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Synthesis and Reactivity of Bimetallic Bridging Haloalkyl Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)X(CH_2)_xM(CO)_5]^+BF_4^-$ (X = I, Br, Cl; M = Re, Mn; x = 1, 4)

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Reactions of $(CO)_5ReCH_2OCH_3$ with $(CH_3)_3SiI$, $(CH_3)_3SiBr$, and HCl gas give the halomethyl complexes $(CO)_5ReCH_2X$ (**4**, 76–92%; X = **a**, I; **b**, Br; **c**, Cl). Reactions of $Na^+[(CO)_5Re]^-$ with ICH_2F and $I(CH_2)_4I$ give $(CO)_5ReCH_2F$ (**4d**, 73%) and $(CO)_5Re(CH_2)_4I$ (**5**, 36%). Reactions of the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**) with **4a** and **5** give bridging haloalkyl complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)I(CH_2)_xRe(CO)_5]^+BF_4^-$ (x = 1, **6a**; x = 4, **7**) in 69–78% yields after workup. A similar reaction of **2** and $(CO)_5MnCH_2I$ gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)ICH_2Mn(CO)_5]^+BF_4^-$ (**9**), which is less stable than **6a** but can be isolated in crude form. The XCH_2 ^{13}C NMR resonances of **6a**, **7**, and **9** show diagnostic downfield shifts, and the diastereotopic XCH_2 protons give distinct ^1H NMR resonances. Reactions of **2** with **4b**,**c** (−80 to −25 °C) give spectroscopically observable adducts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)XCH_2Re(CO)_5]^+BF_4^-$ (X = Br, Cl). Reaction of **2** and **4d** does not yield a detectable bridging fluoroalkyl complex. Addition of PPN^+Br^- to **6a** gives $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (78%) and **4b** (82%), and similar reactions of **9** are described.

Although transition metal complexes of alkyl and aryl halides[1–9] were scarcely known a decade ago, numerous adducts have now been isolated.[1–7] As such, this rapidly expanding branch of coordination chemistry is poised for practical application and architectural extension. In particular, we became interested in the possibility of preparing bimetallic *bridging* haloalkyl complexes derived from ω-haloalkyl compounds $L_nM(CH_2)_xX$ (I), as illustrated in generalized eq i. Numerous complexes of the formula I are readily available, as recently summarized in a comprehensive review.[10]

$$\underset{\textbf{I}}{L_nM(CH_2)_xX} + [M'L'_{n'}]^{m+} \rightarrow \underset{\textbf{II}}{[L_nM(CH_2)_xXM'L'_{n''}]^{m+}} \quad \text{(i)}$$

The target molecules II offer several features of interest in addition to those normally associated with new classes of binuclear complexes. First, they constitute potential models for intermediates in metal-promoted degradations of haloalkanes. For example, several bimetallic or cluster compounds have been isolated that contain bridging CH_2, CH, or CX fragments derived from dihalomethanes.[11] Second, α-halomethyl complexes (I, x = 1) see use in alkene cyclopropanation and metathesis reactions[10] and other carbon–carbon bond forming processes.[12] These chemical properties may be enhanced or modified in useful ways in binuclear derivatives II.

At the outset of this study, we were not certain whether adducts II would be isolable. We were encouraged by an earlier finding that the sulfur atoms in α-(alkylthio)methyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SR)$ were more basic than those in organic thioethers CH_3SR[13] and by

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similar observations with other compounds.[14] Thus, we anticipated that α-halomethyl complexes would be thermodynamically stronger ligands than the corresponding alkyl halides RCH_2X. This also might enhance the prospects of detecting adducts with organofluorine donor groups—a very rare type of species.[5,6] On the other hand, alkyl halide complexes are strongly activated toward nucleophilic attack at carbon.[2,7] Thus, the C–X linkage in I, which is in many cases very substitution-labile,[10] might be even more reactive in II, leading to kinetic instability.

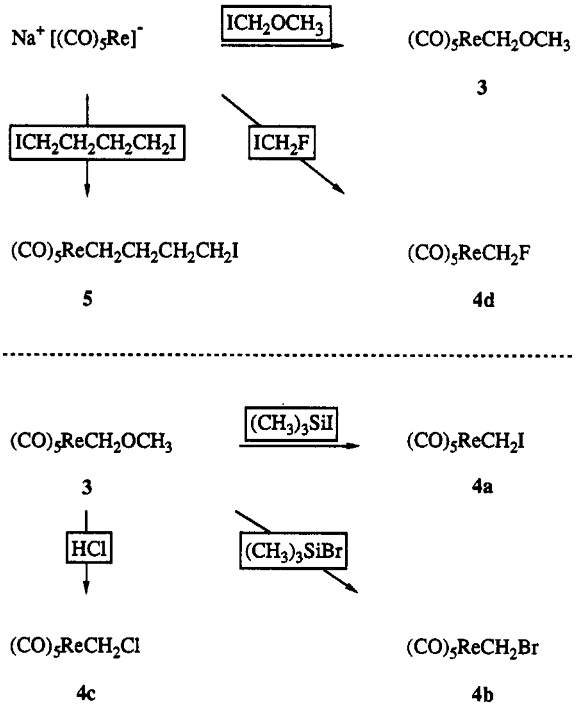
We have previously conducted an extensive study of the synthesis, structure, and reactivity of chiral rhenium alkyl and aryl halide complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(XR)]^+BF_4^-$ (1).[7,8] In general, these are readily available from the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**), which is easily generated in situ.[8a] Complexes in which XR is a primary alkyl iodide are generally isolable in pure form.[7a,b] Some aryl iodide and secondary alkyl iodide complexes have been isolated,[7a,c] and alkyl bromide and alkyl chloride complexes are spectroscopically observable.[7a] Hence, we set out to prepare analogous derivatives of transition metal ω-haloalkyl complexes I and describe the successful realization of this objective in the narrative below.

Results

1. Syntheses of ω-Haloalkyl Complexes $(CO)_5M(CH_2)_xX$. Syntheses of several manganese and rhenium α-halomethyl complexes of the formula $(CO)_5MCH_2X$ have been reported in the literature.[10] Hence, they were targeted for exploratory studies. However, scout reactions with $(CO)_5MnCH_2I$[15] described below gave products with poor stability at room temperature. Since third-row transition metals often given more robust complexes than first-row transition metals, emphasis was shifted to rhenium compounds $(CO)_5ReCH_2X$. For comparative purposes, the entire halide series was sought (X = I, Br, Cl, F).

Thus, the strongly nucleophilic carbonylmetallate[16] $Na^+[(CO)_5Re]^-$ was treated with iodomethyl methyl ether, ICH_2OCH_3 (2.0 equiv).[17] Workup gave the known α-methoxymethyl complex $(CO)_5ReCH_2OCH_3$ (**3**) in 81% yield, as shown in Scheme I. This represented a marked improvement over an earlier preparation utilizing chloromethyl methyl ether.[18] Subsequent reactions with $(CH_3)_3SiI$, $(CH_3)_3SiBr$, and HCl gas gave the corresponding α-halomethyl complexes $(CO)_5ReCH_2I$ (**4a**), $(CO)_5ReCH_2Br$ (**4b**), and $(CO)_5ReCH_2Cl$ (**4c**) in 76–92% yields (Scheme I).

Scheme I. Syntheses of Pentacarbonylrhenium Haloalkyl Complexes $(CO)_5Re(CH_2)_xX$



Analogous reactions of **3** and aqueous or gaseous HF did not give detectable amounts of the α-fluoromethyl complex $(CO)_5ReCH_2F$ (**4d**). Thus, the fluoroacetyl complex $(CO)_5ReCOCH_2F$ was prepared from $Na^+[(CO)_5Re]^-$ and fluoroacetyl chloride, FCH_2COCl.[19] However, all attempts to effect thermal, photochemical, or chemical decarbonylations to **4d** were unsuccessful. Finally, $Na^+[(CO)_5Re]^-$ and the alkylating agent ICH_2F[20] were reacted (Scheme I). Workup gave **4d** in 73% yield. Interestingly, only one other α-fluoromethyl complex, the manganese analog $(CO)_5MnCH_2F$, appears to have been reported previously.[10,21]

In view of the concerns expressed above regarding the stability of target complexes II, we sought a homolog of **4a** with iodide at a site more remote from the rhenium. Thus, a solution of $Na^+[(CO)_5Re]^-$ was slowly added to a solution of excess 1,4-diiodobutane, $I(CH_2)_4I$ (Scheme I). Workup gave the δ-iodobutyl complex $(CO)_5Re(CH_2)_4I$ (**5**) in 36% yield.

Complex **4c** has been synthesized earlier,[18] and the IR and NMR properties of our sample were identical with those reported. Complexes **4a,b,d** and **5** were new compounds and were characterized by microanalysis and IR and ^1H NMR spectroscopy (Experimental Section). The methylene proton ^1H NMR resonances shifted progressively downfield in the series **4a–d** (δ, $CDCl_3$: 2.26, 3.17, 3.59, 5.75), and that in **4d** was strongly coupled to fluorine (J_{HF} = 47.5 Hz).

2. Syntheses of Bridging Haloalkyl Complexes. The dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**2**) was generated in CH_2Cl_2 at −80 °C as previously described[8a] and treated in separate experiments with ω-iodoalkyl complexes **4a** and **5** (1.3–1.5 equiv). Workup gave the bridging iodoalkyl complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)ICH_2Re(CO)_5]^+BF_4^-$ (**6a**) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)I(CH_2)_4Re(CO)_5]^+BF_4^-$ (**7**) as analytically pure powders in 78–69% yields (Scheme II). Both

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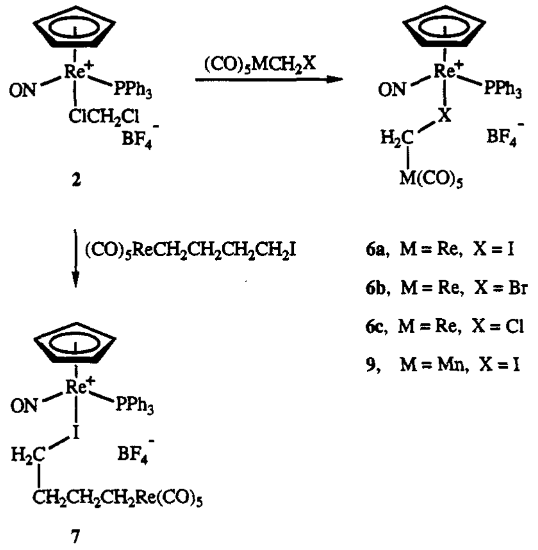
Scheme II. Syntheses of Bridging Haloalkyl Complexes



2

6a, M = Re, X = I

6b, M = Re, X = Br

6c, M = Re, X = Cl

9, M = Mn, X = I

7

6a and **7** showed little or no decomposition in CH_2Cl_2 over the course of 12 h at room temperature.

Complexes **6a** and **7** were characterized by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Experimental Section and Table I). General features resembled those reported earlier for the primary alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2R)]^+BF_4^-$.[7] In particular, the ICH_2 ^{13}C NMR resonances (−12.2, +31.1 ppm) showed characteristic 29–24 ppm downfield shifts from those of the free ligands (−41.3, +6.8 ppm). Also, the ICH_2 protons, which become diastereotopic in the presence of the chiral rhenium end group, exhibited distinct ^1H NMR resonances. Unfortunately, attempts to grow crystals for X-ray diffraction gave powders (low temperature) or decomposition (extended periods, room temperature), and efforts to replace BF_4^- by PF_6^- were not successful.

Next, the deuteriodichloromethane complex **2**-d_2 was generated in a NMR tube. Then a CD_2Cl_2 solution of **4a** (1.5 equiv) was added at −80 °C. The sample was kept at −30 °C for 2 h and cooled to −60 °C. NMR spectra (^1H, ^{13}C, ^{31}P) showed the formation of **6a** to be complete. Analogous experiments were subsequently conducted with α-bromomethyl and α-chloromethyl complexes **4b**,**c**. The bridging halomethyl complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)XCH_2Re(CO)_5]^+BF_4^-$ (**6b**, X = Br; **6c**, X = Cl) formed in >90% yields over the course of 6 h at −25 °C, as assayed by ^1H and ^{31}P NMR (Table I). When identical reactions were attempted above −20 °C, substantial amounts of decomposition products formed.

Similar NMR experiments were conducted with the α-fluoromethyl complex **4d** (3.0 equiv). However, no evidence was observed for the generation of the bridging fluoromethyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)FCH_2Re(CO)_5]^+BF_4^-$ (**6d**). Instead, the bridging chloride complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ formed in ca. 80% yield (^1H NMR, δ 5.40).[8a] This compound has been shown to arise from the independent decomposition of **2**.[8a] NMR-monitored reactions of **4d** and the substitution-labile chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**8**)[8b] also gave no evidence for **6d**.

Analogous preparative and NMR scale reactions of **2**-d_n and the manganese α-iodomethyl complex $(CO)_5MnCH_2I$ were conducted. The heterobimetallic bridging iodomethyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)ICH_2Mn(CO)_5]^+BF_4^-$ (**9**) formed in high yields, as assayed by NMR. However, CD_2Cl_2 solutions showed 50% decomposition after 1.5 h at room temperature. Thus, **9** could only be isolated as a crude powder (78%, ca. 75% purity). Similar results were obtained by utilizing the chlorobenzene complex **8**. Hence, **9** was characterized by IR and NMR in situ (Experimental Section and Table I). The ICH_2 ^{13}C NMR resonance was shifted 31 ppm downfield from that of the free ligand (−20.2 ppm).[15] No adducts were detected when **2**-d_2 or **8**-d_5 were similarly reacted with the manganese α-chloromethyl complex $(CO)_5MnCH_2Cl$.[22]

3. Reactions of Bridging Haloalkyl Complexes. First, the decomposition of iodomethyl complex **9** was investigated. Thus, **9** was generated in CD_2Cl_2 in the presence of an internal standard, Ph_3SiCH_3. After 13 h at room temperature, the known terminal iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**10**)[23] and bridging iodide complex (*RR*,*SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2I^+BF_4^-$ (**11**)[24] had formed in 53% and 42% yields, as assayed by ^1H and ^{31}P NMR. A second, identical sample was analyzed after 48 h. Complexes **10** and **11** were present in 50% and 46% yields, respectively. No significant amounts of the analogous rhenium chloride complexes, which would be solvent-derived, or the α-haloalkyl complexes $(CO)_5MnCH_2Cl$ or $(CO)_5MnCH_2F$ were detected. IR spectra showed the major manganese-containing product to be $Mn_2(CO)_{10}$, and workup gave **10** and **11** in 43% and 32% yields.

Reactions of the iodomethyl complexes with nucleophiles were next examined. Thus, **6a** was treated with an equimolar amount of the bromide salt[25] PPN^+Br^- in CH_2Cl_2 or CD_2Cl_2 at −80 °C (Scheme III). Reaction was complete at −60 °C, as assayed by NMR. Workup gave the iodide complex **10** (78%) and the α-bromomethyl complex **4b** (82%). No bromide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Br)$[23] or α-iodomethyl complex **4a**, which would have arisen from bromide ion attack at the chiral rhenium center, was detected. For comparison, the α-iodomethyl complex **4a** was similarly treated with PPN^+Br^-. NMR monitoring showed that reaction to give α-bromomethyl complex **4b** was very slow at −20 °C, and conversion was only ca. 60% complete after 1 day at room temperature.

A CH_2Cl_2 solution of **6a** was kept under 250 psi of CO for 10 h at room temperature. No reaction was detected. A C_6H_5Cl solution of **6a** was similarly kept under 250 psi of CO for 5 h at 75 °C. A precipitate formed, which was isolated and shown to be the known carbonyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**12**; 42%).[26] Workup of the red-brown supernatant gave unreacted **6a** (46%). Thus, nucleophilic substitution can also occur at the chiral rhenium, and the Re–CH_2IRe bond shows no extraordinary activation toward (net) CO insertion.

When **9** and PPN^+Br^- were combined in CD_2Cl_2 at −80 °C, the spectroscopically quantitative conversion to iodide complex **10** and α-bromomethyl complex $(CO)_5MnCH_2Br$ (δ 3.15, CD_2Cl_2 vs TMS; lit. 3.29, acetone-d_6)[22] was observed. Workup gave **10** and $(CO)_5MnCH_2Br$ in 72% and 68% yields. The IR spectrum of the latter (hexane,

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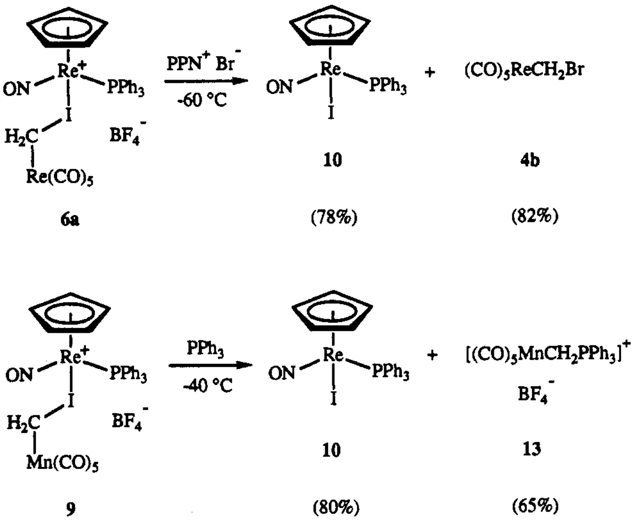
Table I. NMR Characterization of Bridging Haloalkyl Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)X(CH_2)_xM(CO)_5]^+BF_4^-$

complex	^{1}H NMR (δ)[a]	^{13}C{^{1}H} NMR (ppm)[b]	^{31}P{^{1}H} NMR (ppm)[c]
6a ($ReICH_2Re$)	7.48–7.16 (m, 3 C_6H_5) 5.48 (s, C_5H_5) 2.92 (d, J = 8.5, ICH) 2.73 (d, J = 8.5, ICH′)	182.3 (s, cis CO) 179.8 (s, trans CO) 91.9 (s, C_5H_5) −12.2 (br s, CH_2)[d]	13.6 (s)
6b ($ReBrCH_2Re$)	7.53–7.18 (m, 3 C_6H_5) 5.50 (s, C_5H_5) 4.16 (d, J = 8.8, ICH) 3.85 (d, J = 8.8, ICH′)		14.1 (s)
6c ($ReClCH_2Re$)	7.57–7.16 (m, 3 C_6H_5) 5.57 (s, C_5H_5) 4.57 (d, J = 9.6, ICH) 4.20 (d, J = 9.6, ICH′)		14.5 (s)
7[e] ($ReI(CH_2)_4Re$)	7.59–7.23 (m, 3 C_6H_5) 5.62 (s, C_5H_5) 3.79 (dt, J = 9.0, 6.2, ICH) 3.49 (dt, J = 9.0, 6.2, ICH′) 2.13 (m, ICH_2CH_2) 1.76 (m, CH_2CH_2Re) 0.92 (m, CH_2Re)	185.8 (s, cis CO) 181.5 (s, trans CO) 92.1 (s, C_5H_5) 39.3, 39.0 (2s, CCH_2CH_2C) 31.1 (br s, ICH_2) −11.6 (s, CH_2Re)[d]	12.1 (s)
9 ($ReICH_2Mn$)	7.43–7.16 (m, 3 C_6H_5) 5.49 (s, C_5H_5) 2.84 (d, J = 7.0, ICH) 2.64 (d, J = 7.0, ICH′)	208.6 (s, cis CO) 207.4 (s, trans CO) 91.7 (s, C_5H_5) 10.7 (br s, CH_2)[d]	12.9 (s)

[a] ^{1}H NMR spectra were recorded at 300 MHz in CD_2Cl_2 at −60 °C and referenced to TMS (δ 0.00) unless noted. All coupling constants (J) are to hydrogen and in hertz. [b] ^{13}C NMR spectra were recorded at 75 MHz in CD_2Cl_2 at −60 °C and referenced to CD_2Cl_2 (53.8 ppm) unless noted. [c] ^{31}P NMR spectra were recorded with an external lock at 32 MHz in CD_2Cl_2 at −60 °C and referenced to external H_3PO_4 (0.0 ppm) unless noted. [d] The PPh_3 carbons for **6a**/**7**/**9** are at 133.3/133.6/132.7 (d, J_{CP} = 9.2/10.9/9.6 Hz, ortho), 132.2/132.5/131.7 (d, J_{CP} = 50.4/54.9/55.5 Hz, ipso), 131.2/132.1/131.3 (s/d/s, J_{CP} = <2/3.1/<2 Hz, para), 129.1/129.6/128.8 (d, J_{CP} = 10.6/10.9/10.0 Hz, meta). The ICH_2 resonances exhibit widths of 5–8 Hz (half-height). [e] All data for **7** are at room temperature.

Scheme III. Representative Reactions of Bridging Haloalkyl Complexes



cm^{-1}: ν_{CO} 2121 (w), 2060 (w), 2026 (s), 2002 (m)) agreed exactly with that in the literature. A similar reaction with PPh_3 proceeded over the course of 0.5 h at −40 °C (Scheme III). Workup gave **10** (80%) and the new phosphonium salt $[(CO)_5MnCH_2PPh_3]^+BF_4^-$ (**13**, 65%), the structure of which was assigned by IR and ^{1}H/^{31}P NMR spectroscopy (Experimental Section). The unbridged α-iodomethyl complex $(CO)_5MnCH_2I$ was also treated with PPh_3. After 0.5 h in CH_2Cl_2 at room temperature, a ^{31}P NMR spectrum showed that only 2–3% of a phosphonium salt had formed (39.0 ppm).

Finally, **9** and CH_3CN (3 equiv) were combined in CD_2Cl_2 at −70 °C. No reaction occurred below 0 °C. Within 1 h at room temperature, complete conversion to **10** and the known acetonitrile complex[8a] $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (**14**) had occurred, as assayed by ^{1}H and ^{31}P NMR. The latter product requires a displacement at the chiral rhenium. Workup gave **10** and **14** in 33% and 39% yields, respectively.

Discussion

The preceding data clearly demonstrate the capability of haloalkyl fragments to serve as bridging ligands. The relative reactivities of α-halomethyl complexes **4a–d** toward the dichloromethane complex **2** ($-CH_2I > -CH_2Br > -CH_2Cl > -CH_2F$) parallel the expected donor strengths[1] and previous results with simple alkyl halides.[7a] The inability of α-fluoromethyl complex **4d** to displace dichloromethane from **2** may be due to unfavorable thermodynamics. Other strategies for accessing organofluorine donor complexes of the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ have also been unsuccessful.[27]

The relative and absolute kinetic stabilities of the bridging halomethyl complexes **6a–c** are similar to those of the analogous ethyl halide complexes. However, the rhenium/rhenium and rhenium/manganese iodomethyl complexes **6a** and **9** exhibit markedly different stabilities. This shows that the metal fragment attached to the carbon terminus can also exert a significant influence. In an exploratory NMR experiment, no significant stability enhancement was found for an analog of **9** generated from the phosphine-substituted α-iodomethyl complex *cis*-$(CO)_4(Ph_3P)MnCH_2I$.[28] Thus, we believe it probable that many bridging haloalkyl complexes will be unstable at room temperature and that isolable examples will remain rare.

The NMR features of bridging halomethyl complexes **6a–c** exhibit several interesting trends (Table I). For example, the ^{31}P NMR resonances shift progressively downfield, paralleling those of the corresponding ethyl

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[28] (a) Gibson, D. H.; Mandal, S. K.; Owens, K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 1114. (b) Mandal, S. K.; Ho, D. M.; Orchin, M. *J. Organomet. Chem.* **1990**, *397*, 313.

halide complexes (11.8, 12.9, 13.6 ppm).[7a] The cyclopentadienyl ^{1}H NMR resonances show a similar downfield shift. The diastereotopic XCH_2 protons are somewhat less differentiated in **6a** ($\Delta\delta$ 0.19 ppm) than in **6b,c** ($\Delta\delta$ 0.31, 0.37 ppm). This trend is also mirrored in the ethyl halide complexes ($\Delta\delta$ 0.31, 0.45, 0.51 ppm) and might be connected to the expected[1] contraction in Re–X bond lengths. The XCH_2 protons of **6a–c** also show average downfield shifts of 0.57, 0.84, and 0.80 ppm from those of the free ligands **4a–c**.

The reactivity of bridging iodomethyl complexes **6a** and **9** is similar to that of the corresponding alkyl iodide complexes. For example, the ICH_2 carbons are activated toward nucleophilic attack, as qualitatively demonstrated by the accelerated reactions with PPN^+Br^- and PPh_3. Quantitative studies have previously shown rate enhancements as high as 3×10^5 (25 °C).[7a] The thermal decomposition of **9** also features carbon–iodine bond cleavage. As analyzed earlier,[7c] pathways involving BF_4^- or solvent participation, and/or ionization, are likely. In the latter context, cationic methylidene complexes $[L_nM({=}CH_2)]^+X'^-$ have been shown to be kinetically accessible from α-halomethyl complexes under certain conditions.[10] These would constitute plausible intermediates in many of the preceding transformations.

In at least one case, bridging haloalkyl fragments have received consideration as reaction intermediates. A detailed study has been conducted of the reduction of α-iodomethyl complex $[(H_2O)_5Cr(CH_2I)]^{2+}$ by Cr(II), which ultimately gives Cr(III) products and methane.[29] There is good rate evidence that the first step involves a transition state with a $CrCH_2ICr$ linkage (III), as shown in equation ii. Similar species should also be involved in Ag$^+$-assisted reactions of α-halomethyl complexes,[10] although we are unaware of any explicit proposals. Interestingly, bridging dihaloalkane complexes presently appear to be unknown, although several chelates have been prepared.[3a,4a]

$$\mathrm{Cr^{2+} + ICH_2Cr^{2+} \rightarrow \underset{\text{III (intermediate or transition state)}}{[CrICH_2Cr]^{4+}} \rightarrow CrI^{2+} + {}^{\bullet}CH_2Cr^{2+}} \tag{ii}$$

Finally, the bridging halomethyl complexes **6a–c** and **9** provide an important connection between oxidative addition reactions of dihalomethanes[8c,30] and subsequently derived cluster compounds containing CH_2, CH, and CX fragments.[11] Thus, there is now the potential for both further mechanistic definition of and practical refinements in metal-based haloalkane degradation processes. Future reports will describe additional properties of rhenium dihalomethane complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(XCH_2X')]^+BF_4^-$, including mechanistic data on substitution reactions of the dichloromethane complex **2**.[31]

Experimental Section

General Data. General procedures were as described in previous papers,[7] except that workups were conducted in air unless noted. Melting points were determined in open capillaries using a calibrated thermometer.[32] Solvents were purified as follows: CH_2Cl_2 and CH_3CN, distilled from CaH_2; ether and THF, distilled from Na/benzophenone; hexane, distilled from sodium; $CDCl_3$ and CD_2Cl_2, vacuum transferred from CaH_2. The following reagents were used as received: $(CH_3)_3SiI$, $I(CH_2)_4I$, PPh_3 (Aldrich), $(CH_3)_3SiBr$ (Petrarch), HCl gas (Matheson), PPN^+Br^-, Ph_3SiCH_3 (Strem). $HBF_4 \cdot OEt_2$ (Aldrich) was standardized as described earlier.[8a]

(CO)$_5$ReCH$_2$OCH$_3$ (3). A red solution of $Na^+[Re(CO)_5]^-$ (6.20 mmol)[16] in THF (12 mL) was slowly added with stirring to a −80 °C solution of ICH_2OCH_3 (2.13 g, 12.4 mmol)[17] in THF (10 mL). The cooling bath was allowed to gradually warm to room temperature, and the mixture was stirred at room temperature for 0.5 h. Solvent was removed by rotary evaporation and the residue extracted with hexane (3 × 30 mL). Solvent was removed from the extract to give a pale yellow oil, which was sublimed under oil pump vacuum at room temperature onto a CH_3CN/dry ice cooled finger. This gave white crystals of **3** (1.86 g, 5.01 mmol, 81%), mp 22.5 °C. The IR and ^{1}H NMR spectra were identical with literature data.[18]

(CO)$_5$ReCH$_2$I (4a). A Schlenk flask was charged with **3** (0.320 g, 0.862 mmol), CH_2Cl_2 (10 mL), and stir bar and was cooled to −80 °C. Then $(CH_3)_3SiI$ (0.224 g, 0.112 mmol) was added with stirring. The cooling bath was allowed to gradually warm to room temperature. Solvent was removed under oil pump vacuum, and the residue was sublimed under oil pump vacuum at 60 °C onto an ice-cooled finger. This gave white crystals of **4a** (0.369 g, 0.790 mmol, 92%), mp 61.5–62.5 °C. Anal. Calcd for $C_6H_2IO_5Re$: C, 15.43; H, 0.43; I, 27.12. Found: C, 15.54; H, 0.46; I, 27.02. IR (cm^{-1}, hexane): ν_{CO} 2136 (w), 2066 (w), 2024 (vs), 1994 (s). ^{1}H NMR (δ, $CDCl_3$): 2.26 (s, CH_2). $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$): 184.0 (cis CO), 180.2 (trans CO), −41.3 (s, CH_2).

(CO)$_5$ReCH$_2$Br (4b). A Schlenk flask was charged with **3** (0.500 g, 1.35 mmol), CH_2Cl_2 (20 mL), and a stir bar. Then $(CH_3)_3SiBr$ (0.412 g, 2.69 mmol) was added with stirring. After 5 h at room temperature, solvent was removed under oil pump vacuum. The residue was sublimed under oil pump vacuum at 40 °C onto an ice-cooled finger. This gave white crystals of **4b** (0.455 g, 1.18 mmol, 87%), mp 71–72 °C. Anal. Calcd for $C_6H_2BrO_5Re$: C, 17.15; H, 0.48; Br, 19.02. Found: C, 17.40; H, 0.51; Br, 19.18. IR (cm^{-1}, hexane): ν_{CO} 2137 (w), 2022 (vs), 1994 (s). ^{1}H NMR (δ, $CDCl_3$): 3.17 (s, CH_2).

(CO)$_5$ReCH$_2$Cl (4c). Dry HCl gas was bubbled through a solution of **3** (0.400 g, 1.08 mmol) in CH_2Cl_2 (25 mL) for ca. 10 min. Solvent was then removed under oil pump vacuum, and the residue was sublimed under oil pump vacuum at 40 °C onto an ice-cooled finger. This gave white crystals of **4c** (0.307 g, 0.819 mmol, 76%). The IR and ^{1}H NMR spectra were identical with literature data.[18]

(CO)$_5$ReCH$_2$F (4d). A red solution of $Na^+[Re(CO)_5]^-$ (0.960 mmol)[16] in THF (3 mL) was added with stirring to a −80 °C solution of ICH_2F (0.230 g, 1.44 mmol)[20] in THF (2 mL). The cooling bath was allowed to gradually warm to room temperature, and the mixture was stirred at room temperature for 0.5 h. The solution was filtered through silica, and solvent was removed from the filtrate under oil pump vacuum to give a pale yellow solid. The solid was sublimed under oil pump vacuum at 70 °C onto a CH_3CN/dry ice cooled finger. This gave white crystals of **4d** (0.250 g, 0.696 mmol, 73%), mp 117–118 °C. Anal. Calcd for $C_6H_2FO_5Re$: C, 20.06; H, 0.56. Found: C, 20.12; H, 0.61. IR (cm^{-1}, hexane): ν_{CO} 2137 (vw), 2062 (w), 2020 (s), 1995 (m). ^{1}H NMR (δ, $CDCl_3$): 5.75 (d, J_{HF} = 47.5 Hz, CH_2).

(CO)$_5$ReCOCH$_2$F. Acid chloride FCH_2COCl (0.144 g, 1.49 mmol)[19] was added with stirring to a −80 °C solution of $Na^+[Re(CO)_5]^-$ (0.747 mmol) in THF (5 mL). The cooling bath

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(30) Selected examples from ref 10: (a) Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* **1980**, *19*, 3236. (b) Werner, H.; Hofman, L. *J. Organomet. Chem.* **1985**, *289*, 141. (c) Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1543. (d) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Ramirez, J. A. *Ibid.* **1989**, 304.

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was allowed to gradually warm to room temperature, and the mixture was stirred at room temperature for 1 h. The solution was filtered through Celite, and solvent was removed from the filtrate by rotary evaporation to give a pale yellow solid. The solid was dissolved in CH_2Cl_2 (2 mL) and chromatographed on silica in CH_2Cl_2. Solvent was removed from product fractions to give a white solid (0.240 g, 0.620 mmol, 83%), mp 91–92 °C. Anal. Calcd for $C_7H_2FO_6Re$: C, 21.71; H, 0.52. Found: C, 21.82; H, 0.58. IR (cm^{-1}, hexane): ν_{CO} 2137 (w), 2067 (w), 2029 (vs), 2007 (s), 1621 (m). ^1H NMR (δ, $CDCl_3$): 4.14 (d, J_{CF} = 50.3 Hz, CH_2).

$(CO)_5Re(CH_2)_4I$ (5). A red solution of $Na^+[Re(CO)_5]^-$ (4.30 mmol) in THF (10 mL) was added dropwise with stirring to a −20 °C solution of $I(CH_2)_4I$ (6.66 g, 21.5 mmol) in THF (10 mL). The cooling bath was allowed to gradually warm to room temperature, and the mixture was stirred at room temperature for 0.5 h. Solvent was removed by rotary evaporation, and the residue extracted with hexane (3 × 30 mL). Solvent was removed from the extract to give a pale yellow oil, which was sublimed under oil pump vacuum at 72 °C onto a CH_3CN/dry ice cooled finger. Some $I(CH_2)_4I$ was collected first, and further sublimation gave **5** as a colorless oil (0.788 g, 1.55 mmol, 36%). Anal. Calcd for $C_9H_8IO_5Re$: C, 21.23; H, 1.58; I, 24.92. Found: C, 21.33; H, 1.58; I, 25.07. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2126 (w), 2009 (s), 1979 (m). ^1H NMR (δ, $CDCl_3$): 3.21 (t, J_{HH} = 6.5 Hz, ICH_2), 1.82 (m, CCH_2CH_2C), 0.90 (m, CH_2Re). $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$): 185.5 (cis CO), 181.1 (trans CO), 40.7/39.7 (CCH_2CH_2C), 6.8 (ICH_2), −11.6 (CH_2Re).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)ICH_2Re(CO)_5]^+BF_4^-$ (6a). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.179 g, 0.320 mmol),[26] CH_2Cl_2 (15 mL), and a stir bar, capped with a septum, and cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (0.035 mL, 0.320 mmol) was added with stirring. After 5 min, **4a** (0.194 g, 0.415 mmol) was added. The cold bath was allowed to warm to −30 °C and was kept at −30 °C for 3 h. The solution was concentrated to ca. 3 mL under oil pump vacuum and added to ether (30 mL, −80 °C) via cannula. The resulting precipitate was collected by filtration under nitrogen and dried under oil pump vacuum. This gave **6a** as a tan powder (0.274 g, 0.250 mmol, 78%), mp 131–134 °C dec. Anal. Calcd for $C_{29}H_{22}BF_4INO_6PRe_2$: C, 31.74; H, 2.02; N, 1.28. Found: C, 31.55; H, 2.15; N, 1.21. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2137 (w), 2048 (w), 2020 (vs); ν_{NO} 1704 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)I(CH_2)_4Re(CO)_5]^+BF_4^-$ (7). Complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.179 g, 0.320 mmol), $HBF_4{\cdot}OEt_2$ (0.035 mL, 0.320 mmol), and **5** (0.244 g, 0.479 mmol) were combined in a procedure analogous to that given for **6a**. The cold bath was allowed to warm to −20 °C and was kept at −20 °C for 2 h. The solution was concentrated to ca. 3 mL and added to ether (30 mL). The resulting precipitate was collected by filtration under nitrogen and dried under oil pump vacuum. This gave **7** as a tan powder (0.253 g, 0.222 mmol, 69%), mp 115–119 °C dec. Anal. Calcd for $C_{32}H_{28}BF_4INOPRe_2$: C, 33.73; H, 2.48; N, 1.23. Found: C, 33.27; H, 2.47; N, 1.17. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2127 (w), 2053 (w), 2010 (vs), 1981 (s); ν_{NO} 1711 (s).

Generation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)XCH_2Re(CO)_5]^+BF_4^-$ (X = I, Br, Cl, 6a–c). The following procedure is representative. A 5-mm NMR tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.045 g, 0.081 mmol) and CD_2Cl_2 (0.5 mL), capped with a septum, and cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (0.0086 mL, 0.081 mmol) was added. A ^1H NMR spectrum was taken at −60 °C, which showed the formation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCD_2Cl)]^+BF_4^-$ (**2**-d_2).[8a] The sample was cooled to −80 °C, and a solution of **4a** (0.057 g, 0.120 mmol) in CD_2Cl_2 (0.2 mL) was added via cannula. The sample was kept at −25 °C for 6 h, and NMR spectra of **6a** were then recorded at −60 °C (Table I).

Generation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)ICH_2Mn(CO)_5]^+BF_4^-$ (9). Complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.063 g, 0.113 mmol), CD_2Cl_2 (0.5 mL), and $HBF_4{\cdot}OEt_2$ (0.012 mL, 0.11 mmol) were combined in a NMR tube as in the preceding experiment. The sample was cooled to −80 °C, and a solution of $(CO)_5MnCH_2I$ (0.040 g, 0.119 mmol)[15] in CD_2Cl_2 (0.2 mL) was added via cannula. The sample was kept at −30 °C for 3 h, and NMR spectra of **9** were then recorded at −60 °C (Table I). IR (cm^{-1}, CD_2Cl_2): ν_{CO} 2125 (w), 2031 (vs); ν_{NO} 1689 (s).

Decomposition of 9. Complex **9** was generated from $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.063 g, 0.113 mmol) in a NMR tube as above, but in the presence of Ph_3SiCH_3 (0.031 g, 0.113 mmol). The sample was kept at room temperature for 2 days (NMR data: see text). The solution was filtered through a 3-cm plug of silica, which was eluted with additional CH_2Cl_2. The solution was concentrated to ca. 1 mL, and hexane was added. The resulting precipitate was collected by filtration and dried under oil pump vacuum to give $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**10**) as a purple powder (0.033 g, 0.049 mmol, 43%).[23] The plug was eluted with acetone. Solvent was removed under oil pump vacuum to give (*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2I^+BF_4^-$ (**11**) as an orange powder (0.023 g, 0.018 mmol, 32% of theory).[24] NMR data (**10**/**11**, before workup): ^1H δ 5.21/5.41; ^{31}P 12.7/11.8 ppm.

Reaction of 6a and PPN^+Br^-. A Schlenk flask was charged with **6a** (0.263 g, 0.240 mmol), CH_2Cl_2 (15 mL), and a stir bar, and cooled to −80 °C. Then PPN^+Br^- (0.149 g, 0.240 mmol) was added with stirring. The cooling bath was allowed to gradually warm to room temperature. The mixture was filtered through a 3-cm silica plug, which was eluted with additional CH_2Cl_2. The solution was concentrated to ca. 3 mL and added to hexane (20 mL). The resulting precipitate was collected by filtration and dried under oil pump vacuum to give **10** as a purple powder (0.127 g, 0.189 mmol, 78%). Solvent was removed from the filtrate to give **4b** (0.083 g, 0.179 mmol, 82%). Both products were characterized by IR and ^1H NMR spectroscopy.

Reaction of 9 and PPh_3. Complex **9** was generated from $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.063 g, 0.113 mmol) in a NMR tube as above. The solution was frozen in liquid nitrogen, and PPh_3 (0.039 g, 0.147 mmol) was added. NMR spectra (^1H, ^{31}P) were recorded as the sample was warmed (data: see text). The sample was allowed to warm to room temperature and filtered through a 3-cm plug of silica, which was eluted with additional CH_2Cl_2. The solution was concentrated to ca. 1 mL, and hexane was added. The resulting precipitate was collected by filtration and dried under oil pump vacuum to give **10** as a purple powder (0.061 g, 0.091 mmol, 80%). The plug was then eluted with CH_3CN. The solvent was removed under oil pump vacuum, and the residue was dissolved in CH_2Cl_2. A layer of hexane was added, and white crystals slowly formed. These were collected by filtration and dried under oil pump vacuum to give $[(CO)_5MnCH_2PPh_3]^+BF_4^-$ (**13**; 0.041 g, 0.074 mmol, 65%). IR (cm^{-1}, Nujol): ν_{CO} 2132 (w), 2077 (w), 2028 (vs), 2011 (s); ν_{BF} 1058 (s). ^1H NMR (δ, CD_2Cl_2): 7.82–7.58 (m, 3 C_6H_5), 1.62 (d, J_{HP} = 14.5 Hz, CH_2). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2): 38.2 (s).

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Supplementary Material Available: Text giving additional experimental procedures involving **4a**, **6a**, and **9** (2 pages). Ordering information is given on any current masthead page.

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