/benzophenone, collected, and transferred under N_2. Hexamethylphosphoric triamide (HMPA) was purchased from Aldrich Chemical Co. and degassed prior to use. [Caution: HMPA is a potent carcinogen and should be handled with great care.] Other reagents were obtained from standard vendors and used as received. The salt $Li^+BPh_4^-$ was prepared from ion exchange of $Na^+BPh_4^-$ and LiCl in THF solvent according to a literature procedure.[9]

The anions $HM(CO)_5^-$,[10] *cis*-$HW(CO)_4PR_3^-$,[11] and *cis*-$ClW(CO)_4P(OMe)_3^-$ [12] were prepared as their bis(triphenylphosphine)nitrogen(1+) (PPN^+) salts as described previously. The synthesis of a new hydride, PPN^+*cis*-$HCr(CO)_4P(OMe)_3^-$, followed the same method as reported for the tungsten analogue.

Instrumentation. Infrared spectra were recorded of THF solutions in matched, sealed 0.1-mm NaCl or CaF_2 cells on the Perkin-Elmer 283B spectrophotometer calibrated below 2000 cm^{-1}

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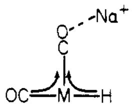
on water vapor. Proton magnetic resonance spectra were measured on a Varian EM390 spectrometer.

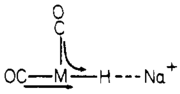
Results and Discussion

The effects of counterions on the THF solution spectra (ν(CO) IR region and ^{1}H NMR) were probed in this work. Previous conductivity measurements have shown that even large counterions such as PPN$^+$, tightly solvated sodium ions (HMPA$_x$Na$^+$), and Et_4N^+ were highly associated with various metal carbonyl anions such as $Mn(CO)_5^-$,[13] $Mn(CO)_4P(OPh)_3^-$,[13] $CpMo(CO)_3^-$,[14] and $V(CO)_5PR_3^-$,[15] as well as the hydridocarbonylate $HFe(CO)_4^-$[16] in THF solution (dielectric constant = 7.6). In these cases such associations were either nonspecific for a particular basic site or so weakly interacting as to not perturb the symmetry of the anion. In fact the spectral characteristics (ν(CO) IR) of such salts were largely independent of solvent polarity and the only measure of the extent of ion pairing was solution conductivity. However, with alkali cations as counterions to the above anions, contact ion pairs were formed that showed specific carbonyl oxygen interaction sites, readily discernible in the ν(CO) infrared spectra. The reported examples of the ion pairs that show cation–anion interaction sites other than a carbonyl oxygen are those in which the negative charge is localized on a ligand such as $Na^+\cdots NCFe(CO)_4^-$,[17a] $Na^+\cdots{}^-ONFe(CO)_3$,[17b] and $Li^+\cdots O{=}C(R)Fe(CO)_3L^-$,[18] or, in cases where a combination of transition-metal basicity and the cation's electrostatic potential are suitable for metal–metal bond formation, as in $(OC)_4Fe^{2-}\cdots Na^+$,[19] $(OC)_4Fe^{2-}\cdots K^+$,[20] $Cp(OC)_2Fe^-\cdots Na^+$,[21] and $Cp(OC)_3Mo^-\cdots Zn^{2+}\cdots Mo(Cp)(CO)_3^-$.[22]

For the hydridocarbonylates we might then expect several prominent possibilities of specific Na$^+$/anion or Li$^+$/anion interactions, affecting the ν(CO) IR as follows. **Type 1.** A low-frequency ν(CO) band is expected to result from Na$^+$ interaction with a carbonyl oxygen, and the creation of such a good π-acceptor ligand should reduce the π-density available for back-donation from M to the other CO groups.[23] The ν(CO) absorptions related to the latter would then be shifted to higher frequencies when compared to their positions in the non-cation-perturbed anion. Of the two types of CO groups in C_{4v} $LM(CO)_5^-$ or $XM(CO)_5^-$ anions, the CO oxygen trans to the substituent ligand is predicted to be the more basic and the site of cation contact.[15] **Type 2.** In contrast, if the cation/anion interaction is selective for the H$^-$ ligand site, all CO groups would be affected similarly. Electron density should be polarized toward the $M{-}H^-\cdots Na^+$ interaction site and the lesser amount of M → CO π-back-bonding should result in all ν(CO) bands being moved to higher frequencies. **Type 3.** A penetration of the coordination sphere to give direct alkali cation···transition metal contact interaction would have a similar effect on ν(CO) as the type 2 interaction.[21] As indicated above the precedent for such intimate contact ion pairing is limited and has not been observed for alkali cation (Na$^+$ and Li$^+$) salts of the less electron-rich and more sterically saturated carbonylates such as $CpM(CO)_3^-$ (M = Cr, Mo, W),[14] $Mn(CO)_5^-$,[13] $Mn(CO)_4PR_3^-$,[13] or $V(CO)_5PR_3^-$.[15] **Type 4** is given as a reasonable alternative to the extremes of types 2 and 3.



type 1



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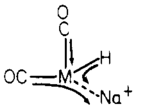

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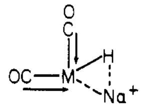

type 4

Table I. ν(CO) Infrared Data for Salts of Cation$^+XM(CO)_5^-$ in THF Solution[a]

			ν(CO), cm^{-1}		
cat$^+$	X	M	A_1^2(vs)	E(s)	A_1^1(m)
PPN	H	Cr	2016	1884	1856
Na[b]	H	Cr	2016	1884	1854
				(1894 sh)	(1814 w)
Na/HMPA[c]	H	Cr	2016	1884	1856
Li	H	Cr	2016	1885	1857
PPN	H	W	2029	1889	1857
Na[b]	H	W	2030	1890	1860
				(1896 sh)	(1822 vw)
Na/HMPA	H	W	2029	1889	1857
Li	H	W	2030	1890	1860
PPN	Cl	W	2060	1916	1849
Na[b]	Cl	W	2066	1921	1867
Na/HMPA	Cl	W	2060	1917	1849
Li	Cl	W	2065	1920	1865

[a] The alkali salts were prepared by adding 1–2 equiv of $NaBPh_4$ or $LiBPh_4$ to a THF solution of the PPN$^+$ salt. No further changes noted when up to 10 equiv of the ion-exchange reagent were added. [b] The low-frequency band in the Na$^+$ salt is presumed to be due to the CO stretch in the $Na^+\cdots OC{-}M$ interaction. [c] Prepared by adding ~10 equiv of HMPA per Na$^+$.

Tables I and II contain ν(CO) IR spectral data for PPN$^+$, Na$^+$, and Li$^+$ salts of $HCr(CO)_5^-$, $HW(CO)_5^-$, and *cis*-$HM(CO)_4P^-$ (M = Cr, W; P = PMe_3, $P(OMe)_3$, PPh_3), as well as the chloride analogues $ClW(CO)_5^-$ and *cis*-$ClW(CO)_4P(OMe)_3^-$. The sodium and lithium salts were generated in situ by ion exchange of the PPN$^+$ salts with $NaBPh_4$ or $LiBPh_4$ in THF. Optimal spectral differences resulted with the addition of only 1–2 equiv of the ion-exchange reagents. No further changes were noted when up to 10 equiv of the alkali cation was added. The $Na^+HW(CO)_5^-$ and $Na^+HW(CO)_4P^-$ salts produced by ion exchange had identical spectral characteristics as the isolated hydride salts produced by MeOH protonation of $(Na^+)_2W(CO)_5^{2-}$ or $(Na^+)_2W(CO)_4P^{2-}$. Furthermore upon addition of HMPA (typically 10 equiv) to the sodium or lithium salts, the same spectral pattern and band positions resulted as was observed for the PPN$^+$ salts. These results may be considered as proof that reversible contact ion pair formation is the source of the spectral changes.

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Table II. ν(CO) Data for Salts of Cation$^+$ *cis*-$XM(CO)_4L^-$ in THF Solution

				ν(CO),[a] cm^{-1}		
cation$^+$	X	M	L	A'(m)	A' + A''(s)	A''(m)
PPN	H	Cr	$P(OMe)_3$	1972	1854	1822
Na[b]	H	Cr	$P(OMe)_3$	1986	1865	1843
PPN	H	W	$P(OMe)_3$	1982	1857	1822
Na	H	W	$P(OMe)_3$	1993	1864	1848
Li[b,c]	H	W	$P(OMe)_3$	1982 (1993)	1872 sh, 1857 (1894 sh, 1868)	1826 (1826 br)
PPN	H	W	PMe_3	1969	1847 sh, 1842	1805
Na	H	W	PMe_3	1982	1858	1823
Li	H	W	PMe_3	1985	1862	1824
PPN	H	W	PPh_3	1974	1851	1815
Na	H	W	PPh_3	1987	1863	1826
Li	H	W	PPh_3	2012	1894	1851
PPN	Cl	W	$P(OMe)_3$	2004	1875	1815
Na	Cl	W	$P(OMe)_3$	2010	1884	1829
Li	Cl	W	$P(OMe)_3$	2010	1885	1829

[a] Assignments for C_s symmetry as discussed in ref 15. [b] Prepared by adding 1-2 equiv of $NaBPh_4$ or $LiBPh_4$ to a THF solution of the PPN$^+$ salt. No further changes noted when up to 10 equiv of the ion-exchange reagent were added. [c] Values in parentheses are for contact ion paired form. Spectrum is composite of ssip form and contact ion paired form in ca. 50:50 ratio.

The $HM(CO)_5^-$ ions in a symmetrical solvent environment (as the PPN$^+$ or $Na(HMPA)_x^+$ salts in THF show a two-band pattern in the ν(CO) IR. The strong intensity E vibrational mode (the asymmetric stretch of the four CO groups cis to the hydride) is at 1884 and 1889 cm^{-1} for M = Cr and W, respectively, and the well-resolved medium A_1^1 band is at 1856 (Cr) and 1857 cm^{-1} (W). Another allowed A_1^2 vibrational mode is at 2016 (Cr) and 2029 cm^{-1} (W) but is extremely weak, in agreement with the distorted octahedral geometry of $HM(CO)_5^-$ and discussed elsewhere.[10] Since the A_1^1 band corresponds primarily to the stretch of the CO group trans to the hydride, spectral perturbations in its intensity and position may be interpreted in terms of site-specific cation contact with CO oxygen.

The IR spectra of the Na$^+$ salts of both $HCr(CO)_5^-$ and $HW(CO)_5^-$ (Figure 1) show diminished absorption maxima and a broadening of both the E and A_1^1 bands. A weak low-frequency band appears at 1814 cm^{-1} for $HCr(CO)_5^-$ and at 1822 cm^{-1} for $HW(CO)_5^-$. Asymmetry of the E band appears as a broadening on the higher frequency side. No attempt was made to deconvolute the spectra; however, in our judgement, a reasonable interpretation is as follows. Approximately 75% of the $HCr(CO)_5^-$ ions are in a symmetrical solvent environment as solvent-separated ion pairs, ssip's, and ca. 25% are in an axial CO oxygen contact ion paired form as illustrated in eq 1. Other simplest contacts (the H$^-$ ligand, the Cr, or the cis O oxygen) should lead to resolution loss between the A_1^1 and E band positions. A $Na^+\cdots H^-$ ligand contact or a $Na^+\cdots Cr$ contact should not produce a low-frequency ν(CO) band. [It should be noted that the M–H and M–D stretches in these anions are not readily observed (at least at room temperature) in the IR or Raman spectra.[24]]

$$Na^+(THF)_xHCr(CO)_5^- \rightleftharpoons \textit{trans}\text{-}HCr(CO)_4CO^-\cdots Na^+(THF)_{x-1} \quad (1)$$

$$\begin{tikzcd} Na^+(THF)_xHW(CO)_5^- \arrow[rr, shift left, ""] & & \textit{trans}\text{-}HW(CO)_4CO^-\cdots Na^+(THF)_{x-1} \arrow[ll, shift left] \arrow[dl, shift left] \\ & (THF)_{x-1}Na^+\cdots HW(CO)_5^- \arrow[ul, shift left] \arrow[ur, shift left] & \end{tikzcd} \quad (2)$$

The differences between the $HCr(CO)_5^-$ and $HW(CO)_5^-$ solution spectra are slight but, in our opinion, indicative of ion pair site selectivity changes. For $Na^+HW(CO)_5^-$ there is a buildup of intensity between the E and A_1^1 band, resulting in a greater loss of resolution than was observed for $Na^+HCr(CO)_5^-$. The low-frequency $W–CO\cdots Na^+$ ν(CO) band is less intense, implying fewer contact ion pairs of the form *trans*-$HW(CO)_4CO^-\cdots Na^+$. As eq 2 illustrates, a new species involving $Na^+\cdots HW^-$ interaction is proposed. As discussed above, forms of this species illustrated by structural types 2, 3, or 4 cannot be distinguished. Neither can the presence of some small amount of the isomer *cis*-$HW(CO)_4CO\cdots Na^+$ be ruled out. Our preference for some form of sodium ion to tungsten metal–hydride bond density interaction is based on other evidence (vide infra).

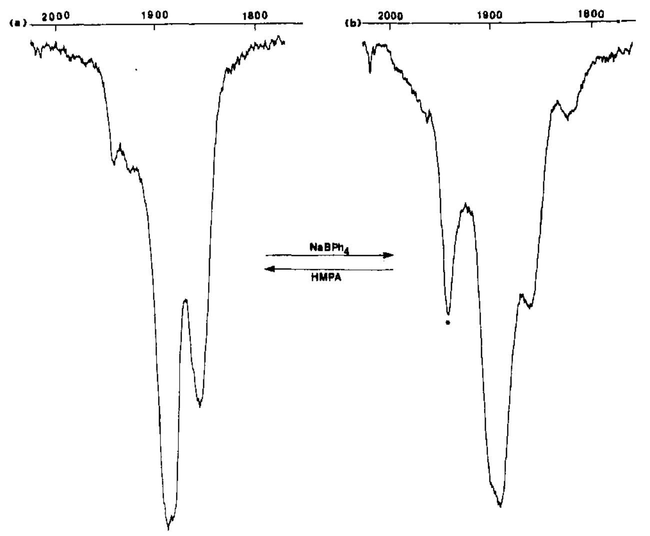

Figure 1. IR spectra in THF solution of (a) $PPN^+HW(CO)_5^-$ and (b) $Na^+HW(CO)_5^-$. The asterisk denotes the decomposition product, assigned to $HW_2(CO)_{10}^-$.

The ion exchange of PPN$^+$ for Li$^+$ produces no change in IR spectra of $HM(CO)_5^-$ (M = Cr, W). Such a lack of contact interaction suggests the pentacarbonyl hydrides to be less competitive than THF for contact with Li$^+$. This finding is consistent with other studies that showed Li$^+$ to be noninteracting with $Mn(CO)_5^-$,[13] $V(CO)_6^-$, or even $V(CO)_5PPh_3^-$.[15] In contrast the CO oxygens of $CpMo(CO)_3^-$ are of sufficient electrostatic potential to displace THF from the coordination sphere of Li$^+$.[14]

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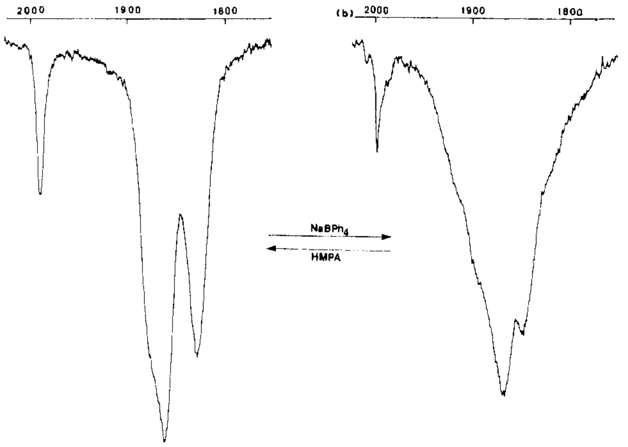

Figure 2. IR spectra in THF solution of (a) $PPN^+HW(CO)_4P(OMe)_3^-$ and (b) $Na^+HW(CO)_4P(OMe)_3^-$ (b).

Both Li^+ and Na^+ form contact ion pairs with $ClM(CO)_5^-$ anions in THF. As Table I indicates, the band pattern of the PPN^+ or $Na^+(HMPA)_x$ salts of $ClM(CO)_5^-$ is the same as the Na^+ or Li^+ salts. However, the frequencies of all bands are shifted to higher values. The greatest shift is in the A_1^1 vibration, the mode involving the CO trans to the chloride. The most reasonable explanation of these observations is contact ion pairing of the form $Na^+\cdots ClM(CO)_5^-$ or $Li^+\cdots ClM(CO)_5^-$. Such ion pair site selectivity is to be expected as the negative charge on the anion is highly localized on the chloride ligand. Compare, for example, the positions of ν(CO) of $HM(CO)_5^-$ with those of $ClM(CO)_5^-$ (Table I); the position of the major ν(CO) band is some 30 cm^{-1} higher in the latter. Irreversible complexities rapidly developed in the Na^+ salt spectra due to the loss of Cl^- and formation of THF-insoluble NaCl and the spectroscopically observable complex $THF{\cdot}M(CO)_5$. The latter eventually decomposed, yielding free CO and $M(CO)_6$. Both the $PPN^+ClM(CO)_5^-$ and the $Li^+ClM(CO)_5^-$ solutions are stable toward decomposition, presumably because both PPN^+Cl^- and LiCl are soluble in THF and reversibly add to the intermediate $THF{\cdot}M(CO)_5$.

The effect of exchanging PPN^+ by Na^+ or Li^+ is approximately the same for both *cis*-$HM(CO)_4PR_3^-$ and *cis*-$ClM(CO)_4PR_3^-$. The ν(CO) IR bands of Na^+ or Li^+ salts of all entries in Table II are shifted to higher frequencies as compared to the PPN^+ or $Na^+(HMPA)_x$ salts. Figure 2 illustrates the broadening of spectral features concomitant with the ion exchange of Na^+ for PPN^+ in $HW(CO)_4P(OMe)_3^-$. Despite this indication of the presence of more than one species in solution, the principal species appears to be one in which the symmetry of the CO groups is not changed. The Na^+ or Li^+ salts of *cis*-$ClW(CO)_4P(OMe)_3^-$ produce well-resolved ν(CO) bands whose band widths are the same as the PPN^+ or $Na^+(HMPA)_x$ salts. The similarity of spectral changes of the hydride derivatives and the chloride derivatives is accepted as evidence for a similarity of site-specific cation/anion contact ion pairing. Since cation contact with the chloride ligand is imminently reasonable, we assume cation–hydride or cation–metal hydride bond density contact with the P-substituted hydridocarbonylates.

Table III. ^{1}H NMR Spectral Data for Salts of $Cation^+HM(CO)_4L^-$ in THF Solution

$HM(CO)_4L^-$	cat$^+$, δ (M–H)($J_{P\text{-}H}$)		
	$PPN^{+\,a}$	$Na^{+\,b,c}$	$Li^{+\,b}$
$HCr(CO)_5^-$	−6.73	−6.75	−6.80
$HW(CO)_5^-$	−4.10	−4.40	−4.35
$HCr(CO)_4P(OMe)_3^-$	−7.00 (53 Hz)	−7.50 (52 Hz)	*d*
$HW(CO)_4P(OMe)_3^-$	−4.35 (35 Hz)	−5.50 (32 Hz)	−5.40 (32 Hz)
$HW(CO)_4PMe_3^-$	−3.60 (31 Hz)	−4.75 (28 Hz)	−5.05 (27 Hz)
$HW(CO)_4PPh_3^-$	−3.00 (28 Hz)	−3.70 (26 Hz)	−3.85 (26 Hz)

[a] The values are ca. identical with those of $M'(HMPA)_x^+$ salt ($M' = Na^+, Li^+$) prepared by titrating HMPA into the M′ solution. [b] Prepared by adding 1-2 equiv $M'BPh_4$ ($M' = Na^+, Li^+$) to a solution of PPN^+ salt. No further changes noted when up to 10 equiv $M'BPh_4$ was added. [c] The values are ca. identical with those of Na^+ salt prepared by reacting $Na_2M(CO)_4L$ (M = Cr, W; L = $P(OMe)_3$, PMe_3, PPh_3) with MeOH in THF. [d] The Li^+ salt is too unstable for measurement.

Our confidence in the above interpretations was bolstered upon comparing proton NMR results in the hydride region. As Table III indicates there is little to no counterion dependence of the hydride chemical shift of $HCr(CO)_5^-$, the anion for which IR results suggested little or no $Na^+\cdots HCr^-$ interaction. This result is consistent with earlier studies of PPN^+ vs. Na^+ salts of $HFe(CO)_4^-$.[6] The THF solution IR spectrum of $Na^+HFe(CO)_4^-$ indicated a ca. 50:50 mixture of solvent-separated ion pairs $Na^+(THF)_xHFe(CO)_4^-$ and contact ion pairs of the form *cis*-$HFe(CO)_3CO\cdots Na^+(THF)_y$. The proton NMR of the sodium salt was practically identical (δ −8.70) with that of the PPN^+ salt (δ −8.68) in THF.

Sodium and lithium counterions induce an upfield chemical shift (in comparison to the PPN^+ or HMPA solvate) for $HW(CO)_5^-$ and all *cis*-$HM(CO)_4P^-$. That shift is only 0.3 ppm for $HW(CO)_5^-$ but is 1.1 ppm for *cis*-$HW(CO)_4P(OMe)_3^-$. Such upfield shifts are typical for the hydride ligand in a bridging environment. For example, the chemical shift of $HW(CO)_5^-$ in THF is −4.1 ppm and that of $PPN^+(\mu\text{-}H)W_2(CO)_{10}^-$ is −12.6 ppm.[10] The most reasonable explanation for such shifts in the case of hydrides locked between transition metals is the large diamagnetic contribution from the proximity of two transition metals. This behavior is however also observed for hydrides bridging transition metals and main-group metals. For example, the hydride signal of $Cp_2Nb(C_2H_4)(H)$ is at δ −3.0, whereas for $Cp_2Nb(C_2H_4)(H\cdots AlEt_3)$ the chemical shift is moved upfield to −9.6 ppm.[25] We propose that the upfield shifts observed in this study are similarly due to formation of "bridging" hydrides $Na^+\cdots H\text{–}M^-$ or $Li^+\cdots H\text{–}M^-$. Polarization of electron density toward the site of interaction producing a greater shielding effect on the hydrogen is proposed as the cause of the upfield shift. The ion pair structures illustrated above as types 2 or 4 are most consistent with this explanation. In the absence of possible complications caused by cation solvation, interaction of the type 3 would be expected to have an opposite effect on M–H bond density, i.e., a deshielding effect. There are however, at this time no definitive examples of the type 3 ion pair with which to compare our data. Note that in the known cases of hydrides bridging transition metals, there is at least some metal–metal interaction. Hence the upfield shift observed here cannot be taken as evidence of a linear bridge (type 2). In other words, neither of the spectral tools used in this study are capable of determining direct cation⋯transition metal interaction and structural types 2, 3, and 4 remain possibilities for the ion pair in which cation contact is not at a CO oxygen.

The abstraction of Cl^- by Na^+ leads to irreversible spectral changes in the $ClW(CO)_4L^-$ (L = CO, $P(OMe)_3$).

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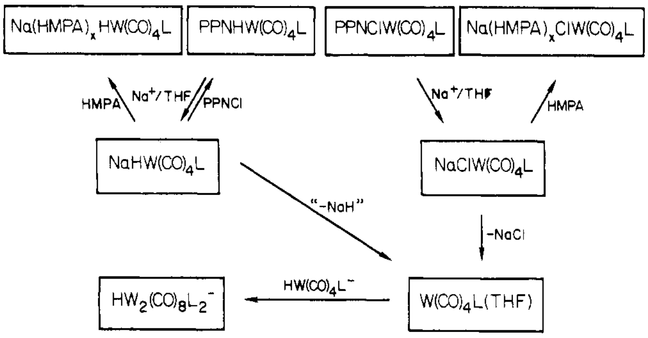
(25) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5412.

Scheme I



The spectroscopically observable $W(CO)_4L{\cdot}THF$ species[26] thus generated ($t_{1/2} \approx 3$ h) can be trapped on time of mixing by various trapping ligands including $HW(CO)_4L^-$. There is an analogous decomposition of the hydrides. Whereas the PPN^+ salts of *cis*-$HW(CO)_4PR_3^-$ are stable in THF solution for extended periods (weeks), the Na^+ salts decompose over the course of a day and the Li^+ salts decompose within minutes to a few hours. As Scheme I illustrates, the decomposition product of the $HM(CO)_4L^-$ ions is $(\mu\text{-}H)M_2(CO)_8L_2^-$, the same product obtained from the decomposition of $ClM(CO)_4L^-$ when $HM(CO)_4L^-$ is added as a trapping agent. Scheme I suggests the alkali-ion-promoted decomposition of the monomeric hydrides to proceed by H^- ion abstraction in the form of "NaH". There is no experimental proof of the presence of NaH at the reaction's end; however, the demands of stoichiometry and earlier reports of the leaving group ability of the H^- ligand[27,28] lend credence to this proposal.

The decomposition products $(\mu\text{-}H)M_2(CO)_8L_2^-$ were identified by comparison of spectral features (ν(CO) IR and ^1H NMR) with those of the well-characterized $(\mu\text{-}H)Mo_2(CO)_8L_2^-$,[29] $(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2CH_2PPh_2)Mo_2(CO)_8^-$,[30] and $(\mu\text{-}H)W_2(CO)_8(PR_3)_2$.[31] In only one case was there a subsequent reaction. The Li^+ ion promoted decomposition of *cis*-$HW(CO)_4PPh_3^-$ yielded as ultimate product the monosubstituted dimer $(\mu\text{-}H)W_2(CO)_9PPh_3^-$, analogous to the crystallographically defined $(\mu\text{-}H)Mo_2(CO)_9PPh_3^-$. The first-formed species, observed within 5 min on addition of $Li^+BPh_4^-$ to a THF solution of $PPN^+HW(CO)_4PPh_3^-$, had IR and NMR spectra similar to the disubstituted dimer hydrides. Over the course of a few hours this transient species changed into the final product via loss of PPh_3 and capture of CO produced by complete decomposition of some of the initial product molecules. This observation is consistent with the reported inability to form $(\mu\text{-}H)Mo_2(CO)_8(PPh_3)_2^-$ by direct substitution.[29] Furthermore the dominant structural characteristic of phosphine-substituted bridging hydrides is the location of phosphines cis to the hydride bridge and exo to the bent molecular framework.[29] Such an arrangement leads to severe ligand steric repulsions for bulky ligands such as PPh_3.

The probability of close cation interaction with hydride was further suggested by the results of eq 3 and 4. Hy-

$$cis\text{-}HW(CO)_4P(OMe)_3^- + PPN^+Cl^- \xrightarrow{THF} \text{no reaction} \quad (3)$$

$$cis\text{-}HW(CO)_4P(OMe)_3^- + LiCl \xrightarrow{THF} LiH + cis\text{-}ClW(CO)_4P(OMe)_3^- \quad (4)$$

$$cis\text{-}HW(CO)_4P(OMe)_3^- + RCl \xrightarrow{THF} RH + cis\text{-}ClW(CO)_4P(OMe)_3^- \quad (5)$$

dride/halide exchange was observed for LiCl as chloride source but not for PPN^+Cl^-. To be sure less electrostatic repulsion is expected for the H^-/Cl^- exchange of (4) as opposed to (3). However the probability of a four-centered transition state for the exchange, involving LiH bond-making simultaneous with W–Cl bond making, is emphasized by this result. Note that eq 4 is the inorganic analogue of (5), the reaction on which the reactivity scale for anionic hydrides is based.[5]

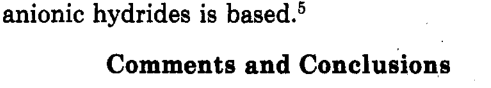
Comments and Conclusions

The points of greatest significance in this accumulation of spectral and chemical data are as follows:

(i) The alkali cation$^+\cdots$anion$^-$ interaction with *cis*-$ClW(CO)_4L^-$ (L = CO, $P(OMe)_3$) is site selective for the chloride ligand.

(ii) The alkali cation$^+\cdots$anion$^-$ interaction with $HM(CO)_4L^-$ shows a dependence on both M and L. Although alkali cation contact of carbonyl oxygen is observed in both $HM(CO)_5^-$ (M = Cr and W), evidence for some ion pairing at the $W\text{-}H^-$ site is fairly strong. Upon substitution of a CO by a phosphine or phosphite ligand, the electrostatic potential of the hydride site (or metal–hydride bond density) is enhanced more than is the CO oxygen basic sites. This has been previously noted,[3] and an explanation of the effect probably lies in the decreased ability of the H^- ligand to donate electrons to the metal in the presence of a good σ-donor phosphorus ligand.[32]

(iii) The results presented here along with those in the literature[33] suggest the following order for sodium ion interaction with hydridocarbonylates:



(iv) With one exception the tendency for alkali cation to interact with the hydride–metal site parallels the relative reactivity of the hydrides toward reduction of nonhindered alkyl halides. That exception is $CpV(CO)_3H^-$ which displays contact ion pairing exclusively of the form $Na^+\cdots OC\text{-}V(Cp)(CO)_2H^-$[33] but whose reactivity rivals that of $HCr(CO)_5^-$.[5] The factors that determine charge apportionment in hydridocarbonylates present an interesting problem to theory that would seem to be also of practical significance.

(v) Finally, alkali cation$\cdots$HM$^-$ interactions result in a weakening of the $M\text{-}H^-$ bond but not an activation of hydride since the NaH or LiH presumed to be generated in the decomposition reactions is quite inert. The original impetus for this study was to define counterion effects in homogeneous metal hydride chemistry that might be useful toward the understanding of alkali promoters in hetero-

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[26] Matching ν(CO) band patterns and positions are obtained upon photolysis of $W(CO)_6$ and $W(CO)_5P(OMe)_3$ in THF. ν(CO) for $W(CO)_5{\cdot}THF$: 2070 (w), 1935 (s), and 1895 (m) cm^{1}. For *cis*-$W(CO)_4P(OMe)_3{\cdot}THF$: 2020 (w), 1898 (s, br), and 1856 (m) cm^{-1}.

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geneous catalytic reduction processes.[7,8] The insight gained by this study is as follows: *If* the hydride-interacting cation could be rendered both less mobile and less attractive electrostatically, then we might expect partial labilization or weakening of the transition metal–hydride bond that might favor processes such as CO insertion or hydride transfer to an adjacent CO ligand site. Whereas such a situation is difficult to achieve in homogeneous systems,[34] the ready availability of rigid basic sites to hold the promoter cation in metal oxide, alumina, or silica supported catalysts would seem to be conducive to CO/H^- activation of precisely this type.

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Registry No. $PPN^+HCr(CO)_5^-$, 78362-94-4; $Na^+HCr(CO)_5^-$, 83399-32-0; $Li^+HCr(CO)_5^-$, 89676-23-3; $PPN^+HW(CO)_5^-$, 78709-76-9; $Na^+HW(CO)_5^-$, 89676-24-4; $Li^+HW(CO)_5^-$, 89676-25-5; $PPN^+ClW(CO)_5^-$, 39048-34-5; $Na^+ClW(CO)_5^-$, 89676-26-6; $Li^+ClW(CO)_5^-$, 89676-27-7; $PPN^+HCr(CO)_4P(OMe)_3^-$, 89676-28-8; $Na^+HCr(CO)_4P(OMe)_3^-$, 89676-29-9; $PPN^+HW(CO)_4P(OMe)_3^-$, 82963-28-8; $Na^+HW(CO)_4P(OMe)_3^-$, 89676-30-2; $Li^+HW(CO)_4P(OMe)_3^-$, 89676-31-3; $PPN^+HW(CO)_4PMe_3^-$, 82963-32-4; $Na^+HW(CO)_4PMe_3^-$, 89676-32-4; $Li^+HW(CO)_4PMe_3^-$, 89676-33-5; $PPN^+HW(CO)_4P(Ph)_3^-$, 82963-30-2; $Na^+HW(CO)_4P(Ph)_3^-$, 89676-34-6; $Li^+HW(CO)_4P(Ph)_3^-$, 89676-35-7; $PPN^+ClW(CO)_5P(OMe)_3^-$, 89676-36-8; $Na^+ClW(CO)_5P(OMe)_3^-$, 89676-37-9; $Li^+ClW(CO)_5P(OMe)_3^-$, 89676-38-0.

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Preparation of Alkenyliron Complexes from the Addition of Anionic Nucleophiles to Cationic Vinylidene Complexes

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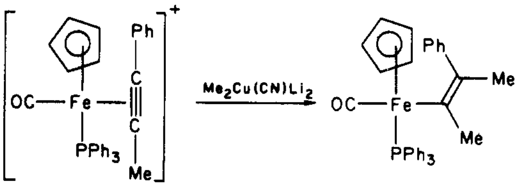
The reaction of $[CpFeCO(PPh_3)(C{=}CMe_2)]BF_4$ with $R_2Cu(CN)Li_2$ (R = Ph, $CH{=}CH_2$) reagents leads to addition at the vinylidene α-carbon atom to produce $CpFeCO(PPh_3)[\eta^1\text{-}C(R){=}CMe_2]$ complexes. For R = $CH{=}CH_2$, this η^1-allyl complex smoothly converts into $CpFe(PPh_3)(\eta^3\text{-}CH_2CHC{=}CMe_2)$, a complex with an unusual η^3-allyl ligand. Addition of $[SPh]^-$ to the vinylidene complex yields $CpFeCO(PPh_3)[C(SPh){=}Me_2]$. The unsymmetrical vinylidene complex $[CpFeCO(PPh_3)\{C{=}C(Ph)Me\}][OSO_2CF_3]$ was prepared and reacts with $Me_2Cu(CN)Li_2$ to produce a 93:7 ratio of the *Z*:*E* isomers of $CpFeCO(PPh_3)[\eta^1\text{-}C(Me){=}C(Ph)Me]$.

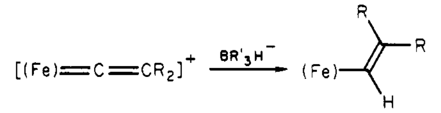
Introduction

We have recently been able to demonstrate that a variety of anionic nucleophiles will add to alkynes η^2-coordinated to cationic iron species to yield η^1-alkenyl complexes.[1] As shown with a specific example in eq 1, the nucleophiles add trans[2] (with the exception of hydride[3]) and for the cases tested, to date, the reaction is regioselective.[1] Because many types of nucleophiles are successful in the reaction, one has considerable control of the β-alkenyl substituent trans to the metal. The other two substituents are controlled by the choice of alkyne. Control of the alkenyl substituents is important because we are developing a variety of reactions that specifically cleave the iron leading to tetrasubstituted olefins.[4]



(1)

Another route to these alkenyl complexes would be the addition of anionic nucleophiles to cationic vinylidene complexes that are isomeric to the η^2-alkyne complexes used in eq 1. Two known examples[5] using hydride as the nucleophile are shown in eq 2. A number of examples using neutral nucleophiles such as PPh_3, pyridine, ROH, RSH, and R_2NH have also been reported.[5a,6]



(2)

(Fe) = $CpFeCO(PPh_3)$, R = H, (Fe) = CpFe(dppe), R = Me

If the reaction of anionic nucleophiles with vinylidene cations were as general as that shown in eq 1, one would gain additional control of the alkenyl substituents. In these vinylidene addition reactions, the nucleophile becomes a substituent at the α-alkenyl carbon atom. In the chemistry shown in eq 1, it becomes a β-alkenyl substituent. Also, a number of attractive routes to these vinylidene starting materials are available (eq 3[5a] and 4[7]), giving one control

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