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## Characterization of MnTc(CO)<sub>10</sub> and TcRe(CO)<sub>10</sub>

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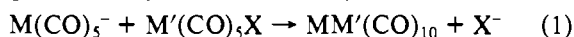
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The heteronuclear decacarbonyls of MnTc and TcRe have been synthesized and characterized according to the infrared and mass spectra. Optimum conditions have been established for their preparation and purification, which may be applicable to the production of mixed-metal carbonyls in general.

### Introduction

The preparation and characterization of ReMn(CO)<sub>10</sub> have been described,<sup>1b</sup> but similar work concerned with the other two heteronuclear decacarbonyls of the group 7B elements has not been reported. DeJong and Wiles<sup>2</sup> speculated that MnTc(CO)<sub>10</sub> was formed in low yields when <sup>99m</sup>Tc(CO)<sub>5</sub>, produced as a result of the β decay of <sup>99</sup>Mo(CO)<sub>6</sub>, reacted with photochemically produced ·Mn(CO)<sub>5</sub>. The compound was however characterized only by its radiochemical properties. Nothing has been reported about TcRe(CO)<sub>10</sub>.

The general approach to the synthesis of the group 7B decacarbonyls is to react a pentacarbonyl anion, M(CO)<sub>5</sub><sup>-</sup>, with a pentacarbonyl halide, M'(CO)<sub>5</sub>X:



Both reactants are readily prepared from the corresponding homonuclear decacarbonyls if they are available. The paucity of Tc<sub>2</sub>(CO)<sub>10</sub> has perhaps been the main reason why MnTc(CO)<sub>10</sub> and TcRe(CO)<sub>10</sub> have not been prepared and characterized in the past. The availability of ~1 g of Tc<sub>2</sub>(CO)<sub>10</sub> here contributed to the success of this project. However, synthesis of the mixed compounds containing technetium needed to be optimized.

Two questions were resolved in order to use eq 1 effectively. Bromine was chosen as the halogen because the pentacarbonyl bromides are easy to prepare in good yield and Br<sup>-</sup> is a good leaving group for the nucleophilic substitution required by eq 1. The other question concerned which pentacarbonyl anion and bromide should be reacted to produce the best yields of a particular heteronuclear decacarbonyl. The dilemma was resolved by using the synthesis of MnRe(CO)<sub>10</sub> as a model.

### Experimental Section

All of the preparations were done at room temperature under an atmosphere of dry nitrogen and in dry solvents. The glassware was dried at 120 °C and assembled immediately before use. Tetrahydrofuran was distilled from lithium aluminum hydride and carbon disulfide from anhydrous calcium sulfate. The decacarbonyls, obtained from Pressure Chemical Co., Pittsburgh, PA 15201, were purified by vacuum sublimation. Technetium decacarbonyl was prepared from the radioactive <sup>99</sup>Tc isotope. This isotope, whose half-life is 2.12 × 10<sup>5</sup> years, is a weak β emitter (β<sub>max</sub> = 0.3 MeV). When used on a small scale (<50 mg), it does not present a serious health hazard because the β rays are absorbed by the glassware and there is no associated γ radiation. When larger quantities are used (>250 mg), a distance of 30 cm must be maintained from the working area to avoid the effect of very soft X-rays produced by the action of the β particles on glass (see ref 3, application I). When Tc<sub>2</sub>(CO)<sub>10</sub> was used, the sample size was limited to 100 mg.

The mixed-metal decacarbonyls were purified by gas chromatography using an Aerograph Model A-700 gas chromatograph equipped with a 0.25 in. × 15 ft 3% SE-30 glass column. The compounds were

collected in glass capillary tubes loosely plugged at one end with glass wool and fitted directly to the exit port of the thermal conductivity detector. Once the retention times were established, the compounds were collected with the filaments of the detector turned off to prevent sample decomposition. Twenty 45-μL injections of a saturated pentane solution produced 2–10 mg of each heteronuclear decacarbonyl.

All products were identified by their infrared spectra in the carbonyl absorption region (2150–1900 cm<sup>-1</sup>). The infrared spectra were obtained in cyclohexane. Positions of the peaks were determined with use of an expanded-scale recorder calibrated with gaseous CO. The mixed-metal decacarbonyls were also identified from their mass spectra.

**Pentacarbonyl Bromides of Mn, Tc, and Re.** The pentacarbonyl bromides were prepared by a modification of the method of Abel and Wilkinson.<sup>4</sup> The reactions were done at 25 °C (instead of 40 °C) in carbon disulfide (instead of carbon tetrachloride) with use of a 10% molar excess of bromine (instead of a 30% excess).

**Mn(CO)<sub>5</sub>Br.** A suspension of Mn<sub>2</sub>(CO)<sub>10</sub> (2.0 g, 5.13 mmol) in 40 mL of carbon disulfide was stirred while Br<sub>2</sub> (0.3 mL, 5.64 mmol) in 15 mL of carbon disulfide was added dropwise during a period of 30 min. After removal of the solvent, a yellow-orange product was collected by vacuum sublimation in 90% yield. IR (cyclohexane): 2051 s, 2019 w, 2001 m cm<sup>-1</sup>.

**Tc(CO)<sub>5</sub>Br.** A 5-mL aliquot of a solution of Br<sub>2</sub> (0.1 mL, 1.95 mmol) in carbon disulfide (40 mL) was added slowly (10 min) to a suspension of Tc<sub>2</sub>(CO)<sub>10</sub> (0.10 g, 0.21 mmol) in 10 mL of carbon disulfide. The solvent was removed under reduced pressure, and 74 mg of product was obtained from the residue by vacuum sublimation at 50–70 °C.

The infrared spectrum of the sublimate revealed the presence of [Tc(CO)<sub>4</sub>Br]<sub>2</sub> as an impurity. IR for Tc(CO)<sub>5</sub>Br (cyclohexane): 2055 s, 2024 w, 1994 m cm<sup>-1</sup>. IR for [Tc(CO)<sub>4</sub>Br]<sub>2</sub>: 2045 s, 2012 m, 1974 m cm<sup>-1</sup>.

**Re(CO)<sub>5</sub>Br.** Bromine (0.1 mL, 1.95 mmol) in 10 mL of carbon disulfide was added dropwise during a period of 10 min to Re<sub>2</sub>(CO)<sub>10</sub> (1.0 g, 1.54 mmol) in 25 mL of carbon disulfide. After the solution was evaporated to dryness under reduced pressure, the white crystalline product, Re(CO)<sub>5</sub>Br, was separated from the residue by vacuum sublimation. The desired compound was obtained in 90% yield. IR (methylcyclohexane): 2044 s, 2012 w, 1982 m cm<sup>-1</sup>.

**Mixed-Metal Decacarbonyls.** The general procedure for synthesizing and purifying the heteronuclear decacarbonyls of Mn, Tc, and Re was developed through the preparation of MnRe(CO)<sub>10</sub>. This approach was dictated by the radioactive nature, and the limited amount (1.111 g), of Tc<sub>2</sub>(CO)<sub>10</sub> available. The reaction was scaled for the use of 100–150 mg of reactants. The conditions for optimizing the yield of MnRe(CO)<sub>10</sub> were developed as was the methodology for its separation and purification from the Mn<sub>2</sub>(CO)<sub>10</sub> and Re<sub>2</sub>(CO)<sub>10</sub> side products.

The major obstacle to the synthesis of MnRe(CO)<sub>10</sub> proved to be the choice of reactants. Either Re(CO)<sub>5</sub><sup>-</sup> or Mn(CO)<sub>5</sub><sup>-</sup> can be chosen as the nucleophile. The logical option was to react Re(CO)<sub>5</sub><sup>-</sup> with Mn(CO)<sub>5</sub>Br since Re(CO)<sub>5</sub><sup>-</sup> is the stronger nucleophile.<sup>5</sup> When this was done, a gas chromatographic analysis of the product gave Mn<sub>2</sub>(CO)<sub>10</sub> (22%), ReMn(CO)<sub>10</sub> (8%), and Re<sub>2</sub>(CO)<sub>10</sub> (70%). The alternate procedure was to react stoichiometric amounts of Mn(CO)<sub>5</sub><sup>-</sup> and Re(CO)<sub>5</sub>Br. The sublimate from this reaction contained Mn<sub>2</sub>(CO)<sub>10</sub> (11%), MnRe(CO)<sub>10</sub> (77%), and Re<sub>2</sub>(CO)<sub>10</sub> (12%). This dramatic increase in the yield of MnRe(CO)<sub>10</sub> was realized by

(1) (a) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Director for Energy Research, Office of Basic Energy Science, WPAS-KC-01-02-01-2. (b) N. Fliteroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964).

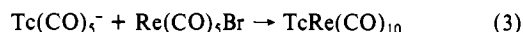
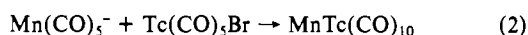
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changing to the less reactive nucleophile  $\text{Mn}(\text{CO})_5^-$ . A general explanation for this phenomenon has been given by Desay and Weissman.<sup>6</sup> When the Mn-Re bond is formed during a reaction,  $\text{Re}(\text{CO})_5^-$  will cleave it, forming the more stable  $\text{Re}_2(\text{CO})_{10}$  molecule and  $\text{Mn}(\text{CO})_5^-$ , which is oxidized to  $\text{Mn}_2(\text{CO})_{10}$  upon exposure to air. The nucleophilic strength of  $\text{Mn}(\text{CO})_5^-$  is insufficient to break the Mn-Re bond. The large percentage of  $\text{Re}_2(\text{CO})_{10}$  formed from the reaction with  $\text{Re}(\text{CO})_5^-$  provides additional evidence for this explanation. As a result, the optimum method for synthesizing the heteronuclear decacarbonyls is to react the *weakest* nucleophile with the corresponding bromide. Thus,  $\text{MnTc}(\text{CO})_{10}$  and  $\text{TcRe}(\text{CO})_{10}$  were prepared according to the reactions



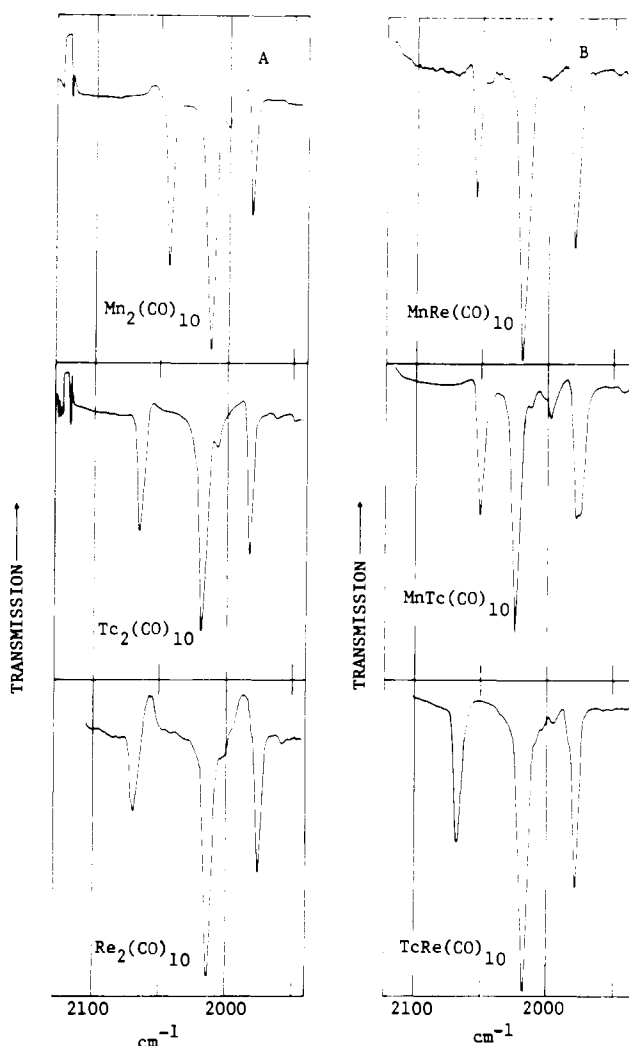
**$\text{MnRe}(\text{CO})_{10}$ .** Manganese decacarbonyl (102 mg, 0.26 mmol) was reduced to  $\text{Mn}(\text{CO})_5^-$  by stirring for 45 min in 25 mL of THF with excess sodium amalgam (0.7 g (20.4 mmol) of Na and 10 mL of Hg). The liquid amalgam was removed through a stopcock at the bottom of the flask. Rhenium pentacarbonyl bromide (205 mg, 0.51 mmol) in 15 mL of THF was added dropwise during a period of 30 min. The solvent was removed under reduced pressure, leaving a reddish brown residue. Sublimation at 60 °C under a high vacuum onto a water-cooled probe yielded a mixture of  $\text{Mn}_2(\text{CO})_{10}$  (11%),  $\text{MnRe}(\text{CO})_{10}$  (77%), and  $\text{Re}_2(\text{CO})_{10}$  (12%).

**$\text{MnTc}(\text{CO})_{10}$ .** A solution of  $\text{Mn}_2(\text{CO})_{10}$  (41 mg, 0.11 mmol) in 25 mL of THF was stirred for 45 min with excess sodium amalgam (0.7 g (30.4 mmol) of Na and 10 mL of Hg). After the liquid amalgam was removed,  $\text{Tc}(\text{CO})_5\text{Br}$  (approximately 60 mg, 0.19 mmol) in 20 mL of THF was added slowly. When the addition was completed (30 min), the solution was evaporated to dryness under reduced pressure. The volatile components of the residue were collected by vacuum sublimation. Gas chromatographic analysis of the sublimate showed that a mixture of  $\text{Mn}_2(\text{CO})_{10}$  (42%),  $\text{MnTc}(\text{CO})_{10}$  (55%), and  $\text{Tc}_2(\text{CO})_{10}$  (3%) had been produced.

**$\text{TcRe}(\text{CO})_{10}$ .** Technetium decacarbonyl (103 mg, 0.22 mmol) in 25 mL of THF was stirred with sodium amalgam (0.7 g (30.4 mmol) of Na and 10 mL of Hg) for 15 min. The liquid amalgam was removed, and  $\text{Re}(\text{CO})_5\text{Br}$  (165 mg, 0.41 mmol) in 20 mL of THF was added dropwise during a period of 15 min. The reaction mixture was evaporated and sublimed. The sublimate was found to contain  $\text{Tc}_2(\text{CO})_{10}$  (37%),  $\text{TcRe}(\text{CO})_{10}$  (52%), and  $\text{Re}_2(\text{CO})_{10}$  (11%).

**Purification and Identification of the Compounds.** The infrared spectra of the group 7B pentacarbonyl bromides in the CO stretching region agreed with the literature spectra<sup>7</sup> within 2  $\text{cm}^{-1}$ . Except for the  $\text{Tc}(\text{CO})_5\text{Br}$  preparation there was no indication of any impurities. No attempt was made to isolate pure  $\text{Tc}(\text{CO})_5\text{Br}$ . This halide was extracted from the tetracarbonyl dimer with THF immediately before use.

The homonuclear and heteronuclear decacarbonyls are separated readily on nonpolar columns by gas chromatography according to their molecular weights. Dimanganese decacarbonyl is eluted first followed by  $\text{MnTc}(\text{CO})_{10}$ ,  $\text{Tc}_2(\text{CO})_{10}$ ,  $\text{MnRe}(\text{CO})_{10}$ ,  $\text{TcRe}(\text{CO})_{10}$ , and  $\text{Re}_2(\text{CO})_{10}$ . The difference in retention times between the mixed-metal carbonyls and the corresponding monometal complexes is sufficient for preparative work. However it is necessary to operate the injector, column, and detector at relatively low temperatures to avoid decomposition of the compounds. In this work the 3% SE-30 column was held at 130 °C, and the injector and detector were held at 135 °C. A flow rate of 150 mL/min of the helium carrier gas was used. When the filaments of the thermoconductivity detector were turned off, the recovery of  $\text{Mn}_2(\text{CO})_{10}$  increased from 60 to 70%. The 150 mL/min flow rate is required to obtain good peak shapes and to allow a reasonable time for one collection (15 min). The resolution between  $\text{MM}'(\text{CO})_{10}$  and the  $\text{M}_2(\text{CO})_{10}$  and  $\text{M}'_2(\text{CO})_{10}$  impurities is sufficient in every case to allow two injections within 30 s to be separated and collected simultaneously. The size of an injection (45  $\mu\text{L}$ ) was limited by the low solubility of the decacarbonyls in pentane. Very pure  $\text{MnRe}(\text{CO})_{10}$  and  $\text{TcRe}(\text{CO})_{10}$  (>99%) were obtained in this manner. The Mn-Tc compound could not be separated from a small impurity of  $\text{Mn}_2(\text{CO})_{10}$  (1–3%). The collected homonuclear and MnRe



**Figure 1.** Carbonyl region of the infrared spectra of the group 7B dimetal (A) and mixed-metal (B) decacarbonyls.

decacarbonyls were identified by their infrared spectra in the carbonyl stretching region (1950–2100  $\text{cm}^{-1}$ ).<sup>4</sup>

## Results and Discussion

The identification of  $\text{MnTc}(\text{CO})_{10}$  and  $\text{TcRe}(\text{CO})_{10}$  was based upon gas chromatographic retention times and qualitative comparison of their infrared spectra with those of the other decacarbonyls. Both compounds are eluted between the respective homonuclear decacarbonyls as expected. The infrared spectra of the compounds are compared in Figure 1. The  $\text{M}_2(\text{CO})_{10}$  species belong to the  $D_{4d}$  point group and have three infrared-active C–O stretching modes,  $2B_2$  and  $E_1$ . The energy of these vibrations decrease in the order  $B_2 > E_1 > B'_2$  with respective intensities of medium, very strong, and medium as shown in the figure. The mixed-metal derivatives most likely belong to the  $C_{4v}$  point group for which there are six infrared-active C–O vibrations ( $4A_1$  and  $2E$ ). The spectrum of  $\text{MnRe}(\text{CO})_{10}$  however (Figure 1b) does not contain six bands but rather three bands in qualitative agreement with the homonuclear complexes (Figure 1a). The explanation as proposed by Flitcroft, Huggins, and Kaesz<sup>1b</sup> is that the six bands are grouped into the three sets  $2A_1$ ,  $2E$ , and  $2A'_1$ . One mode of each set is either weak and cannot be observed or is superimposed upon the other intense band. The spectra of  $\text{MnTc}(\text{CO})_{10}$  and  $\text{TcRe}(\text{CO})_{10}$  are in qualitative agreement with the spectrum of  $\text{MnRe}(\text{CO})_{10}$ . The shoulder on the low-energy  $A'_1$  band of  $\text{MnTc}(\text{CO})_{10}$  cannot be accounted for on the basis of an impurity and lends support to an argument of superimposition. The small band at 2013  $\text{cm}^{-1}$  in this

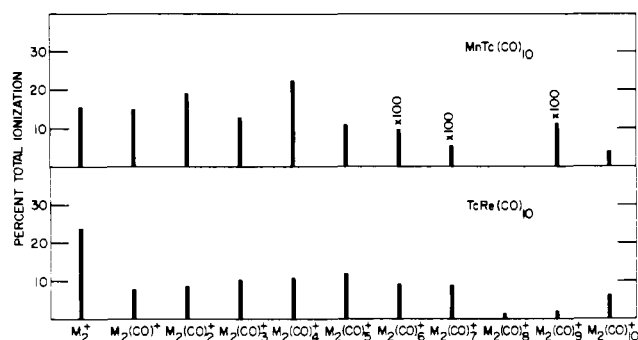
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**Table I.** Carbonyl Stretching Frequencies (cm<sup>-1</sup>) for the Metal and Mixed-Metal Decacarbonyls of Mn, Tc, and Re<sup>a</sup>

compd	str freq					
	found			reported <sup>b</sup>		
Mn <sub>2</sub> (CO) <sub>10</sub>	2044	2013	1983	2044	2013	1983
Tc <sub>2</sub> (CO) <sub>10</sub>	2065	2017	1984	2064	2017	1984
Re <sub>2</sub> (CO) <sub>10</sub>	2070	2014	1976	2070	2014	1976
MnRe(CO) <sub>10</sub>	2054	2017	1978	2054	2017	1978
MnTc(CO) <sub>10</sub>	2051	2024	1979, 1975			
TcRe(CO) <sub>10</sub>	2067	2017	1979			

<sup>a</sup> Measured in cyclohexane solution. <sup>b</sup> Reference 4.

**Figure 2.** The 50-eV mass spectra of MnTc(CO)<sub>10</sub> and TcRe(CO)<sub>10</sub>.

spectrum is due to the presence of Mn<sub>2</sub>(CO)<sub>10</sub>. The numerical results for the spectra of Figure 1 are tabulated in Table I.

The mixed-metal decacarbonyls were also identified by their mass spectra. For MnRe(CO)<sub>10</sub>, MnTc(CO)<sub>10</sub>, and TcRe(CO)<sub>10</sub> the mass-to-charge ratios of the molecular ions were found to be 522, 434, and 566, respectively. The fragmentation patterns of the compounds are characterized by the stepwise loss of CO. The spectrum of MnTc(CO)<sub>10</sub> is monoisotopic. Each dimetal fragment of MnRe(CO)<sub>10</sub> and TcRe(CO)<sub>10</sub> has two isotopes in the approximate ratio of 5:3 due to the presence of Re. The 50-eV anisotropic mass spectra of the dimetal ions from MnTc(CO)<sub>10</sub> and TcRe(CO)<sub>10</sub> are shown in Figure 2. The spectra of the remaining decacarbonyls were similar to those reported previously.<sup>8</sup> The fragmentation patterns of MnTc(CO)<sub>10</sub> and TcRe(CO)<sub>10</sub> are very similar to those of Mn<sub>2</sub>(CO)<sub>10</sub> and Tc<sub>2</sub>(CO)<sub>10</sub>, respectively. The low abundance of the M<sub>2</sub>(CO)<sub>9</sub><sup>+</sup> to M<sub>2</sub>(CO)<sub>6</sub><sup>+</sup> ions from MnTc(CO)<sub>10</sub> is in

**Table II.** Ionization Energies (eV) of the Group 7B Metal and Mixed-Metal Decacarbonyls

compd	electron	photoelectron <sup>a</sup>
Mn <sub>2</sub> (CO) <sub>10</sub>	8.32 ± 0.01	8.02
Tc <sub>2</sub> (CO) <sub>10</sub>	8.22 ± 0.01	
Re <sub>2</sub> (CO) <sub>10</sub>	8.49 ± 0.02	8.07
MnTc(CO) <sub>10</sub>	8.16 ± 0.02	
MnRe(CO) <sub>10</sub>	8.22 ± 0.01	

<sup>a</sup> Reference 9.

agreement with the equally low intensities of these ions for Mn<sub>2</sub>(CO)<sub>10</sub> and MnRe(CO)<sub>10</sub>. This trend is undoubtedly related to the presence of manganese in the complexes but is yet unexplained. The spectra of Tc<sub>2</sub>(CO)<sub>10</sub>, Re<sub>2</sub>(CO)<sub>10</sub>, and TcRe(CO)<sub>10</sub> show a similar trend in low abundances for the M<sub>2</sub>(CO)<sub>9</sub><sup>+</sup> and M<sub>2</sub>(CO)<sub>8</sub><sup>+</sup> ions.

Ionization energies (IE) are recorded in Table II for all members of the group 7B decacarbonyls except TcRe(CO)<sub>10</sub>. Due to instrumental limitations and sample size no information about the energetics of this compound was obtained. The results of this study are in good agreement with those obtained previously.<sup>8</sup> However, the electron ionization values are significantly higher than the photoelectron results<sup>9</sup> for Mn<sub>2</sub>(CO)<sub>10</sub> and Re<sub>2</sub>(CO)<sub>10</sub>. This discrepancy may be attributed to the inability of the electron ionization method to distinguish between ionization from the 6a<sub>1</sub> level (given in Table II) and the 6e<sub>3</sub> level (8.35 and 8.57 eV for Mn<sub>2</sub>(CO)<sub>10</sub> and Re<sub>2</sub>(CO)<sub>10</sub>, respectively). The data appear to indicate however that the metal orbitals from which the electron is lost in the heteronuclear decacarbonyls are destabilized with respect to those in the corresponding homonuclear compounds. This results in a lower IE for the heteronuclear compounds than for either of the pertinent homonuclear compounds.

**Acknowledgment.** We wish to acknowledge the many helpful discussions we had with Gerald D. Flesch as the results of this work developed. G.D.M. also acknowledges the helpful discussions he had with fellow graduate students, especially Michael Quick, concerning synthesis problems.

**Registry No.** Mn<sub>2</sub>(CO)<sub>10</sub>, 10170-69-1; Tc<sub>2</sub>(CO)<sub>10</sub>, 78498-97-2; Re<sub>2</sub>(CO)<sub>10</sub>, 14285-68-8; MnRe(CO)<sub>10</sub>, 14693-30-2; MnTc(CO)<sub>10</sub>, 41375-72-8; TcRe(CO)<sub>10</sub>, 78498-98-3; Mn(CO)<sub>5</sub>Br, 14516-54-2; Tc(CO)<sub>5</sub>Br, 78514-64-4; Re(CO)<sub>5</sub>Br, 14220-21-4; Mn(CO)<sub>5</sub>Na, 13859-41-1; Tc(CO)<sub>5</sub>Na, 78498-99-4.

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