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I^+-abstraction versus I^--displacement in the reactions of diiodoacetylene with metal carbonyl anions: X-ray structure of $[(OC)_5MnC{\equiv}CMn(CO)_5]$

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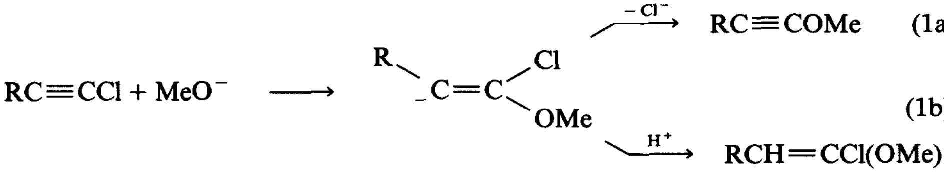
Abstract

Solid diiodoacetylene, IC≡CI, reacts with THF solutions of the highly basic, third row, metal carbonyl anion, $Re(CO)_5^-$, exclusively by a formal I^+-abstraction process producing $ReI(CO)_5$ and $Re_2I_2(CO)_8$. Under the same conditions, the less basic, first row, metal carbonyl anion, $Mn(CO)_5^-$ reacts to produce not only $Mn_2I_2(CO)_8$ by formal I^+-abstraction but also $(OC)_5MnC{\equiv}CMn(CO)_5$ by I^--displacement. These results may be rationalized by HSAB arguments and consideration of charge distribution in the substrate as indicated by molecular orbital calculations. The X-ray structure of $(OC)_5MnC{\equiv}CMn(CO)_5$ is reported. Crystals are triclinic, space group $P\bar{1}$, with $Z = 1$ in a unit cell of dimensions *a* 6.421(2), *b* 6.425(2), *c* 9.520(2) Å, α 81.86(2), β 88.55(2), γ 82.06(2)°, and D_{calc} 1.79 g cm^{-3}. The structure was solved by the Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.024$, $R_w = 0.033$ for 1372 observed reflections with $F_o^2 > 3.0\sigma(F_o^2)$. The complex is centrosymmetric and thus exhibits an eclipsed geometry in the solid state.

Introduction

Both haloalkynes [1], RC≡CX, and dihaloalkynes [1], XC≡CX, are potential C_2-building blocks for organometallic compounds [2] whose reactivity patterns illustrate significant departures from the reactivity patterns of simple alkynes [3]. The reactions with nucleophilic bases are illustrative [1b]. Thus, RC≡CCl reacts with methoxide ion by competing pathways [4] involving attack at C_1, C_2, and at X. Attack at C_1 leads to displacement of X^- (eq. 1a) with competing trapping of the intermediate carbanion by H^+, resulting in regiospecific 1,2-addition (eq. 1b).


(1a)
(1b)

Attack at C_2 produces the opposite regioisomer of the alkene [4] (eq. 2).

$$RC{\equiv}CCl + MeO^- \longrightarrow \underset{MeO}{\overset{R}{>}}C{=}C^{-}\diagdown_{Cl} \xrightarrow{H^+} RC(OMe){=}CHCl \qquad (2)$$

Finally, attack directly at X results in the formal abstraction of X^+ with substitution by H^+ (eq. 3) [4].

$$RC{\equiv}CCl + NaOMe \longrightarrow RC{\equiv}CNa + MeOCl \xrightarrow{MeOH} RC{\equiv}CH + Me_2O + NaOCl \qquad (3)$$

Of the competing pathways illustrated in eqs. 1–3, the absence of proton donors closes down all possible reactions except for the nucleophilic displacement of X^-, shown in eq. 1a. This illustrates the essential difference between haloalkynes, RC≡CX, and simple alkynes, RC≡CH. Thus, in the absence of proton sources, RC≡CX exhibits reactivity umpolung [5] and reacts with nucleophiles by displacement of X^-, i.e. RC≡CX acts as a source of $RC{\equiv}C^+$ equivalents. Conversely, simple alkynes react with nucleophilic bases by H^+-abstraction to produce alkynyl anions [6], $RC{\equiv}C^-$ (eq. 4).

$$RC{\equiv}CH + NaOMe \rightleftharpoons RC{\equiv}CNa + MeOH \qquad (4)$$

Far from being a mechanistic curiosity, the X^--displacement pathway illustrated in eq. 1a has been used to develop synthetic routes to heteroatom-substituted alkynes, RC≡CNu, where Nu^- = alkoxide [7], thiolate [8], amine [9], phosphine [10] etc. Useful C–C bond formation strategies have similarly evolved from the Michael addition of tertiary enolates [11] to RC≡CX. The utility of haloalkynes in organic chemistry has been thoroughly reviewed [1].

Given this comparison of RC≡CX and RC≡CH, a similar comparison of XC≡CX and HC≡CH is possible. Here we find that XC≡CX reacts with nucleophiles by double displacement of X^-, e.g. the Arbuzov reaction [12] shown in eq. 5.

$$2\ R_2POR' + ClC{\equiv}CCl \longrightarrow R_2P(O)C{\equiv}CP(O)R_2 + 2\ R'Cl \qquad (5)$$

The reaction shown in eq. 5 indicates that XC≡CX will act as the synthetic equivalent of $[C{\equiv}C]^{2+}$ in its reactions and thus is complementary or umpolung to HC≡CH which acts as a $[C{\equiv}C]^{2-}$ equivalent [13] (e.g. eq. 6).

$$HC{\equiv}CH + 2\ {}^{n}BuLi \longrightarrow LiC{\equiv}CLi + 2\ {}^{n}BuH \qquad (6)$$

Based upon this known chemistry, we have sought to utilize dihaloalkynes as C_2-building blocks for organometallic compounds [14*] by exploiting their potential as $[C{\equiv}C]^{2+}$ equivalents in areas where analogous chemistry employing $[C{\equiv}C]^{2-}$ equivalents fails.

Accordingly we have investigated the reaction of IC≡CI with metal carbonyl

* Reference number with asterisk indicates a note in the list of references.

anions. The considerations described above suggest that novel routes to $(OC)_nMC{\equiv}CM(CO)_n$ complexes might evolve if X^--displacement is successful. General routes to $L_nMC{\equiv}CML_n$ complexes are not routinely available [15] and the few fully characterized complexes of this type have typically been prepared by attack of nucleophilic carbon on an electrophilic metal center [15]. This approach is known to fail [16] in attempts to synthesize $(OC)_5MnC{\equiv}CMn(CO)_5$ (eq. 7).

$$2\ MnCl(CO)_5 + LiC{\equiv}CLi \longrightarrow Mn_2(CO)_{10} + 2\ LiCl + 2\ C \qquad (7)$$

Similarly, $(OC)_5ReC{\equiv}CRe(CO)_5$ cannot be prepared [17] by the reaction of $Re(CO)_5FBF_3$ with either Li_2C_2 or Na_2C_2. Despite these synthetic failures, there can be no inherent thermodynamic instability in $(OC)_nMC{\equiv}CM(CO)_n$ complexes since the rhenium compound, $(OC)_5ReC{\equiv}CRe(CO)_5$, has been prepared by Beck [18] via an ingenious multistep route, which involves sequential nucleophilic attacks on electrophilic rhenium and which avoids direct use of highly reducing $[C{\equiv}C]^{2-}$ synthons (eq. 8).

$$[Re(CO)_5FBF_3] + Me_3SiC{\equiv}CH \longrightarrow Re(CO)_5C{\equiv}CH + FSiMe_3 + BF_3$$

$$Re(CO)_5C{\equiv}CH \xrightarrow{[Re(CO)_5FBF_3]} \left[\begin{array}{c}(OC)_5ReC{\equiv}CH \\ \quad\quad | \\ \quad\quad Re(CO)_5\end{array}\right]^+ [BF_4]^-$$

$$(OC)_5ReC{\equiv}CRe(CO)_5 + NaBF_4 + EtOH \xleftarrow{NaOEt} \left[\begin{array}{c}(OC)_5ReC{\equiv}CH \\ \quad\quad | \\ \quad\quad Re(CO)_5\end{array}\right]^+ [BF_4]^- \qquad (8)$$

Based on these reports, we have investigated the reactions of both $Re(CO)_5^-$ and $Mn(CO)_5^-$ with $IC{\equiv}CI$ in order to determine the utility of this dihaloalkyne as a $[C{\equiv}C]^{2+}$ equivalent in a system where the direct use of $[C{\equiv}C]^{2-}$ synthons is known to fail [16,17].

Experimental

$Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ used to generate the corresponding $Mn(CO)_5^-$ and $Re(CO)_5^-$ anions, were purchased from Strem Chemical Company and used without further purification. Reagent grade tetrahydrofuran (THF) was distilled from sodium metal and benzophenone under nitrogen. All reactions were done using Schlenk techniques and employing a nitrogen atmosphere. Infrared spectra were recorded using a Nicolet 60-SX FTIR spectrometer. Mass spectra were recorded using an HP5988A spectrometer. X-Ray data for the structure determination of **1** were collected using an Enraf–Nonius CAD4 diffractometer.

The ab initio calculations were performed using the GAUSSIAN 86 program [19] on a MicroVAX II or a Cray Y-MP/864. Restricted Hartree–Fock minima were calculated using the STO-3G* basis set [20], and all stationary points on the potential energy hypersurface were confirmed by force calculations. Geometries were constrained to be linear; the bond lengths were optimized using symmetry where applicable. Output data are summarized in the supplementary material.

Reaction of $Mn(CO)_5^-$ with IC≡CI

A solution of 0.2 g (1.02×10^{-3} mol) of $Mn(CO)_5^-$, prepared according to the literature method [21], in 28 ml of dry and degassed THF was added dropwise to 0.14 g (5.03×10^{-4} mol) of solid diiodoacetylene. The reaction mixture was stirred under nitrogen overnight (14 h), during which time the color changed to dark brown. The reaction mixture was then concentrated under vacuum and cooled overnight at $-13°$C. A pale yellow crystalline product separated (0.032 g, 15.2%) which was isolated by filtration and identified as $(OC)_5MnC{\equiv}CMn(CO)_5$: IR (KBr disk): ν(CO) 1939w, 1986m, 2012m, 2037w, 2068s, 2117vs cm^{-1}, MS (70 eV, EI): M^+ (414), $M^+ - CO$ (386), $M^+ - 2CO$ (358), $M^+ - 3CO$ (330), $M^+ - 4CO$ (302), $M^+ - 5CO$ (274), $M^+ - 6CO$ (246), $M^+ - 7CO$ (218), $M^+ - 8CO$ (190), $M^+ - 9CO$ (162), $Mn_2C_2^+$ (134), MnC_2^+ (79), Mn^+ (55). The reaction mixture was then further concentrated *in vacuo*, treated with hexanes, and cooled at ~ 13°C for 15 h to produce a dark brown crystalline product (0.07 g, 23.3%) which was identified as $Mn_2I_2(CO)_8$: IR (KBr disk): ν(CO) 1844vw, 1868w, 1890w, 1951m, 1960w, 1978s, 2004m, 2026m, 2036m, 2087vs cm^{-1}, MS (70 eV, EI): M^+ (588), $M^+ - 3CO$ (504), $M^+ - 4CO$ (476), $M^+ - 5CO$ (448), $M^+ - 6CO$ (420), $M^+ - 7CO$ (392), $Mn_2I_2^+$ (364), Mn_2I^+ (237), MnI^+ (182), I^+ (127), Mn^+ (55). The rest of the solution was then evaporated *in vacuo* to produce a high melting point black residue.

Reaction of $Re(CO)_5^-$ with IC≡CI

A solution of 0.2 g (6.11×10^{-4} mol) of $Re(CO)_5^-$, prepared according to the literature method [21*], in 28 ml of dry and degassed THF was added dropwise to 0.085 g of solid IC≡CI. The reaction mixture was stirred under nitrogen overnight (17 h), during which time the color changed from red to dark violet. The reaction mixture was then concentrated *in vacuo* and cooled at $-13°$C to give a pale yellow crystalline product (0.068 g, 24.5%) identified as $ReI(CO)_5$: IR (KBr disk): ν(CO) 1948w, 1984s, 2029s, 2146vs cm^{-1}, MS (70 eV, EI): M^+ (454), $M^+ - CO$ (426), $M^+ - 2CO$ (398), $M^+ - 3CO$ (370), $M^+ - 4CO$ (342), ReI^+ (314), Re^+ (187), I^+ (127). The reaction mixture was then treated with hexanes and cooled to $-13°$C to produce a yellow crystalline product (0.18 g, 34.5%) which was filtered and identified as $Re_2I_2(CO)_8$: IR (KBr disk): ν(CO) 1936m, 1966m, 2030m, 2107vs cm^{-1}. MS (70 eV, EI): M^+ (852), $M^+ - CO$ (824), $M^+ - 2CO$ (796), $M^+ - 3CO$ (768), $M^+ - 4CO$ (740), $M^+ - 5CO$ (712), $M^+ - 6CO$ (684), $M^+ - 7CO$ (656), $Re_2I_2^+$ (628), Re_2^+ (374), Re^+ (185, 187), I^+ (127). The rest of the solvent was then evaporated *in vacuo* to produce a high melting point black residue.

Results and discussion

When $Mn(CO)_5^-$ generated by NaK alloy reduction of $Mn_2(CO)_{10}$ in THF, is added to one half equivalent of IC≡CI and stirred overnight, a dark brown solution is produced. Concentration *in vacuo* and cooling to $-13°$C resulted in the formation of a pale yellow crystalline product, **1**. After filtration, addition of hexanes, followed by further cooling to $-13°$C, led to precipitation of **2**, which was isolated by filtration. Removal of solvent *in vacuo* from the remaining solution produced a black material, **3**.

The compound **1** was initially identified as $(OC)_5MnC{\equiv}CMn(CO)_5$ from its EI mass spectrum. The spectrum showed a molecular ion, ($m/e = 414$) and peaks

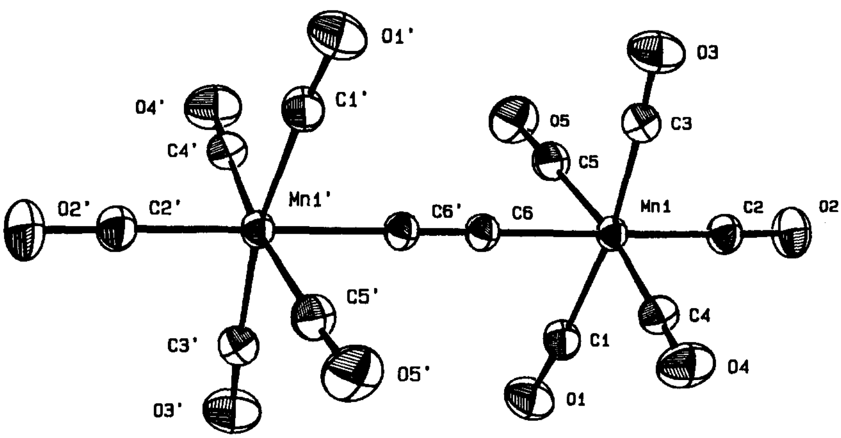


Fig. 1. An ORTEP view of $(OC)_5MnC{\equiv}CMn(CO)_5$ showing 50% probability elipsoids.

corresponding to the sequential loss of each of the ten carbonyl groups. Loss of one manganese, then the other, completed the fragmentation. The IR spectrum of **1** showed the expected bands in the carbonyl region (see Experimental) based on a comparison with Beck's rhenium compound [17,18] (see eq. 8). The X-ray structure of **1** is shown in Fig. 1 with crystal data, atomic positional parameters, and bond lengths and angles presented in Tables 1, 2, and 3 respectively. The X-ray crystal structure of Beck's rhenium compound has recently been described (Re–C≡ 2.14(2), C≡C 1.20(3) Å) [17] and both the rhenium and manganese compounds have an unusual eclipsed geometry when viewed along the four-fold axis (Fig. 2). Similarly,

Table 1

Crystal data for $(OC)_5MnC{\equiv}CMn(CO)_5$

FW	414
Crystal syst.	triclinic
Space group	$P\bar{1}$
a, Å	6.421(2)
b, Å	6.425(2)
c, Å	9.520(2)
α, deg	81.86(2)
β, deg	88.55(2)
γ, deg	82.06(2)
V, Å^3	385.1
Z	1
D_{calc}, g cm^{-3}	1.79
Cryst. dimens., mm	0.24×0.14×0.16
Radiation	Mo-K_α (λ 0.71073 Å)
Monochrometer	graphite
2θ limits, deg	52.0
Temp., °C	21±1
No. of refl. measured	1637 total, 1497 unique
μ, cm^{-1}	16.2
R, %	2.40
R_w, %	3.30

Table 2

Atomic positional parameters and equivalent isotropic displacement parameters for $(OC)_5MnC{\equiv}CMn(CO)_5$ [a]

Atom	x	y	z	B (Å^2)
Mn1	0.63293(4)	0.18531(3)	0.25897(2)	2.759(5)
C1	0.7772(3)	−0.0817(3)	0.2402(2)	3.88(4)
C2	0.7263(3)	0.3205(3)	0.0914(2)	3.81(4)
C3	0.4683(3)	0.4276(3)	0.3084(2)	3.60(4)
C4	0.8545(3)	0.2399(3)	0.3671(2)	3.68(4)
C5	0.3975(3)	0.1106(3)	0.1802(2)	3.90(4)
C6	0.5306(3)	0.0421(3)	0.4444(2)	3.09(3)
O1	0.8568(3)	−0.2466(3)	0.2328(2)	6.04(4)
O2	0.7809(3)	0.4065(3)	−0.0121(2)	5.83(4)
O3	0.3661(3)	0.5677(2)	0.3421(2)	5.73(4)
O4	0.9835(2)	0.2696(3)	0.4354(2)	5.82(4)
O5	0.2534(3)	0.0625(3)	0.1356(2)	6.19(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

both compounds exhibit typical C≡C bond lengths, implying acetylenic (MC≡CM), rather than allene-like (M=C=C=M), character.

The second product isolated from the reaction of IC≡CI with $Mn(CO)_5^-$, **2**, was identified by EI–MS, IR methods, and X-ray crystallography as $Mn_2(\mu\text{-}I)_2(CO)_8$. The X-ray crystal structure of this compound is routine and will be described elsewhere [22]. The black residue remaining after isolation of **1** and **2** proved to be an insoluble, high melting point material which we believe to be a carbonaceous deposit.

Table 3

Bond lengths (Å) and angles (°) for $(OC)_5MnC{\equiv}CMn(CO)_5$ (numbers in parentheses are estimated standard deviations in the least significant digits)

Mn1–C1	1.863(2)	C1–O1	1.122(2)
Mn1–C2	1.834(2)	C2–O2	1.132(2)
Mn1–C3	1.868(2)	C3–O3	1.118(2)
Mn1–C4	1.877(2)	C4–O4	1.11993)
Mn1–C5	1.854(2)	C5–O5	1.126(3)
Mn1–C6	2.011(2)	C6–C6	1.201(2)
C1–Mn1–C2	95.95(8)	C3–Mn1–C6	84.52(7)
C1–Mn1–C3	169.43(8)	C4–Mn1–C5	170.56(8)
C1–Mn1–C4	90.03(9)	C4–Mn1–C6	84.72(8)
C1–Mn1–C5	89.39(9)	C5–Mn1–C6	85.84(8)
C1–Mn1–C6	84.93(8)	Mn1–C1–O1	176.7(2)
C2–Mn1–C3	94.60(8)	Mn1–C2–O2	178.8(2)
C2–Mn1–C4	94.66(9)	Mn1–C3–O3	177.2(2)
C2–Mn1–C5	94.77(9)	Mn1–C4–O4	177.8(2)
C2–Mn1–C6	178.93(9)	Mn1–C5–O5	178.3(2)
C3–Mn1–C4	89.65(8)	Mn1–C6–C6	179.5(2)
C3–Mn1–C5	89.20(9)		

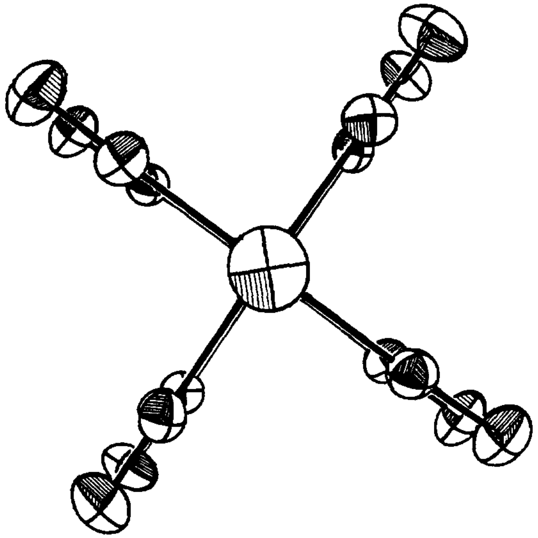


Fig. 2. An ORTEP view of $(OC)_5MnC{\equiv}CMn(CO)_5$ along the four-fold axis showing 50% probability elipsoids.

Thus, by analogy to the known reactions [1] of dihaloalkynes with basic, organic nucleophiles (eqs. 1–3) we interpret the results of the reaction of IC≡CI with $Mn(CO)_5^-$ in terms of two competing pathways, one involving I^--displacement (analogous to eq. 1a) and one involving formal I^+-abstraction (analogous to eq. 3). These pathways are illustrated in eqs. 9 and 10. We have excluded possible radical pathways for the formation of **1** and **2** since $Mn_2(CO)_{10}$, which is typically formed in related processes involving radical mechanisms [23], is not a product of this reaction.

$$2\,M[Mn(CO)_5] + IC{\equiv}CI \longrightarrow \underset{\textbf{(1)}}{(OC)_5MnC{\equiv}CMn(CO)_5} + 2\,MI \qquad (9)$$

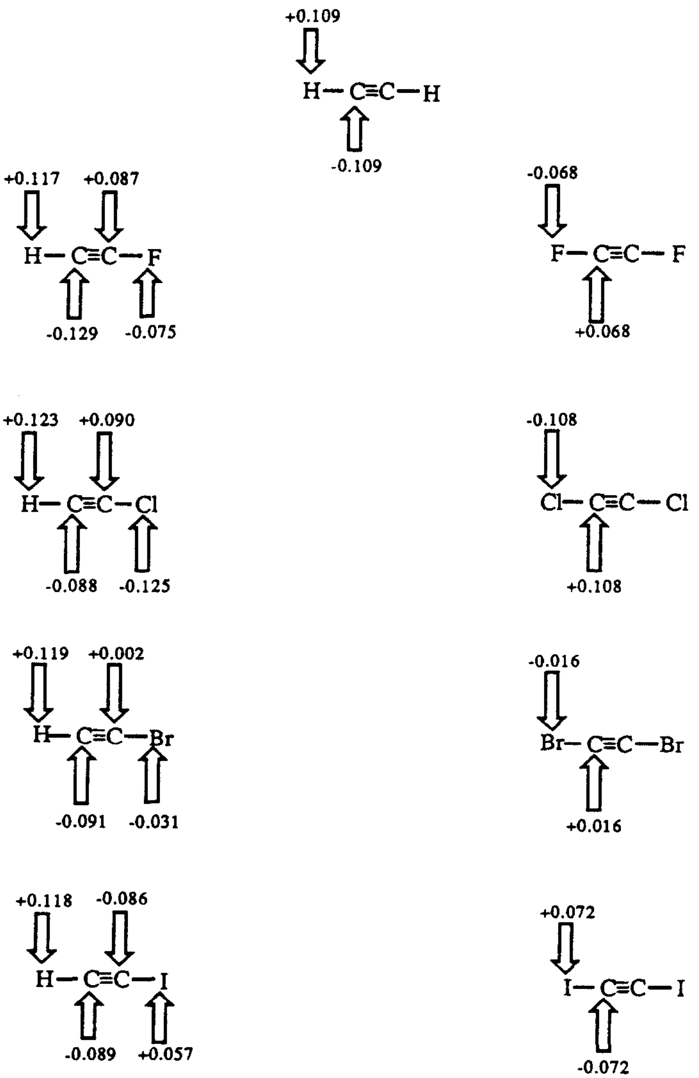
$$M[Mn(CO)_5] + IC{\equiv}CI \longrightarrow MnI(CO)_5 \xrightarrow{-CO} \underset{\textbf{(2)}}{1/2\,Mn_2I_2(CO)_8}$$

$$+\,\underset{\textbf{(3)}}{MC{\equiv}CI \longrightarrow \text{Black residue}} \qquad (10)$$

Analogous treatment of solid IC≡CI with two equivalents of $Re(CO)_5^-$ produced two crystalline products, **4** and **5**, and an insoluble black residue, **6**. Neither **4** nor **5** proved to be $(OC)_5ReC{\equiv}CRe(CO)_5$. Compound **4** was identified by EI-MS, IR methods and X-ray crystallography as $ReI(CO)_5$. The X-ray structure of this compound is routine and will also be described elsewhere [22]. The compound **5** was identified by EI-MS methods, and comparison of unit cell parameters to those extant in the literature [24], as $Re_2(\mu\text{-}I)_2(CO)_8$. Thus, $Re(CO)_5^-$ reacts with IC≡CI by a process analogous to that illustrated in eq. 10. We were able to find no evidence for a competing process analogous to eq. 9.

To summarize, $Mn(CO)_5^-$ reacts by both I^--displacement and formal I^+-abstraction whereas $Re(CO)_5^-$ reacts by formal I^+-abstraction only. In the rhenium case we isolate both $ReI(CO)_5$ and $Re_2(\mu\text{-}I)_2(CO)_8$ whereas in the case of manganese, since the dimerization of $MnI(CO)_5$ is known [25] to be rapid, only $Mn_2(\mu\text{-}I)_2(CO)_8$ is isolated.

We believe that the difference in reactivity between $Re(CO)_5^-$ and $Mn(CO)_5^-$ can be explained by simple hard-soft acid-base (HSAB) arguments [26*]. Thus, the low electronegativity of iodine leads to a build up of negative charge on carbon (*vide infra*) in IC≡CI, making the iodine itself an electrophilic site. Attack of the third row, strongly basic [27*] anion, $Re(CO)_5^-$, occurs exclusively at this site. With the first row, less basic [27*] anion, $Mn(CO)_5^-$, attack directly at iodine will be less favored on HSAB grounds and so attack at the harder carbon site becomes competitive.



Scheme 1. Calculated total charges on HC≡CX and XC≡CX.

In order to explore possible methods of enhancing site selectivity in the reactions of metal carbonyl anions with haloalkynes, we have performed *ab initio* molecular orbital calculations [28] on optimized HC≡CX and XC≡CX structures at the RHF/STO-3G* level [20]. Scheme 1 shows some selected examples from the series where total electronic charges are displayed by each atom. As mentioned in a qualitative way in the above paragraphs, IC≡CI is subject to formal I^+-abstraction because the low electronegativity of iodine leads to a build up of negative charge on carbon [28*]. By consideration of the charge distributions shown in Scheme 1, it is clear that ClC≡CCl will be the substrate of choice to maximize X^--displacement and minimize formal X^+-abstraction.

Indeed, after completion of this work we became aware of work from the USSR [29] which demonstrates that the reactions of the anions $MCp(CO)_3^-$ (M = Cr, Mo, W) with XC≡CX also proceed by both X^+-abstraction and X^--displacement. These workers find that X^+-abstraction increases in the order X = Cl < Br < I as HSAB considerations suggest.

Acknowledgments

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