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Preliminary communication

A REACTIVITY STUDY OF ADDITION OF ORGANIC HALIDES TO $CpMo(CO)_3^-$: COUNTERION AND RX DEPENDENCES

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Summary

Rates of reaction of $CpMo(CO)_3^-$ with organic halides to yield $CpMo(CO)_3R$ showed opposite counterion effects according to the type of RX reagent.

The reactions of benzyl and allyl chloride with $M^+Mn(CO)_4L^-$ ($M^+ = Na^+, Li^+, Na(HMPA)_x^+, Na(15\text{-crown-}5)^+$ or PPN^+; L = CO, $P(OPh)_3$, PPh_3, PMe_2Ph) [1] as well as the reactions of benzyl chloride and substituted benzyl chlorides with $M^+Co(CO)_4^-$ (M^+ = alkali cations and PPN^+) [2] have shown a counterion or solvent effect somewhat unexpected for a process of nucleophilic displacement of halides from RX molecules by the transition metal nucleophile. Rates of reaction and the derived second-order rate constants were observed to decrease as the anionic transition metal carbonylate was placed in a symmetrical solvent environment, freed from the spectroscopially observable influence of the alkali cation as well as its charge neutralizing capabilities. The importance of contact ion pairs and cation involvement in the transition state, presumably via cation assistance in R—X bond cleavage, was emphasized in both studies.

In contrast, oxidative addition of n-alkyl halides to $Na_2Fe(CO)_4$ and of $CH_3C{\equiv}C(CH_2)_4I$ to $Na^+CpW(CO)_3^-$ to yield $Na^+RFe(CO)_4^-$ and $CpW(CO)_3(CH_2)_4C{\equiv}CCH_3$ as first-formed products respectively showed normal counterion or solvent effects [3,4]. The separation of ion aggregates enhanced rates of reaction. Herein we report that the discrepancy is based not on the transition metal nucleophiles but rather on the organic halides used in the various studies.

Using ν(CO) infrared and conductivity techniques as previously described [5] it was established that sodium salts of $CpMo(CO)_3^-$ in tetrahydrofuran (THF) exist as contact ion pairs with cation—anion interactions exclusively of the $Na^+\cdots OC{-}Mo$ type. Ion pairs of bis(triphenylphosphino)iminium (PPN^+)-$CpMo(CO)_3^-$ or $Na(HMPA)_x^+CpMo(CO)_3^-$ are the predominant forms of such

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TABLE 1

SECOND ORDER RATE CONSTANTS FOR REACTION OF METAL CARBONYLATES WITH ORGANIC HALIDES AT 22 ± 1°C IN TETRAHYDROFURAN

Salt[a]	Ion-paired status[b]	RX[c]	k_2 ($\mathrm{mol^{-1}\,l^{-1}\,sec^{-1}}$)[d]
$Na^+CpMo(CO)_3^-$	100% contact	n-C_4H_9I	1.37 ± 0.35[e] × 10^{-4}
$Na(HMPA)_x{}^+CpMo(CO)_3^-$	s.s.f.	n-C_4H_9I	2.68 ± 0.10[f] × 10^{-3}
$PPN^+CpMo(CO)_3^-$	s.s.f.	n-C_4H_9I	2.60 ± 0.13[g] × 10^{-3}
$Na^+CpMo(CO)_3^-$	100% contact	n-C_4H_9Br	2.82 ± 0.14[f] × 10^{-6}
$Na(HMPA)_x{}^+CpMo(CO)_3^-$	s.s.f.	n-C_4H_9Br	1.36 ± 0.03[f] × 10^{-5}
$Na^+CpMo(CO)_3^-$	100% contact	BzCl	1.94 ± 0.04[f] × 10^{-4}
$Na(HMPA)_x{}^+CpMo(CO)_3^-$	s.s.f.	BzCl	6.18 ± 0.07[f] × 10^{-5}
$PPN^+CpMo(CO)_3^-$	s.s.f.	BzCl	6.27 ± 0.19[g] × 10^{-5}
$Na^+Mn(CO)_5^-$	50% contact 50% s.s.f.	BzCl	1.35 ± 0.05[h] × 10^{-3}
$Na(HMPA)_x{}^+Mn(CO)_5^-$	s.s.f.	BzCl	1.49 ± 0.03[h] × 10^{-4}

[a] The separation of ion-pairs by addition of HMPA is assured by providing a 20-fold excess of HMPA per Na^+. See text. [b] "s.s.f." stands for symmetrical solvent field about the carbonylate; "contact" refers to M—CO··· Na^+ interaction in all cases. [c] Reactions were run with RX in 20-fold excess of the carbonylate concentration, which was 0.022 *M*. [d] These values were derived by dividing the k_{obs} obtained from the ln $(A_t - A_\infty)$ vs. time plots, which were linear over the entire reaction, by [RX]. [e] The value for k_2 is the average of 5 runs, utilizing 10—15 individual measurements per run. This error is an expression of the 90% confidence limit for replication, neglecting the smaller errors in individual runs. [f] These k_2 values are averaged over two runs in which reproducibility is < 10%. The error is the average of errors of individual runs, calculated at 95% confidence level. [g] k_2 values obtained from one run; error is calculated at 95% confidence level. [h] Data taken from ref. 1.

salts in THF. However, the C_{3v} symmetry of free $CpMo(CO)_3^-$ is not perturbed by such large counterions.

The reaction described by eq. 1 was shown to obey a second order rate expression, eq. 2, for the RX molecules listed in Table 1. The second order rate constants given in Table 1 were determined at 22 ± 1°C, at which temperature

$$M^+CpMo(CO)_3^- + RX \rightarrow CpMo(CO)_3R + M^+X^- \qquad (1)$$

$$\text{rate} = k_2[M'CO^-][RX] \qquad (2)$$

the product was stable and the reaction appeared (by comparison of the band areas under the reactant and product peaks) to yield $CpMo(CO)_3R$ quantitatively under all counterion and solvent situations.

The reaction of $CpMo(CO)_3^-$ with benzyl chloride (BzCl) proceeds most rapidly when the carbonylate is polarized by Na^+. Both counterions which would yield a symmetrical carbonylate structure, PPN^+ or $Na(HMPA)_x{}^+$, affect the k_2 value the same; there is a three-fold diminution of the rate constant. This counterion effect is less dramatic than that observed for the difference in analogous k_2 values for BzCl reactions of $Mn(CO)_5^-$ as Na^+ vs. $Na(HMPA)_x{}^+$ salts [1]. However, the direction of the effect is unquestionably the same.

In marked contrast, sodium-perturbed $CpMo(CO)_3^-$ reacts with n-C_4H_9I ~20 times slower than does the PPN^+ salt of $CpMo(CO)_3^-$. The THF solution of $Na^+CpMo(CO)_3^-$ containing a 20/1 molar ratio of HPMA/Na^+ also shows a rate enhancement with $k_2(\mathrm{Na(HMPA)}_x^+)/k_2(\mathrm{Na}^+)$ ~20/1. A smaller cation effect is noted for the similar and slower reactions with n-BuBr, with $k_2(\mathrm{Na(HPMA)}_x^+)/k_2(\mathrm{Na}^+) \simeq 5/1$. Although the reaction of n-BuCl with $\mathrm{CpMo(CO)_3^-}$ is immeasurably slow, the rate of reaction of n-BuCl with contact $\mathrm{CpFe(CO)_2^-Na^+}$ in THF is about one-fifth that of the analogous reaction of solvent-separated $\mathrm{CpFe(CO)_2^-(HMPA)_xNa^+}$.

Further studies established that the observed rate constant for reaction of $\mathrm{Na^+CpMo(CO)_3^-}$ with n-BuI was directly dependent on the amount of added HMPA at levels (<20 equivalents) of incomplete sodium ion complexation by HMPA, as monitored by ν(CO) IR. Contrary to this, rate constants gradually decreased upon incremental addition of HMPA to the $\mathrm{CpMo(CO)_2CO^-\cdots Na^+}$ + BzCl reaction.

It is apparent that counterion effects on oxidative addition reactions of transition metal carbonylates will add their own mechanistic subtleties to an already significant list of reaction pattern characteristics [6], The reason for the reversal of counterion effect for RX = BzCl vs. n-BuI or n-BuBr surely lies in a complete or partial mechanism change. Since the benzylic moiety is known to stabilize both radical and carbonium ion species, as well as to provide opportunity for remote site attack, attempts are being made to detect or rationalize such intermediates.

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