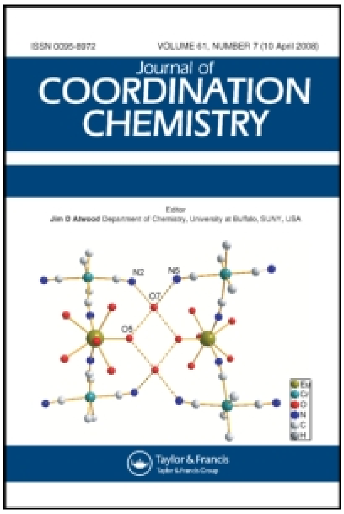

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HALIDE EXCHANGE REACTIONS BETWEEN $CpW(CO)_3^-$ AND $CpMo(CO)_3X$

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Halogen atom transfer from $CpMo(CO)_3X$ (X = Cl, Br and I) to $CpW(CO)_3^-$ forming $CpMo(CO)_3^-$ and $CpW(CO)_3X$ occurs with a first-order dependence on the oxidant and the reductant. The rate constants show a very small dependence on the identity of X, suggesting a mechanism involving nucleophilic attack by $CpW(CO)_3^-$ on a carbonyl of $CpMo(CO)_3X$.

KEYWORDS: Halide exchange, electron transfer, kinetics, metal carbonyl anions, atom transfer

Electron transfer and atom transfer reactions involving organometallic compounds continue to be of great interest. Atom transfer reactions have been defined by Taube[1] as those in which an atom from either the oxidizing or reducing species is transferred through an activated complex in which both species are bound to the transferred atom. Among the species whose transfer has been effected between metal carbonyl anions are H^+,[2,3] R^+ (R = Me, Et, and CH_2Ph)[2,4] and CO.[5] Halide transfer reactions have gotten less attention.[6,7]

Our previous research[8] involving metal carbonyl anions and metal carbonyl halides indicated that in reactions represented by Eq (1), transfer of the halide occurred in those instances where the reactant anion M^- was more nucleophilic[9] than an anion M'^- resulting from the atom transfer.

$$M^- + M'-X \longrightarrow M-X + M'^- \qquad (1)$$

In the opposite situation (M'^- more nucleophilic than M^-), no halide transfer is seen, only single electron transfer.[9]

As an extension of his theory of electron transfer, Marcus developed a treatment for cross-exchange reactions.[10] Kristjánsdóttir and Norton showed that proton transfer between the group 6 complexes $HMCp(CO)_3$ and $M'Cp(CO)_3^-$ follows relative Marcus theory.[3]

Schwarz *et al.* examined the kinetics and mechanism for the halide self-exchange reactions between $CpM(CO)_3^-$ and $CpM(CO)_3X$ (M = Cr, Mo,W; X = Cl, Br, I).[7] They proposed an outer-sphere mechanism, with a significant influence on the rate constants (Table 1) from the halide.

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Table 1 Rate constants for self-exchange reactions between $CpM(CO)_3^-$ or $(Cp\text{-}d_5)Mo(CO)_3^-$ with $CpM(CO)_3X$ at 298 K.[a]

Metal carbonyl anion	Metal carbonyl halide	$k_{ex}(M^{-1}s^{-1})$
$CpMo(CO)_3^-$	$CpMo(CO)_3I$	1.5×10^4
$CpMo(CO)_3^-$	$CpMo(CO)_3Br$	16
$(Cp\text{-}d_5)Mo(CO)_3^-$	$CpMo(CO)_3Cl$	9.0×10^{-2}
$CpW(CO)_3^-$	$CpW(CO)_3I$	4.5×10^3
$CpW(CO)_3^-$	$CpW(CO)_3Br$	1.5
$(Cp\text{-}d_5)W(CO)_3^-$	$CpW(CO)_3Cl$	2.1×10^{-3}

[a]Data from Reference 8.

In this manuscript, we examine the halide cross-exchange reactions between $CpW(CO)_3^-$ and $CpMo(CO)_3X$ (X = Cl, Br, I) to supplement the self-exchange reactions.

EXPERIMENTAL

$W(CO)_6$ and $Cp_2Mo_2(CO)_6$ were purchased from Strem Chemical Co., [PPN][Cl] (PPN = bis(triphenylphosphine)nitrogen(1 +)), $CHBr_3$, and dicyclopentadiene from Aldrich Chemical Corp., $CHCl_3$ and iodine from Fisher Scientific, and all were used as received. The compounds $[PPN][CpW(CO)_3]$,[11] [PPN] $[CpMo(CO)_3]$,[12] $CpMo(CO)_3X$ (X = Cl, Br, I),[13] and $CpW(CO)_3X$ (X = Cl,[14]I[15]) were prepared by literature methods. $CpW(CO)_3Br$ was prepared by the same method as $CpMo(CO)_3Br$. Infrared spectra were recorded on a Mattson Polaris FTIR. THF was refluxed over Na/benzophenone and distilled under N_2.

Product Studies

Each of the samples was prepared, and the reactions run, by the same method. In an inert-atmosphere glovebox, approximately 1×10^{-5} moles of metal carbonyl anion were dissolved in THF in a 10 mL volumetric flask. An equimolar quantity of halide was prepared in the same way. These solutions were then combined in a 5 dram vial, capped, and shaken vigorously. An infrared cell was filled with a solution, removed from the drybox, and a spectrum recorded.

Kinetics

All data were collected at 25°C under *pseudo* first-order conditions by following the disappearance of the infrared absorptions of the metal carbonyl anion, with at least a 5-fold excess of halide complex.

THF solutions were prepared in volumetric flasks in the drybox, with anion solution concentrations between 5×10^{-4} and 1×10^{-3}M. Concentrations of the halide complex ranged from 5×10^{-3} to 3×10^{-2}M. These flasks were then capped with rubber septa and removed for analysis on our stopped-flow instrument, which has been described previously.[16] The data collected were analyzed using the stopped-flow operating system (OLIS).

All rate constants are averages of multiple reactions of independently prepared solutions. Error limits are standard deviations for k_{obs}, and 95% confidence limits for second-order rate constants.

RESULTS

Products

The products of the reactions between $CpW(CO)_3^-$ and $CpMo(CO)_3X$ are shown in Table 2. In each case, the halide was transferred quantitatively to the anion, forming a new metal carbonyl halide $CpW(CO)_3X$, and $CpMo(CO)_3^-$. In addition, reaction between $CpW(CO)_3^-$ and $(C_9H_7)Mo(CO)_3Br$ resulted in halide transfer, with $CpW(CO)_3Br$ and $(C_9H_7)Mo(CO)_3^-$ as products. The reactions were all sufficiently rapid that the final products were the only species present in the first infrared spectrum obtained after mixing (approximately five minutes). Infrared absorption data are listed in Table 3.

Kinetics

These reactions were overall second order (first order in both $CpW(CO)_3^-$ and $CpMo(CO)_3X$) with a rate law

$$\text{rate} = k[CpW(CO)_3^-][CpMo(CO)_3X]$$

normal for electron transfer reactions. Second order rate constant data were obtained under *pseudo* first-order conditions with halide in excess. The rate constants are listed in Table 4. Reaction between $CpW(CO)_3^-$ and $(C_9H_7)Mo(Co)_3Br$ gave a second order rate constant of 220 ± 20 $M^{-1}s^{-1}$.

DISCUSSION

Reaction of $CpW(CO)_3^-$ with $CpMo(CO)_3X$ results in quantitative transfer of halide to the tungsten, coupled with a two electron change; alternatively, this could be considered as X^+ transfer. The reactions were first order in $[CpW(CO)_3^-]$ and first order in $CpMo(CO)_3X$. Table 4 shows calculated equilibrium constant values from using relative Marcus theory and the self-exchange rate data from Table 1. The calculated values vary tremendously and cannot be accurate. The failure of the rate constants to agree with relative Marcus theory is likely an indication of a mechanistic change.[17,18] The very small dependence of the rate on X for the cross

Table 2 Products of the reaction of $CpW(CO)_3^-$ with $CpMo(CO)_3X$ (X = Cl, Br, I).

$CpMo(CO)_3X$	Products
$CpMo(CO)_3Cl$	$CpMo(CO)_3^-$, $CpW(CO)_3Cl$
$CpMo(CO)_3Br$	$CpMo(CO)_3^-$, $CpW(CO)_3Br$
$CpMo(CO)_3I$	$CpMo(CO)_3^-$, $CpW(CO)_3I$

Table 3 Infrared absorption frequencies in THF.

Compound	IR (cm^{-1})
$CpMo(CO)_3^-$	1898(s), 1781(vs)
$CpW(CO)_3^-$	1891(s), 1777(vs)
$(C_9H_7)Mo(CO)_3$	1902(s), 1789(s)
$CpMo(CO)_3Cl$	2051(s), 1972(s, br), 1957(sh)
$CpMo(CO)_3Br$	2047(s), 1971(sh), 1960(s, br)
$CpMo(CO)_3I$	2039(s), 1962(s)
$CpW(CO)_3Cl$	2043(s), 1954(vs, br)
$CpW(CO)_3Br$	2041(s), 1953(vs)
$CpW(CO)_3I$	2033(s), 1949(vs, br)
$(C_9H_7)Mo(CO)_3Br$	2045(m), 1969(s), 1952(sh)

Table 4 Experimental second order rate constants for the reactions between $CpW(CO)_3^-$ and $CpMo(CO)_3X$ and calculated K_{12} Values.

$CpMo(CO)_3X$	$k(m^{-1}s^{-1})$	K_{12}
$CpMo(CO)_3I$	390 ± 50	2×10^{-3}
$CpMo(CO)_3br$	210 ± 30	2×10^{3}
$CpMo(CO)_3Cl$	160 ± 30	1×10^{8}

reactions reported herein, is quite different than the dependence on halide for the self-exchange reactions.[7]

An inner-sphere mechanism is proposed for these reactions involving nucleophilic attack. One site for attack in halogen transfer reactions is the halide, forming a halide-bridging dimer in the activated complex. However, a reaction intermediate involving a bridged halide can be discounted by the experimental rate constant data in Table 4. Attack at the halide should show a wide variation in the rate constant when X is varied from Cl to Br to I, in the order Cl < Br < I, similar to the self-exchange data. While our data showed this order of rate constants, the rate dependence was not large enough for attack at halide.

A second possible site for attack is the metal center of the reactant halide complex. Attack at the metal center can also be discounted, however, for two reasons. Formation of bimetallic complex (even in very low yield) would be expected from attack at the metal. In addition, the large rate enhancements ("indenyl effect") indicative of a ring slippage mechanism were not evident when idenyl ligand was substituted for Cp in the reactant halide complex.

Attack at a third possible site, the carbon atom of a carbonyl *cis* to the halide is possible, as suggested for reactions between metal carbonyl anions and metal carbonyl halides previously described.[8] Attack at the CO *cis* to X is consistent with the relatively small dependence on X. Nucleophilic attack at CO has been reviewed.[19] That the cross-exchange reactions (reaction 2) occur by a different mechanism than the self-exchange partially accounts for the failure of relative Marcus theory to correctly predict the reaction rates.

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