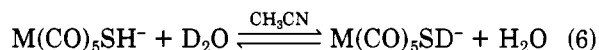


$^{13}\text{C}$ -enriched sample was determined at  $-50\text{ }^\circ\text{C}$  to avoid subsequent processes leading to CO rearrangement in the sample during the acquisition of the NMR data.

Thus the thiol ligand represents another example of a cis-labilizing ligand.<sup>31</sup> That is, the  $\text{SH}^-$  ligand stabilizes the intermediate afforded upon CO dissociation,  $[\text{M}(\text{CO})_4\text{SH}]^-$ , by exhibiting a strong preference for the equatorial site in the square-pyramidal structure.<sup>31</sup> A characteristic feature seen in other  $\text{M}(\text{CO})_5\text{L}$  complexes where L is a CO-labilizing ligand, which is absent in this instance, is a trans shortening of the axial M-CO bond relative to that of the equatorial M-CO bonds (e.g., see Table IV).

The  $\text{M}(\text{CO})_5\text{SH}^-$  species were shown to undergo proton exchange in protic medium; i.e., the reversible reaction (6)



was observed at ambient temperature. On the other hand, Gingerich and Angelici<sup>7</sup> have reported that they were unable to deprotonate  $\text{W}(\text{CO})_5\text{SH}^-$  with large excesses of very

strong bases, e.g., NaOEt, NaH, or LiMe. It is hoped to resolve this apparent inconsistency by performing more detailed studies aimed at determining the acidity of the thiol ligand's proton in these derivatives, for the resulting  $\text{M}(\text{CO})_5\text{S}^{2-}$  complexes might serve as quite useful models for metal carbonyls adsorbed at sulfide sites on surfaces.<sup>32</sup>

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**Registry No.**  $[\text{Na}(\text{cryptand})][\text{Cr}(\text{CO})_5\text{SH}]$ , 82374-30-9;  $[\text{Na}(\text{cryptand})][\text{Mo}(\text{CO})_5\text{SH}]$ , 82374-31-0;  $[\text{Na}(\text{cryptand})][\text{W}(\text{CO})_5\text{SH}]$ , 82374-32-1;  $[\text{Na}(\text{kryptofix-221})]^+\text{SH}^-$ , 82374-33-2;  $\text{Cr}(\text{CO})_6$ , 13007-92-6;  $\text{Mo}(\text{CO})_6$ , 13939-06-5;  $\text{W}(\text{CO})_6$ , 14040-11-0.

**Supplementary Material Available:** Tables of the structure factor amplitudes, anisotropic thermal parameters, cation bond lengths and angles, anisotropic thermal parameters, cation bond lengths and angles, and the idealized atomic coordinates for cation hydrogen atoms (19 pages). Ordering information is given on any current masthead page.

(32) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* 1980, 102, 7456 and references therein.

(31) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* 1976, 98, 3160.

## Enthalpy of Formation of Acyl-, Alkyl-, and Hydridopentacarbonylmanganese Complexes. The Enthalpy Contributions of Manganese-Hydrogen and Manganese-Carbon Bonds in these Molecules. Thermochemical Aspects of Models in Fischer-Tropsch Reactions

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Microcalorimetric measurements at elevated temperatures of the enthalpies of sublimation, thermal decomposition, bromination, and iodination of pentacarbonylmanganese complexes,  $[\text{Mn}(\text{CO})_5\text{R}]$ , have been made to obtain the standard enthalpies of formation,  $\Delta H_f^\circ(\text{c})$  and  $\Delta H_f^\circ(\text{g})$  (in that order) as follows (values in  $\text{kJ mol}^{-1}$ ):  $[\text{Mn}_2(\text{CO})_{10}]$   $-1675 \pm 8$ ,  $-1585 \pm 5$ ;  $[\text{Mn}(\text{CO})_5\text{Br}]$   $-964 \pm 4$ ,  $-876 \pm 5$ ;  $[\text{Mn}(\text{CO})_5\text{I}]$   $-911 \pm 5$ ,  $-834 \pm 5$ ;  $[\text{Mn}(\text{CO})_5\text{H}](\text{l})$   $-778 \pm 10$ ,  $-740 \pm 10$ ;  $[\text{Mn}(\text{CO})_5\text{CH}_3]$   $-813 \pm 4$ ,  $-753 \pm 4$ ;  $[\text{Mn}(\text{CO})_5\text{CF}_3]$   $-1464 \pm 4$ ,  $-1386 \pm 4$ ;  $[\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5]$   $-675 \pm 5$ ,  $-590 \pm 7$ ;  $[\text{Mn}(\text{CO})_5\text{CH}_2\text{C}_6\text{H}_5]$   $-726 \pm 8$ ,  $-642 \pm 8$ ;  $[\text{Mn}(\text{CO})_5\text{COCH}_3]$   $-977 \pm 7$ ,  $-897 \pm 10$ ;  $[\text{Mn}(\text{CO})_5\text{COCF}_3]$   $-1587 \pm 5$ ,  $-1508 \pm 8$ ;  $[\text{Mn}(\text{CO})_5\text{COC}_6\text{H}_5]$   $-848 \pm 5$ ,  $-725 \pm 6$ . The enthalpy of formation of  $[\text{Mn}(\text{CO})_5\text{H}]$  was obtained from solution calorimetric measurements at 298 K of the heat of reaction of the liquid hydride with excess iodine in benzene solvent. The  $\Delta H_f^\circ(\text{g})$  values are used to derive the bond enthalpy contributions  $D(\text{R}-\text{Mn}(\text{CO})_5)$ , relative to an accepted value of  $94\text{ kJ mol}^{-1}$  for  $D(\text{Mn}-\text{Mn})$  in  $[\text{Mn}_2(\text{CO})_{10}]$  at 298 K. For the organic radicals  $\text{R} = \text{CH}_3$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5$ , and  $\text{COC}_6\text{H}_5$ , values of  $D(\text{R}-\text{Mn}(\text{CO})_5)$  vary with changes in R in the same way as the values of  $D(\text{R}-\text{H})$  and  $D(\text{R}-\text{CH}_3)$ . For  $\text{R} = \text{CF}_3$  and  $\text{COCH}_3$ , the values of  $D(\text{R}-\text{Mn}(\text{CO})_5)$  are slightly higher than expected from direct comparison with  $D(\text{R}-\text{H})$ . The energetics of carbonylation of  $[\text{Mn}(\text{CO})_5\text{R}]$  to give  $[\text{Mn}(\text{CO})_5\text{COR}]$  ( $\text{R} = \text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{CF}_3$ ) are considered. The formation of the unknown  $[\text{Mn}(\text{CO})_5\text{CHO}]$  from  $[\text{Mn}(\text{CO})_5\text{H}]$  is shown to be unfavorable. Reductive elimination reactions between  $[\text{Mn}(\text{CO})_5\text{H}]$  and  $[\text{Mn}(\text{CO})_5\text{R}]$  or  $[\text{Mn}(\text{CO})_5\text{COR}]$  to form  $\text{Mn}_2(\text{CO})_{10}$  and RH or RCHO or  $\text{RCH}_2\text{OH}$ , respectively, are shown to be favorable on the basis of the calculated enthalpy change.

### Introduction

A previous study reported<sup>1</sup> microcalorimetric measurements of the enthalpy of iodination of methylpentacarbonylmanganese from which the enthalpy of formation

was derived. The present work reexamines this complex and extends the study to other derivatives,  $[\text{Mn}(\text{CO})_5\text{R}]$  ( $\text{R} = \text{H}$ , Br, I,  $\text{CF}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ,  $\text{COCH}_3$ ,  $\text{COCF}_3$ , and  $\text{COC}_6\text{H}_5$ ). The microcalorimetric measurements include enthalpies of sublimation, of thermal decomposition, of

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(1) Brown, D. L. S.; Connor, J. A.; Skinner, H. A. *J. Organomet. Chem.* 1974, 81, 403.

iodination, and of bromination. The microcalorimetric bromination technique, not applied previously, has an advantage over iodination for the study of organometallic compounds in that reaction takes place at lower temperatures, often below the temperature of onset of thermal decomposition of the compound under investigation. In the case of  $[Mn(CO)_5H]$ , solution calorimetric measurements of the enthalpy of iodination in benzene solvent were made in 298 K.

The enthalpies of formation of gaseous  $[Mn(CO)_5R]$  compounds are related to the bond enthalpy contribution<sup>2</sup>  $D(R-Mn(CO)_5)$  through the enthalpy of formation  $\Delta H_f^\circ[Mn(CO)_5, g]$  of the  $(Mn(CO)_5)$  radical. The latter quantity remains to be firmly established, although the available evidence does provide limiting values. The data now reported provide limits to values of  $D(R-Mn(CO)_5)$  for the range of radicals (or atoms), R, investigated. A more reliable determination of any single  $D(R-Mn(CO)_5)$  will thereby fix the values for all the others.

### Experimental Section

**Calorimeter.** The Calvet twin-cell high-temperature microcalorimeter (Setaram, Lyon) and the drop microcalorimetric technique have been described elsewhere.<sup>3</sup> The calorimeter was calibrated by recording the thermograms for vaporization of known masses of iodine, benzoic acid, naphthalene, or water, depending on the temperature of operation. The solution calorimeter, as described elsewhere,<sup>4</sup> was calibrated electrically.

**Materials.** The complexes  $[Mn(CO)_5R]$  ( $R = CH_3, C_6H_5, CH_2C_6H_5$ ) were prepared by reaction<sup>5</sup> between  $Na[Mn(CO)_5]$  and the corresponding bromide or iodide,  $RX$  ( $X = Br, I$ ). The products were isolated by sublimation.  $[Mn(CO)_5CF_3]$  was prepared<sup>5</sup> by decarbonylation of  $[Mn(CO)_5COCF_3]$ .  $[Mn(CO)_5Br]$  was prepared from the reaction between  $[Mn_2(CO)_{10}]$  and bromine in carbon disulfide solution and  $[Mn(CO)_5I]$  by reacting  $[Mn_2(CO)_{10}]$  and iodine.<sup>6</sup>  $[Mn(CO)_5H]$  was prepared from reaction between  $Na[Mn(CO)_5]$  and phosphoric acid.<sup>7</sup>  $[Mn(CO)_5COR]$  ( $R = CH_3, C_6H_5, CF_3$ ) was prepared from reaction<sup>5</sup> between  $Na[Mn(CO)_5]$  and  $RCOCl$  ( $R = CH_3, C_6H_5$ ) or  $(RCO)_2O$  ( $R = CF_3$ ). All of these products were characterized by microanalysis and by IR, NMR, and mass spectrometry in agreement with standards.

**Auxiliary Data.** The following auxiliary heat of formation data (in  $\text{kJ mol}^{-1}$ ) were used in evaluating the calorimetric results:  $CO(g) = -(110.524 \pm 0.17)$ ;<sup>8</sup>  $[Mn_2(CO)_{10}, c] = -(1677.8 \pm 4)$ ;<sup>3,8</sup>  $Br_2(g) = (30.907 \pm 0.11)$ ;<sup>9</sup>  $I_2(g) = (62.42 \pm 0.08)$ ;<sup>9</sup>  $HI(g) = (26.36 \pm 0.8)$ ;<sup>9</sup>  $Br(g) = (111.84 \pm 0.12)$ ;<sup>9</sup>  $I(g) = (106.76 \pm 0.04)$ ;<sup>9</sup>  $H(g) = (218.0 \pm 0.01)$ ;<sup>9</sup>  $MnF_2(c) = -(849 \pm 20)$ ;<sup>10</sup>  $MnBr_2(c) = -(385.8 \pm 1.7)$ ;<sup>11</sup>  $MnI_2(c) = -(248.5 \pm 4)$ ;<sup>3</sup>  $CH_3I(g) = (15.4 \pm 0.9)$ ;<sup>12</sup>  $CH_3Br(g) = -(37.2 \pm 0.9)$ ;<sup>12</sup>  $CF_3Br(g) = -(651.8 \pm 1.5)$ ;<sup>12</sup>  $C_6H_5I(g) = (162.2 \pm 4.6)$ ;<sup>12</sup>  $C_6H_5Br(g) = (104.3 \pm 3)$ ;<sup>12</sup>  $C_6H_5CH_2I(g) = (100.1 \pm 5.4)$ ;<sup>12</sup>  $C_6H_5CH_2Br(g) = (63.6 \pm 4.4)$ ;<sup>12</sup>  $C_2H_6(g) = -(84.0 \pm 0.2)$ ;<sup>12</sup>  $1,1'$ -biphenyl(g) =  $(182.3 \pm 1.4)$ ;<sup>12</sup>  $PhCH_2CH_2Ph(g) = (143.0 \pm 1.8)$ ;<sup>12</sup>  $CF_{1.12}(c) = -(197.0 \pm 0.8)$ ;<sup>13</sup>  $Mn(g) = (283.5 \pm 0.2)$ ;<sup>14</sup>  $CH_3(g) =$

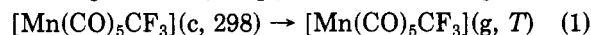
Table I. Sublimation and Thermal Decomposition of  $[Mn(CO)_5CF_3]$

A. Vacuum Sublimation			
T/K	$[Mn(CO)_5CF_3]/$ mg	$\Delta H_1^T/$ $\text{kJ mol}^{-1}$	$\Delta H_1^{298}/$ $\text{kJ mol}^{-1}$
336	2.380	86.1	77.6
355	3.030	91.6	78.8
362	3.175	91.5	77.1
B. Thermal Decomposition			
T/K	$[Mn(CO)_5CF_3]/$ mg	$\Delta H_2^T/$ $\text{kJ mol}^{-1}$	$\Delta H_2^{298}/$ $\text{kJ mol}^{-1}$
475	2.825	-70.7	-114.7
475	2.890	-65.7	-109.9
475	4.165	-60.6	-123.3

$(146.2 \pm 1.0)$ ;<sup>15,16</sup>  $CF_3(g) = -(468.2 \pm 5)$ ;<sup>17</sup>  $C_6H_5(g) = (325.1 \pm 8)$ ;<sup>18</sup>  $C_6H_5CH_2(g) = (190.8 \pm 8)$ ;<sup>19</sup> The enthalpies of reaction,  $\Delta H^T$ , measured at temperature,  $T$ , were adjusted to refer to 298 K by using  $(H_T - H_{298})$  data for organic compounds from Stull, Westrum, and Sinke<sup>20</sup> and for inorganic compounds ( $Mn, Br_2, I_2, MnBr_2, MnI_2$ ) from Barin and Knacke<sup>21</sup> and the JANAF tables.<sup>22</sup>

### Results

1. (Trifluoromethyl)pentacarbonylmanganese,  $[Mn(CO)_5CF_3]$ . Measurements of the enthalpy of the sublimation process (1),  $\Delta H_1^T$ , were made at temperatures,



$T = 355\text{--}362$  K, by using the vacuum sublimation microcalorimetric technique.<sup>23</sup> At temperatures  $T = 395\text{--}422$  K, sublimation was accompanied by thermal decomposition, and at  $T > 473$  K thermal decomposition appeared to be total within the hot zone. The solid residue was partially soluble in water (the solution contained fluoride ion), the insoluble residue being a polymeric product,  $(CF)_n$ , arising from the thermal decomposition reaction (2).  $[Mn(CO)_5CF_3] \rightarrow MnF_2(c) + (1/n)[(CF)_n](c) + 5CO(g)$  (2)

The thermograms for thermal decomposition showed an exothermic peak following the initial endotherm, with slow return of the exotherm trace to the base line. The measured heats of sublimation and of thermal decomposition,  $\Delta H_2^T$ , are given in Table I.

The mean value of  $\Delta H_2^{298} = -(116 \pm 8) \text{ kJ mol}^{-1}$  for thermal decomposition leads to  $\Delta H_f^\circ([Mn(CO)_5CF_3], c) = -(1462 \pm 22) \text{ kJ mol}^{-1}$ . In this evaluation, we have estimated<sup>24</sup> that  $\Delta H_f^\circ = -(176 \pm 1) \text{ kJ mol}^{-1}$  for each monomer unit of the polymer product,  $(CF)_n$ , and used the

(2) Pilcher, G.; Skinner, H. A. In "The Chemistry of the Metal-Carbon Bond"; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; p 43.  
(3) Connor, J. A.; Virmani, Y.; Skinner, H. A. *J. Chem. Soc., Faraday Trans. 1* 1972, 68, 1754.

(4) Bickerton, J. M.Sc. Thesis, Manchester University, 1981.

(5) Beck, W.; Hieber, W.; Tengler, H. *Chem. Ber.* 1961, 94, 862. See also: Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *Inorg. Synth.* 1978, 18, 57.

(6) Quick, M. H.; Angelici, R. J. *Inorg. Synth.* 1979, 19, 160, 161.

(7) Hieber, W.; Wagner, G. Z. *Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* 1958, 13, 339.

(8) Wagman, D. D. *NBS Tech. Note (U.S.)* 1965-1971, No. 270-1-270-5.

(9) CODATA, *J. Chem. Thermodyn.* 1978, 10, 903.

(10) Ehlert, T. C.; Hsia, M. *J. Fluorine Chem.* 1972, 2, 33.

(11) Glyshko, V. P.; Medvedev, V. A. "Thermochemical Constants of Compounds"; Akad. Nauk SSSR: Moscow, 1974, p 7.

(12) Pedley, J. B.; Rylance, J. Sussex-NPL Computer Analysed Thermochemical Data, University of Sussex, 1977.

(13) Wood, J. L.; Badachape, R. B.; Lagow, R. J.; Margrave, J. L. *J. Phys. Chem.* 1969, 73, 3139.

(14) Smoes, S.; Pattje, W. R.; Drowart, J. *High Temp. Sci.* 1978, 10, 109.

(15) Chupka, W. A. *J. Chem. Phys.* 1968, 48, 2337.

(16) Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* 1979, 11, 147.

(17) Ferguson, K. C.; Whittle, E. *J. Chem. Soc., Faraday Trans. 1* 1972, 68, 295.

(18) Chamberlain, G. A.; Whittle, E. *Trans. Faraday Soc.* 1971, 67, 2077.

(19) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* 1979, 101, 1230.

(20) Stull, D. R.; Westrum, E. F.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1960.

(21) Barin, I.; Knacke, O. "Thermochemical Properties of Inorganic Substances"; Springer-Verlag: Berlin, 1973.

(22) Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* 1971, NSRDS-NBS 37.

(23) Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M. L.; Paz Andrade, I. M.; Skinner, H. A. *J. Organomet. Chem.* 1975, 97, 221.

(24) Measurements of the energy of combustion of the polymer  $(CF_{1.12})_n$  in fluorine gas gave<sup>13</sup>  $\Delta H_f^\circ(CF_{1.12}, c) = -(197.0 \pm 0.8) \text{ kJ mol}^{-1}$ . The estimate equates  $\Delta H_f^\circ(CF_{1.0}, c)$  to  $(1/1.12)\Delta H_f^\circ(CF_{1.12}, c)$ .

(25) Good, W. D.; Fairbrother, D. M.; Waddington, G. *J. Phys. Chem.* 1958, 62, 863.

(26) Baev, A. K.; Dem'yanchuk, V. V.; Mirzoev, G.; Novikov, G. I.; Kolobova, N. E. *Russ. J. Phys. Chem. (Engl. Transl.)* 1971, 45, 777.

Table II. Bromination of  $[\text{Mn}(\text{CO})_5\text{CF}_3]$ 

T/K	$[\text{Mn}(\text{CO})_5\text{CF}_3]/$ mg	$\Delta H_3^T/$ kJ mol <sup>-1</sup>	$\Delta H_3^{298}/$ kJ mol <sup>-1</sup>
384	2.090	-154	-175.6
386	2.285	-151	-172.9
401	1.220	-149	-173.6
403	1.642	-143	-168.1
404	1.296	-149.5	-174.9
406	1.450	-144.7	-170.5

Table III. Bromination of  $[\text{Mn}_2(\text{CO})_{10}]$ 

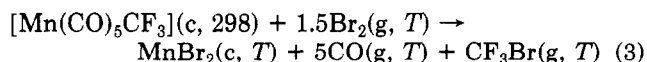
T/K	$[\text{Mn}_2(\text{CO})_{10}]/$ mg	$\Delta H_4^T/$ kJ mol <sup>-1</sup>	$\Delta H_4^{298}/$ kJ mol <sup>-1</sup>
415	2.490	-224.1	-268
418	3.210	-212.1	-257
421	2.310	-208.0	-254
421	2.060	-215.4	-262
421	2.330	-230.7	-277

value of  $\Delta H_f^\circ([\text{MnF}_2, c) = -(849 \pm 20)$  kJ mol<sup>-1</sup> recommended by Ehlert and Hsia.<sup>10</sup>

Iodination studies on  $[\text{Mn}(\text{CO})_5\text{CF}_3]$  proved unhelpful. Samples dropped into iodine vapor at 418 K decomposed to give mainly  $\text{MnF}_2$ ; only small amounts of iodine were taken up in the reaction. At lower temperatures, ca. 393 K, reaction with iodine was too slow to prevent the escape of appreciable quantities of unreacted  $[\text{Mn}(\text{CO})_5\text{CF}_3]$  (as vapor) from the reaction zone; moreover, the solid residue from reaction contained both  $\text{MnF}_2$  and  $\text{MnI}_2$ .

Studies of bromination at 384–406 K were more satisfactory. Samples dropped into bromine vapor reacted rapidly, the solid residue ( $\text{MnBr}_2$ ) being completely soluble in water, without leaving any film of  $(\text{CF})_n$  as residue. The thermograms showed an initial endotherm and followed by an exothermic peak; the return to the base line was often rather slow. In some experiments the initial bromine calibration drop was followed by dropping two capillary containers, one carrying the sample and the other additional bromine. This procedure gave thermograms which returned more rapidly and completely to the base line.

After each experiment, the reaction vessel was evacuated to remove excess bromine and volatile products in order to facilitate examination of the solid residue, a whitish powder. The powder deposited mainly within the reaction vessel itself, but traces of powder were also deposited in the inlet tube. The residue within the reaction vessel was dissolved in water and the solution ( $\text{MnBr}_2$ ) analyzed for total manganese content (atomic absorption spectroscopy). Analysis showed that 80–90% of the total manganese added was retained as  $\text{MnBr}_2$  within the reaction vessel, the remainder escaping as very fine  $\text{MnBr}_2$  particles into the exit tube. Results of the bromination studies are summarized in Table II, where  $\Delta H_3^T$  refers to the cell reaction which is assumed to be eq 3. The mean value



of  $\Delta H_3^{298} = -(172.6 \pm 3)$  kJ mol<sup>-1</sup> leads to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CF}_3, c) = -(1464 \pm 4)$  kJ mol<sup>-1</sup>, in agreement with that indicated by the thermal decomposition studies. With  $\Delta H_{\text{sub}}^{298} = (77.8 \pm 1)$  kJ mol<sup>-1</sup>, the vapor state enthalpy of formation becomes  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CF}_3, g) = -(1386 \pm 4)$  kJ mol<sup>-1</sup>.

The bromination technique was tested by separate measurements on the enthalpy of bromination of decacarbonyldimanganese at temperatures in the range 415–421 K. The measured  $\Delta H_4^T$  refers to the cell reaction (4) and

$$[\text{Mn}_2(\text{CO})_{10}](c, 298) + 2\text{Br}_2(g, T) \rightarrow 2\text{MnBr}_2(g, T) + 10\text{CO}(g, T) \quad (4)$$
Table IV. Sublimation of  $[\text{Mn}_2(\text{CO})_{10}]$ 

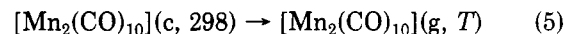
T/K	$[\text{Mn}_2(\text{CO})_{10}]/$ mg	$\Delta H_5^T/$ kJ mol <sup>-1</sup>	$\Delta H_5^{298}/$ kJ mol <sup>-1</sup>
336	1.846	107.3	93.8
345	2.511	109.1	92.4
373	2.087	116.8	88.1
385	3.110	123.4	91.4
387	2.171	122.7	92.4
387	2.768	127.1	95.8

Table V. Sublimation of  $[\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5]$ 

T/K	$[\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5]/$ mg	$\Delta H_{\text{sub}}^T/$ kJ mol <sup>-1</sup>	$\Delta H_{\text{sub}}^{298}/$ kJ mol <sup>-1</sup>
366	7.645	104.3	87.6
393	2.390	103.4	80.6
393	2.095	109.3	86.5

results are summarized in Table III. The mean value of  $\Delta H_f^\circ([\text{Mn}_2(\text{CO})_{10}, c) = -(1675 \pm 8)$  from bromination is in good agreement with that obtained by Good et al. from combustion calorimetry<sup>27</sup> and from iodination studies previously reported.<sup>3</sup>

The vacuum sublimation microcalorimetric technique<sup>23</sup> applied to  $[\text{Mn}_2(\text{CO})_{10}]$  over the range 336–387 K gave the results listed in Table IV, where  $\Delta H_5^T$  refers to the sublimation process (5). The value of  $\Delta H_{\text{sub}}^{298} = (92.3 \pm 2.1)$



kJ mol<sup>-1</sup> is higher than that previously accepted<sup>1</sup> which was based on vapor pressure measurements<sup>26</sup> over the range 351–463 K.

**2. Phenylpentacarbonylmanganese,  $[\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5]$ .** The vacuum sublimation microcalorimetric technique was applied to determine the enthalpy of sublimation in the range 366–383 K (Table V). Sublimation was accompanied by thermal decomposition at temperatures near to 423 K, and at 513 K thermal decomposition appeared to be total and within the hot zone. 1,1'-Biphenyl was the major product of thermal decomposition, but other hydrocarbon products were also detected. The measured enthalpy  $\Delta H_6^{298} = 55$  kJ mol<sup>-1</sup> was less than expected for the simple decomposition reaction (6) comparing in this

$$[\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5] \rightarrow \text{Mn}(c) + 5\text{CO}(g) + 0.5\text{C}_{12}\text{H}_{10}(g) \quad (6)$$

respect with earlier thermal decomposition studies<sup>3</sup> on  $[\text{Mn}_2(\text{CO})_{10}]$ , due to exothermic surface reactions of carbon monoxide on the thin-film deposits of manganese metal.

The iodination of  $[\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5]$  was studied over the temperature range 482–519 K; samples were dropped into excess iodine vapor in the hot reaction vessel, and unused iodine was removed by evacuation after each experiment, the amounts being determined titrimetrically. Traces of biphenyl sublimed with the iodine, condensing as a thin white film on cool parts of the exit line. The involatile residue ( $\text{MnI}_2$ ) was dissolved in dilute nitric acid and the iodide content determined by titration. The iodine balance indicated some loss of iodine (by formation of iodobenzene) but usually barely more than was to be expected from manipulative losses. The measured enthalpies of reaction,  $\Delta H_7^T$ , are assumed to refer to reaction 7. Values of  $n$  were

$$[\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5](c, 298) + 0.5(n+1-m)\text{I}_2(g, T) \rightarrow \text{MnI}_n(c, T) + 5\text{CO}(g, T) + (m/2)[\text{C}_{12}\text{H}_{10}(g, T)] + (1-m)\text{C}_6\text{H}_5\text{I}(g, T) \quad (7)$$

obtained from analysis of the solid residue and values of  $m$  from the iodine balance. The results are summarized in Table VI. The values of  $\Delta H_7^{298}$  refer to reaction 7

(27) Hieber, W.; Wagner, G. *Justus Liebigs Ann. Chem.* 1958, 618, 24.

Table VI. Iodination of [Mn(CO)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>]

T/K	[Mn(CO) <sub>5</sub> C <sub>6</sub> H <sub>5</sub> ]/ mg	I <sub>2</sub> /mg	n	m	ΔH <sub>7</sub> <sup>T</sup> / kJ mol <sup>-1</sup>	ΔH <sub>7</sub> <sup>298</sup> / kJ mol <sup>-1</sup>
512	2.150	8.675	1.83	0.8	4.8	-58.7
514	2.165	9.305	1.85	0.8	21.9	-42.5
516	2.145	8.765	1.71	0.7	1.2	-63.5
519	3.335	8.635	1.88	0.7	-21.0	-86.8
482	2.195	8.580	2.0	0.4	-16.4	-71.0

Table VII. Bromination of [Mn(CO)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>]

T/K	[Mn(CO) <sub>5</sub> C <sub>6</sub> H <sub>5</sub> ]/ mg	ΔH <sub>9</sub> <sup>T</sup> / kJ mol <sup>-1</sup>	ΔH <sub>9</sub> <sup>298</sup> / kJ mol <sup>-1</sup>
383	2.160	-184.3	-208.3
384	2.045	-177.7	-201.9
385	2.365	-177.0	-201.5
399	2.395	-177.7	-207.2
402	2.765	-179.5	-208.9

Table VIII. Sublimation and Thermal Decomposition of [Mn(CO)<sub>5</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]

## A. Vacuum Sublimation

T/K	[Mn(CO) <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]/ mg	ΔH <sub>sub</sub> <sup>T</sup> / kJ mol <sup>-1</sup>	ΔH <sub>sub</sub> <sup>298</sup> / kJ mol <sup>-1</sup>
388	2.780	109.4	85.1
389	9.180	109.2	84.6
384	3.500	107.0	83.6

## B. Thermal Decomposition

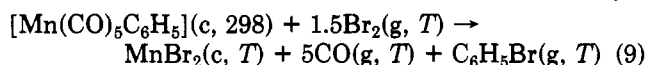
T/K	[Mn(CO) <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]/ mg	ΔH <sub>10</sub> <sup>T</sup> / kJ mol <sup>-1</sup>	ΔH <sub>10</sub> <sup>298</sup> / kJ mol <sup>-1</sup>
518	3.115	197	127
518	2.100	208	138
518	4.210	199	129
518	5.880	206	136

carried out isothermally at 298 K; ΔH<sub>f</sub><sup>o</sup>[Mn(CO)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>, c] was then obtain from

$$\Delta H_f^o = (-421.6 - 155.5n - 39.8m - \Delta H_7^{298}) \text{ kJ mol}^{-1} \quad (8)$$

The mean value of ΔH<sub>f</sub><sup>o</sup> = -(673 ± 16) kJ mol<sup>-1</sup> was obtained.

Bromination studies were made over the temperature range 383–402 K when the reaction occurred readily, and the thermograms (which showed an exothermal peak following the initial endotherm) returned satisfactorily to the base line. Separate measurements showed no significant enthalpy of interaction between bromine and bromobenzene vapors in this temperature range. The measured enthalpies (ΔH<sub>9</sub><sup>T</sup> in Table VII) are accordingly referred to the cell reaction (9). The mean value of ΔH<sub>9</sub><sup>298</sup>



= -(205.6 ± 3.2) kJ mol<sup>-1</sup> leads to a value of ΔH<sub>f</sub><sup>o</sup>([Mn(CO)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>], c) = -(675 ± 5) kJ mol<sup>-1</sup> from bromination

Table IX. Iodination and Bromination of [Mn(CO)<sub>5</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]

## A. Iodination

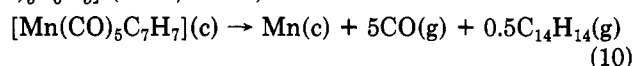
T/K	[Mn(CO) <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]/ mg	I <sub>2</sub> /mg	n	ΔH <sub>11</sub> <sup>T</sup> /kJ mol <sup>-1</sup>	ΔH <sub>11</sub> <sup>298</sup> /kJ mol <sup>-1</sup>
482	2.285	9.885	1.87	11.7	-45.0
518	2.650	9.795	2.0	-3.9	-75.1

## B. Bromination

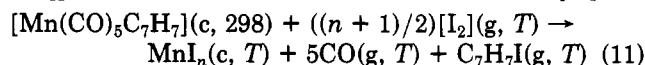
T/K	[Mn(CO) <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ]/mg	ΔH <sub>13</sub> <sup>T</sup> /kJ mol <sup>-1</sup>	ΔH <sub>13</sub> <sup>298</sup> /kJ mol <sup>-1</sup>
376	4.325	-160.8	-185
384	2.410	-167.7	-195
390	2.505	-176.0	-204
390	2.240	-166.1	-194

which is in good agreement with that from iodination but is subject to less uncertainty. Taking ΔH<sub>sub</sub><sup>298</sup> = (84.9 ± 4.4) kJ mol<sup>-1</sup> gives the enthalpy of formation in the gas state ΔH<sub>f</sub><sup>o</sup>([Mn(CO)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>], g) = -(590 ± 7) kJ mol<sup>-1</sup>.

**3. Benzylpentacarbonylmanganese, [Mn(CO)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>].** Vacuum sublimation studies were made at temperatures in the range 384–389 K with results shown in Table VIII. Thermal decomposition in argon at 518 K was rapid, giving a black powder and a relatively involatile liquid. Traces of a white solid (1,2-diphenylethane) condensed in cooler parts of the exit tube. Mass spectra analysis of the liquid products showed the presence of C<sub>7</sub>H<sub>8</sub>, C<sub>14</sub>H<sub>12</sub>, C<sub>14</sub>H<sub>14</sub>, and also C<sub>21</sub> hydrocarbons. The thermal measurements are given in Table VIII; the measured enthalpy of decomposition ΔH<sub>10</sub><sup>298</sup> = (132 ± 4) kJ mol<sup>-1</sup> was less than expected for the simple thermal decomposition (10) comparing in this respect with [Mn(CO)<sub>5</sub>C<sub>6</sub>H<sub>5</sub>] (see 2, above).



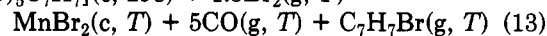
Iodination measurements were made from 482 to 518 K, and two typical results included in Table IX. The iodine consumption indicated appreciable formation of benzyl iodide, either by direct methods or from iodination of primary thermal decomposition products. The measured ΔH<sub>11</sub><sup>T</sup> are attributed to reaction 11 and ΔH<sub>f</sub><sup>o</sup>([Mn-



(CO)<sub>5</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>], c) was evaluated from the corresponding thermochemical equation (12). Bromination studies made

$$\Delta H_f^o = -483.7 - 155.5n - \Delta H_{11}^{298} \text{ kJ mol}^{-1} \quad (12)$$

at temperatures ranging from 376 to 390 K are included in Table IX. The measured ΔH<sub>13</sub><sup>T</sup> relate to the cell reaction (13), and ΔH<sub>f</sub><sup>o</sup>(c) values were obtained from the



corresponding thermochemical equation (14). Separate ΔH<sub>f</sub><sup>o</sup>([Mn(CO)<sub>5</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>], c) =

$$-919.2 - \Delta H_{13}^{298} \text{ kJ mol}^{-1} \quad (14)$$

measurements established that thermal corrections from mixing benzyl bromide vapor with bromine gas were not

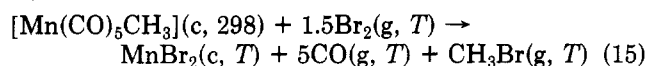
Table X. Bromination of  $[\text{Mn}(\text{CO})_5\text{CH}_3]$ 

T/K	$[\text{Mn}(\text{CO})_5\text{CH}_3]/$ mg	$\Delta H_{15}^T/$ $\text{kJ mol}^{-1}$	$\Delta H_{15}^{298}/$ $\text{kJ mol}^{-1}$
386	2.400	-192.3	-211.8
387	2.505	-184.2	-203.8
387	2.040	-189.3	-208.9
389	2.130	-186.9	-206.9
390	2.070	-189.7	-209.9
403	2.605	-191.1	-214.4
403	2.620	-185.3	-208.6

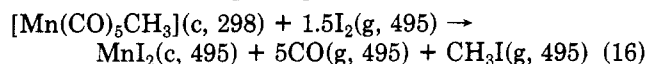
significant. In bromination experiments, the reaction vessel was evacuated before terminating the thermogram trace to ensure complete evaporation of benzyl bromide from the reaction vessel. The mean value of  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CH}_2\text{C}_6\text{H}_5], \text{c}) = -(726 \pm 8) \text{ kJ mol}^{-1}$  from bromination overlaps that from iodination,  $-(725 \pm 9) \text{ kJ mol}^{-1}$ . We accept the former as the best value from these studies. Taking  $\Delta H_{\text{sub}}^{298} = (84.5 \pm 0.7) \text{ kJ mol}^{-1}$  gives the enthalpy of formation in the vapor state  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CH}_2\text{C}_6\text{H}_5], \text{g}) = -(642 \pm 8) \text{ kJ mol}^{-1}$ .

#### 4. Methylpentacarbonylmanganese, $[\text{Mn}(\text{CO})_5\text{CH}_3]$ .

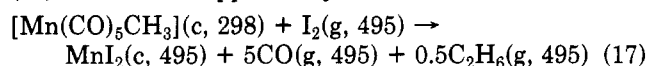
Bromination of  $[\text{Mn}(\text{CO})_5\text{CH}_3]$  was studied over the temperature range 386–403 K; the measured enthalpies (Table X) refer to the cell reaction (15). The mean value of



$\Delta H_{15}^{298} = -(209 \pm 3) \text{ kJ mol}^{-1}$  corresponds to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CH}_3], \text{c}) = -(813 \pm 4) \text{ kJ mol}^{-1}$ . Earlier iodination studies (at 495 K) interpreted on the basis of complete iodination according to eq 16 led<sup>1</sup> to  $\Delta H_f^\circ = -(791 \pm 8)$



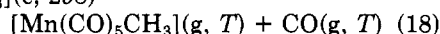
$\text{kJ mol}^{-1}$ , in rather poor agreement with the present value. The iodine balance was,<sup>1</sup> however, barely sufficient to allow for iodination as required by reaction 16; small manipulative losses of iodine vapor (probable at temperatures as high as 500 K) would imply that the decomposition process (17) contributed appreciably to the overall cell reaction.



The measured reaction heat, if attributed entirely to reaction 17, gives  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CH}_3], \text{c}) = -(816 \pm 6) \text{ kJ mol}^{-1}$ , in closer agreement with the value obtained from bromination.

The enthalpy of sublimation of  $[\text{Mn}(\text{CO})_5\text{CH}_3]$  from vapor pressure measurements over the range 298–400 K is reported<sup>27</sup> as  $\Delta H_{\text{sub}} = (60.3 \pm 1.7) \text{ kJ mol}^{-1}$  which, combined with the value of  $\Delta H_f^\circ(\text{c}) = -(813 \pm 4) \text{ kJ mol}^{-1}$ , gives the enthalpy of formation of the gaseous compound,  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CH}_3], \text{g}) = -(753 \pm 4) \text{ kJ mol}^{-1}$ .

**5. Acetylpentacarbonylmanganese,  $[\text{Mn}(\text{CO})_5\text{COCH}_3]$ .** Microcalorimetric studies of the sublimation of  $[\text{Mn}(\text{CO})_5\text{COCH}_3]$  were made over the temperature range 332–416 K. In some experiments, the reaction vessel was evacuated almost immediately after the sample was dropped into the argon-filled hot zone; in others the vacuum was applied later, to ensure that sublimation of the same was complete. At the higher temperatures it is probable<sup>5</sup> that the sublimation is essentially the decomposition (decarbonylation) reaction (18), and even at the



lowest temperatures used (332–335 K), the sublimation may be accompanied in part by decomposition. The changing results as the temperature increases reflect the

Table XI. Sublimation of  $[\text{Mn}(\text{CO})_5\text{COCH}_3]$ 

T/K	$[\text{Mn}(\text{CO})_5\text{COCH}_3]/$ mg	$\Delta H_{18}^T/$ $\text{kJ mol}^{-1}$	$\Delta H_{18}^{298}/$ $\text{kJ mol}^{-1}$
332	3.570	90.3 <sup>a</sup>	82.3
332	3.030	116.4	108.4
335	3.485	97.1 <sup>a</sup>	88.4
369	3.590	137.7	121.0
370	2.938	135.7	118.8
379	3.325	138.9	119.9
396	3.869	142.1 <sup>a</sup>	118.0
396	3.955	143.2	120.3
401	3.869	142.1 <sup>a</sup>	118.0
416	3.498	146.5	118.8

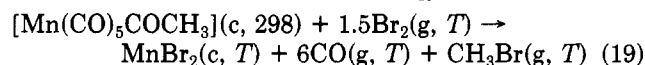
<sup>a</sup> Vacuum applied early.

Table XII. Bromination of  $[\text{Mn}(\text{CO})_5\text{COCH}_3]$ 

T/K	$[\text{Mn}(\text{CO})_5\text{COCH}_3]/$ mg	$\Delta H_{19}^T/$ $\text{kJ mol}^{-1}$	$\Delta H_{19}^{298}/$ $\text{kJ mol}^{-1}$
401	1.220	-138.1	-163.7
405	0.945	-125.4	-151.7
409	1.450	-134.0	-161.0
409	1.485	-135.3	-162.3
411	2.015	-139.4	-166.4

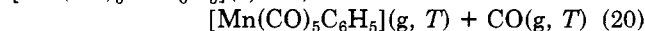
onset of the decomposition (Table XI). The approximate constancy of  $\Delta H_{18}^{298}$  at temperatures  $T \geq 369 \text{ K}$  suggests that decomposition was virtually complete in the higher range of temperature. The mean value of  $\Delta H_{18}^{298} = (119.3 \pm 0.9) \text{ kJ mol}^{-1}$  with the value of  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CH}_3], \text{g}) = -(753 \pm 4) \text{ kJ mol}^{-1}$  corresponds to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{COCH}_3], \text{c}) = -(982 \pm 4) \text{ kJ mol}^{-1}$ . The lowest measured sublimation enthalpy ( $82.3 \text{ kJ mol}^{-1}$  at 332 K) may be influenced slightly by coincident partial decarbonylation, and a value of  $\Delta H_{\text{sub}}^{298} \leq 80 \text{ kJ mol}^{-1}$  is suggested for the pure sublimation process.

The bromination of  $[\text{Mn}(\text{CO})_5\text{COCH}_3]$  was studied over the temperature range 401–411 K, and results are summarized in Table XII, where  $\Delta H_{19}^T$  refers to the cell reaction (19). The mean value of  $\Delta H_{19}^{298} = -(161 \pm 5) \text{ kJ}$



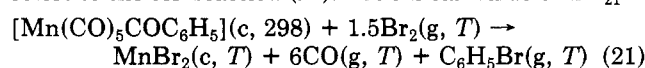
$\text{mol}^{-1}$  leads to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{COCH}_3], \text{c}) = -(971.5 \pm 5.5) \text{ kJ mol}^{-1}$ , as compared with  $-(982 \pm 5) \text{ kJ mol}^{-1}$  from the sublimation/decarbonylation reaction. The intermediate value of  $-(977 \pm 7) \text{ kJ mol}^{-1}$  is accepted for present purposes so that  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{COCH}_3], \text{g}) = -(897 \pm 10) \text{ kJ mol}^{-1}$ .

**6. Benzoylpentacarbonylmanganese,  $[\text{Mn}(\text{CO})_5\text{COC}_6\text{H}_5]$ .** Sublimation measurements over the temperature range 349–401 K are summarized in Table XIII. The measured enthalpy varies with temperature in a similar manner to  $[\text{Mn}(\text{CO})_5\text{COCH}_3]$ , due to the thermal decarbonylation process (20) which becomes increasingly im-



portant above 370 K and predominates at the more elevated temperatures.<sup>6</sup> The mean value of  $\Delta H_{20}^{298}$  (from measurements at  $T > 375 \text{ K}$ ) =  $(148.3 \pm 3) \text{ kJ mol}^{-1}$  attributed to sublimation with decarbonylation and corresponds to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{COC}_6\text{H}_5], \text{c}) = -(849 \pm 7) \text{ kJ mol}^{-1}$ .

Bromination measurements, summarized in Table XIV, were made at 400–402 K. The measured enthalpy  $\Delta H_{21}^T$  refers to the cell reaction (21). The mean value of  $\Delta H_{21}^{298}$



=  $-(143.1 \pm 2) \text{ kJ mol}^{-1}$  leads to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{COC}_6\text{H}_5],$

Table XIII. Sublimation of  $[Mn(CO)_5COC_6H_5]$ 

T/K	$[Mn(CO)_5COC_6H_5]/$ mg	$\Delta H_{20}^T/$ kJ mol <sup>-1</sup>	$\Delta H_{20}^{298}/$ kJ mol <sup>-1</sup>
349	1.945	138.7	126.0
359	2.080	134.9	119.7
375	0.830	161.1 <sup>a</sup>	141.9
375	2.640	165.8	146.6
392	1.675	168.4 <sup>a</sup>	145.0
395	1.670	170.8 <sup>a</sup>	146.7
395	1.540	173.8	151.7
401	2.500	175.5	149.9

<sup>a</sup> Vacuum applied after delay.Table XIV. Bromination of  $[Mn(CO)_5COC_6H_5]$ 

T/K	$[Mn(CO)_5COC_6H_5]/$ mg	$\Delta H_{21}^T/$ kJ mol <sup>-1</sup>	$\Delta H_{21}^{298}/$ kJ mol <sup>-1</sup>
400	2.740	-110.2	-142.0
401	2.980	-112.9	-145.0
401	2.710	-112.1	-144.2
401	2.945	-108.9	-141.0

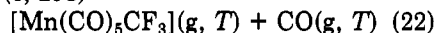
Table XV. Sublimation of  $[Mn(CO)_5COCF_3]$ 

T/K	$[Mn(CO)_5COCF_3]/$ mg	$\Delta H_{22}^T/$ kJ mol <sup>-1</sup>	$\Delta H_{22}^{298}/$ kJ mol <sup>-1</sup>
335	2.390	88.2 <sup>a</sup>	78.8
370	3.235	100.7	82.4
379	4.035	111.1	90.6
390	4.155	116.1	91.0
392	2.738	114.2	90.4
392	2.068	113.4 <sup>a</sup>	89.6
392	3.012	116.1	92.3

<sup>a</sup> Vacuum applied early.

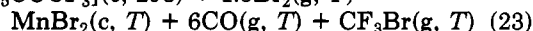
c) =  $-(847 \pm 4)$  kJ mol<sup>-1</sup>, in close agreement with that obtained from sublimation/decarbonylation. Assuming that the sublimation measurements made in the temperature range 349–359 K (Table XIII) refer to sublimation per se, giving  $\Delta H_{sub}^{298} \approx (123 \pm 3)$  kJ mol<sup>-1</sup>, we obtain  $\Delta H_f^\circ([Mn(CO)_5COC_6H_5], g) = -(724 \pm 5)$  kJ mol<sup>-1</sup>.

7. (Trifluoroacetyl)pentacarbonylmanganese,  $[Mn(CO)_5COCF_3]$ . Sublimation measurements over the temperature range 335–392 K are summarized in Table XV. There was visible decomposition (formation of  $MnF_2$ ) at temperatures  $T > 410$  K. The increase in the enthalpy of sublimation with increasing temperature, although less pronounced than for  $[Mn(CO)_5COCH_3]$ , indicates that thermal decarbonylation is increasingly important above 370 K and that complete decomposition according to eq 22 may occur at temperatures above 380 K. The mean  $[Mn(CO)_5COCF_3](c, 298) \rightarrow$



value of  $\Delta H_{22}^{298} = (90.8 \pm 0.9)$  kJ mol<sup>-1</sup> for measurements in the temperature range 379–392 K, combined with  $\Delta H_f^\circ([Mn(CO)_5CF_3], g) = -(1386 \pm 4)$  kJ mol<sup>-1</sup>, leads to  $\Delta H_f^\circ([Mn(CO)_5COCF_3], c) = -(1587 \pm 4)$  kJ mol<sup>-1</sup>.

Bromination studies were made over the temperature range 396–404 K. The measured enthalpies  $\Delta H_{23}^T$  referring to the cell reaction (23) are summarized in Table XVI.  $[Mn(CO)_5COCF_3](c, 298) + 1.5Br_2(g, T) \rightarrow$



The mean value of  $\Delta H_{23}^{298} = -(161.4 \pm 2)$  kJ mol<sup>-1</sup>, corresponds to  $\Delta H_f^\circ([Mn(CO)_5COCF_3], c) = -(1586 \pm 3)$  kJ mol<sup>-1</sup>, in good agreement with the value from the sublimation/decarbonylation studies. Assuming that the enthalpy measured at 335 K (Table XV) refers to sublimation per se, giving  $\Delta H_{sub}^{298} = 79$  kJ mol<sup>-1</sup>, we obtain  $\Delta H_f^\circ([Mn(CO)_5COCF_3], g) = -(1508 \pm 6)$  kJ mol<sup>-1</sup>.

Table XVI. Bromination of  $[Mn(CO)_5COCF_3]$ 

T/K	$[Mn(CO)_5COCF_3]/$ mg	$\Delta H_{23}^T/$ kJ mol <sup>-1</sup>	$\Delta H_{23}^{298}/$ kJ mol <sup>-1</sup>
396	2.928	-138.0	-164.4
403	2.900	-132.0	-160.1
403	3.006	-133.1	-161.2
403	1.507	-133.6	-161.7
403	2.095	-135.2	-163.3
404	2.628	-129.2	-157.6

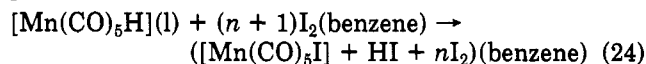
Table XVII. Iodination of  $[Mn(CO)_5H]$ 

$[Mn(CO)_5H]/$ g	$\Delta T^a/$ K	$C^b/$ J K <sup>-1</sup>	$q^c/$ K	$\Delta H_{24}/$ kJ mol <sup>-1</sup>
0.3760	0.9252	268.0	248.0	-129.2
0.4440	1.052	264.7	278.5	-123.0
0.4344	0.9651	269.4	260.0	-117.3
0.5895	1.4005	268.5	376.0	-125.1

<sup>a</sup> Corrected temperature rise. <sup>b</sup> Calorimeter heat capacity. <sup>c</sup> Heat evolved by reaction.

### 8. Hydridopentacarbonylmanganese, $[Mn(CO)_5H]$ .

Addition of the liquid complex to a solution of iodine in benzene at room temperature resulted in a rapid reaction. The consumption of iodine is consistent with the displacement reaction (24). Measurements were made at 298

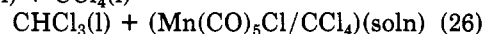


K by releasing samples of the complex (sealed in thin-walled glass ampules) below the surface of the calorimetric solvent (ca. 130 mL of benzene, containing ca. 1.2 g of dissolved iodine). The calorimeter temperature (measured by the resistance of a thermistor) was registered as a function of time by a digital voltmeter (Solartron Microprocessor 7065), and the output data were processed by using a microcomputer. The calorimeter was calibrated electrically after each run. The results are shown in Table XVII. Separate measurements were made of the enthalpy of solution of iodine in benzene and of  $[Mn(CO)_5I]$  in the iodine/benzene solvent, in proportions to match the experiments listed in Table XVII. Data are not available on the enthalpy of solution of HI(g) in benzene solvent, although for solution of HBr(g) in benzene a value of  $\Delta H_{soln}$  [ $\sim -18$  kJ mol<sup>-1</sup>] is available.<sup>8</sup> Where comparisons can be made,  $\Delta H_{soln}$  values in hydrocarbon solvents are generally more exothermic<sup>28</sup> for HBr(g) than for HCl(g); on this basis,  $\Delta H_{soln}[HI]$  in benzene is expected to be more exothermic than for HBr and probably of the order  $\Delta H_{soln}$  ca.  $-(25 \pm 5)$  kJ mol<sup>-1</sup>. With this estimate and the solution measurements  $\Delta H_{soln}(I_2/\text{benzene}) = (17.7 \pm 0.4)$  kJ mol<sup>-1</sup> and  $\Delta H_{soln}([Mn(CO)_5I]/\text{benzene}) = (26.7 \pm 0.5)$  kJ mol<sup>-1</sup>, in combination with  $\Delta H_{24} = -(123.7 \pm 5)$  kJ mol<sup>-1</sup>, we obtained  $\Delta H_{25} = -(107.7 \pm 8)$  kJ mol<sup>-1</sup> for the idealized reaction (25), leading to  $\Delta H_f^\circ([Mn(CO)_5H], l) = -(777.4$



$\pm 9.5)$  kJ mol<sup>-1</sup>. From vapor-pressure measurements over the temperature range 290–320 K,  $\Delta H_{vap}[Mn(CO)_5H] = (37.8 \pm 0.8)$  kJ mol<sup>-1</sup> is derived,<sup>7</sup> and with this  $\Delta H_f^\circ([Mn(CO)_5H], g) = -(740 \pm 10)$  kJ mol<sup>-1</sup>.

Measurements were also made of the enthalpy of reaction of  $[Mn(CO)_5H]$  with carbon tetrachloride according to eq 26, but these gave unconvincing results, as the re-



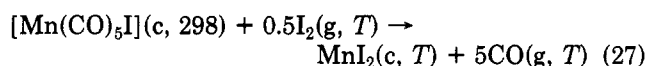
(28) Iogansen, A. V.; Kurkchi, G. A.; Levina, O. V. *Russ. J. Phys. Chem. (Engl. Transl.)* 1975, 49, 1396.

Table XVIII. Sublimation and Iodination of  $[\text{Mn}(\text{CO})_5\text{I}]$ 

A. Vacuum Sublimation			
T/K	$[\text{Mn}(\text{CO})_5\text{I}]$ / mg	$\Delta H_{\text{sub}}^T$ / $\text{kJ mol}^{-1}$	$\Delta H_{\text{sub}}^{298}$ / $\text{kJ mol}^{-1}$
378	5.937	91.4	76.7
377	8.830	93.0	78.1
B. Iodination			
T/K	$[\text{Mn}(\text{CO})_5\text{I}]$ / mg	$\Delta H_{27}^T$ / $\text{kJ mol}^{-1}$	$\Delta H_{27}^{298}$ / $\text{kJ mol}^{-1}$
474	5.779	113.7	77.4
475	5.779	119.6	83.1
476	6.521	115.6	78.9
476	5.984	114.0	77.3

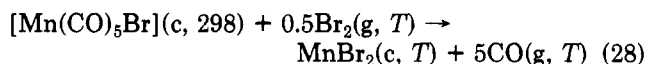
action was too slow to reach completion under the conditions used. In two of the experiments, it was possible reasonably to extrapolate the temperature-time curves to completion; these gave  $\Delta H_{26}^{298} \approx -(193 \pm 10) \text{ kJ mol}^{-1}$  which corresponds to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{H}], \text{l}) \approx -(788 \pm 17) \text{ kJ mol}^{-1}$ , overlapping the result from iodination, within the combined error limits of the measurements.

**9. Iodopentacarbonylmanganese,  $[\text{Mn}(\text{CO})_5\text{I}]$ .** The iodination of this complex was studied at 474–476 K, and the measured enthalpies of the reaction according to eq 27 are given in Table XVIII, together with measurements



of the sublimation enthalpy of  $[\text{Mn}(\text{CO})_5\text{I}]$  obtained by the vacuum sublimation microcalorimetric technique at 377–378 K. The mean value of  $\Delta H_{27}^{298} = (79.2 \pm 2.8) \text{ kJ mol}^{-1}$  corresponds to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{I}], \text{c}) = -(911.5 \pm 5) \text{ kJ mol}^{-1}$ . Taken with the mean value of  $\Delta H_{\text{sub}}^{298} = (77.4 \pm 1.4) \text{ kJ mol}^{-1}$  leads to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{I}], \text{g}) = -(834 \pm 5) \text{ kJ mol}^{-1}$ .

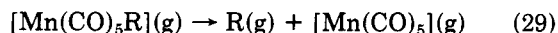
**10. Bromopentacarbonylmanganese,  $[\text{Mn}(\text{CO})_5\text{Br}]$ .** The bromination of this complex was studied at 374–376 K, and analyses confirmed that reaction was complete according to eq 28 even at these slightly elevated tem-



peratures. The measured enthalpies  $\Delta H_{28}^{298}$  are given in Table XIX, together with measurements of the sublimation enthalpy of  $[\text{Mn}(\text{CO})_5\text{Br}]$ , obtained by the vacuum sublimation microcalorimetric technique in the temperature range 365–375 K. The mean value of  $\Delta H_{28}^{298} = (9.9 \pm 1.8) \text{ kJ mol}^{-1}$  corresponds to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{Br}], \text{c}) = -(964 \pm 4) \text{ kJ mol}^{-1}$ . Taken with the mean value of  $\Delta H_{\text{sub}}^{298} = (88.0 \pm 2) \text{ kJ mol}^{-1}$ , this leads to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{Br}], \text{g}) = -(876 \pm 5) \text{ kJ mol}^{-1}$ .

### Discussion

The enthalpies of formation of various  $[\text{Mn}(\text{CO})_5\text{R}]$  complexes from the present study and earlier studies<sup>3</sup> are collected in Table XX. The final column of this table lists bond dissociation enthalpies  $D(\text{R}-\text{Mn}(\text{CO})_5)$  relating to the process at 298 K



and calculated from

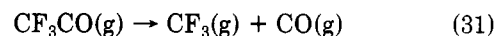
$$D(\text{R}-\text{Mn}(\text{CO})_5) = \Delta H_f^\circ(\text{R}, \text{g}) + \Delta H_f^\circ([\text{Mn}(\text{CO})_5], \text{g}) - \Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{R}], \text{g}) \quad (30)$$

Established values,  $\Delta H_f^\circ(\text{R}, \text{g})$  for the relevant atoms and radicals, are given as auxiliary data earlier. For the acetyl

Table XIX. Sublimation and Bromination of  $[\text{Mn}(\text{CO})_5\text{Br}]$ 

A. Vacuum Sublimation			
T/K	$[\text{Mn}(\text{CO})_5\text{Br}]$ / mg	$\Delta H_{\text{sub}}^T$ / $\text{kJ mol}^{-1}$	$\Delta H_{\text{sub}}^{298}$ / $\text{kJ mol}^{-1}$
365	2.105	98.5	86.1
365	2.180	101.5	89.1
375	2.170	103.2	88.9
B. Bromination			
T/K	$[\text{Mn}(\text{CO})_5\text{Br}]$ / mg	$\Delta H_{28}^T$ / $\text{kJ mol}^{-1}$	$\Delta H_{28}^{298}$ / $\text{kJ mol}^{-1}$
374	2.465	23.8	8.1
374	2.240	29.3	13.6
376	2.200	24.2	8.1

radical, the value of  $\Delta H_f^\circ(\text{CH}_3\text{CO}, \text{g}) = -(22.6 \pm 5) \text{ kJ mol}^{-1}$  is accepted, as recommended by Benson<sup>29</sup> and by Hole and Mulcahy.<sup>30</sup> For the benzoyl radical, a value of  $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{CO}, \text{g}) = (109.2 \pm 8) \text{ kJ mol}^{-1}$  has been reported,<sup>31</sup> which is also accepted here; a lower value, however, is indicated from thermal decomposition kinetic studies on benzoyl chloride.<sup>32</sup> There has been no direct determination of  $\Delta H_f^\circ(\text{CF}_3\text{CO}, \text{g})$ ; however, following an estimate by Walsh,<sup>33</sup> based on  $\Delta H^\circ$  for the process



of  $\Delta H_{31} = (37.7 \pm 12.5) \text{ kJ mol}^{-1}$ , gives  $\Delta H_f^\circ(\text{CF}_3\text{CO}, \text{g}) = -(616 \pm 12) \text{ kJ mol}^{-1}$ .

The value of  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5], \text{g})$  remains to be firmly established and is linked to the dissociation enthalpy of the Mn–Mn bond in  $[\text{Mn}_2(\text{CO})_{10}]$ . The structure of  $[\text{Mn}_2(\text{CO})_{10}]$  has recently been redetermined by two groups.<sup>34,35</sup> The metal–metal bond is longer (2.895 (1) Å at 74 K,<sup>34</sup> 2.904 (1) Å at 296 K<sup>35</sup>) than in manganese metal (average value 2.74 Å<sup>36</sup>). Formation of this long single bond has very little effect on the electron density of the  $[\text{Mn}(\text{CO})_5]$  fragments, and there is no evidence of significant charge density accumulation in the Mn–Mn bond, in agreement with detailed molecular orbital calculations.<sup>37</sup> The structure of the  $[\text{Mn}(\text{CO})_5]$  radical, observed following photodissociation of  $[\text{Mn}_2(\text{CO})_{10}]$  in a cold matrix, shows<sup>38</sup> that the  $\text{C}_{\text{ax}}\text{MnC}_{\text{eq}}$  angle ( $96 \pm 3^\circ$ ) is very little greater than the comparable angle ( $94 \pm 3^\circ$ ) in  $[\text{Mn}_2(\text{CO})_{10}]$ . Measurements of  $D(\text{Mn}-\text{Mn})$  in  $[\text{Mn}_2(\text{CO})_{10}]$  have ranged from<sup>39</sup> 79 to 154  $\text{kJ mol}^{-1}$ .<sup>40</sup> A value of 104  $\text{kJ mol}^{-1}$  is calculated<sup>41</sup> for the dissociation enthalpy at the mean temperature (530 K) of measurements of the equilibrium constant for the gas-phase dissociation  $[\text{Mn}_2(\text{CO})_{10}] \rightleftharpoons 2[\text{Mn}(\text{CO})_5]$  over a substantial temperature range (483–573

(29) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(30) Hole, K. J.; Mulcahy, M. F. R. *J. Phys. Chem.* **1969**, *73*, 177.

(31) Solly, R. K.; Benson, S. W. *J. Am. Chem. Soc.* **1971**, *93*, 1592.

(32) Pritchard, H. O.; Moselhy, G. M. *J. Chem. Thermodyn.* **1975**, *7*, 977.

(33) Walsh, R. University of Reading, Personal communication, 1982.

(34) Martin, M.; Rees, B.; Mitschler, A. *Acta Crystallogr., Sect. B* **1982**, *B38*, 6.

(35) Churchill, M. R.; Amoh, K. N.; Wasserman, H. *J. Inorg. Chem.* **1981**, *20*, 1609.

(36) Oberteufer, J. A.; Ibers, J. A. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1499.

(37) Heijser, W.; Baerends, E. J.; Ros, P. *Symp. Faraday Soc.* **1981**, *14*, 211.

(38) Church, S. P.; Poliakov, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7515.

(39) Bidinosti, D. R.; McIntyre, N. S. *Chem. Commun.* **1966**, 555.

(40) Hopgood, D.; Poë, A. J. *Chem. Commun.* **1966**, 831.

(41) Bidinosti, D. R.; McIntyre, N. S. *Can. J. Chem.* **1970**, *48*, 593.

Table XX. Enthalpies of Formation  $\Delta H_f^\circ$  ( $[Mn(CO)_5R]$ ) and Bond Dissociation Enthalpy Contributions  $D([R-Mn(CO)_5])$ 

complex	$\Delta H_f^\circ$ (c)/kJ mol <sup>-1</sup>	$\Delta H_f^\circ$ (g)/kJ mol <sup>-1</sup>	$D([R-Mn(CO)_5])^a$ /kJ mol <sup>-1</sup>
$[Mn(CO)_5CF_3]$	-(1464 ± 4)	-(1386 ± 4)	(172 ± 7)
$[Mn(CO)_5C_6H_5]$	-(675 ± 5)	-(590 ± 7)	(170 ± 11)
$[Mn(CO)_5CH_2C_6H_5]$	-(726 ± 8)	-(642 ± 8)	(87 ± 12)
$[Mn(CO)_5CH_3]$	-(813 ± 4)	-(753 ± 4)	(153 ± 5)
$[Mn(CO)_5COCH_3]$	-(977 ± 7)	-(897 ± 10)	(129 ± 12)
$[Mn(CO)_5COC_6H_5]$	-(847 ± 4)	-(724 ± 5)	(89 ± 10)
$[Mn(CO)_5COCF_3]$	-(1586 ± 3)	-(1508 ± 6)	(147 ± 11)
$[Mn(CO)_5H]$	-(778 ± 10)(e)	-(740 ± 10)	(213 ± 10)
$[Mn(CO)_5I]$	-(911 ± 5)	-(834 ± 5)	(195 ± 6)
$[Mn(CO)_5Br]$	-(964 ± 4)	-(876 ± 5)	(242 ± 6)
$[Mn(CO)_5Cl]$	-(1009 ± 8)	-(918 ± 10)	(294 ± 10)
$[Mn_2(CO)_{10}]$	-(1677 ± 4)	-(1585 ± 5)	94

<sup>a</sup> Relative to  $D([(CO)_5Mn-Mn(CO)_5]) = 94$  kJ mol<sup>-1</sup>.

K), which agrees with an independent mass spectrometric study.<sup>42</sup> It is argued<sup>43</sup> that the low values of  $D(Mn-Mn)$  are unacceptable because they imply a "totally unreasonable" low value of the entropy of activation for the homolytic fission process. We have redetermined the He I photoelectron spectrum of  $[Mn_2(CO)_{10}]$  with significantly improved resolution and find  $IP(adiabatic) = (7.69 \pm 0.01)$  eV and  $IP(vertical) = (8.02 \pm 0.01)$  eV, in good agreement with the values  $[(7.7 \pm 0.1), (8.01 \pm 0.05)$  eV] derived from a spectrum published<sup>44</sup> earlier. These are significantly lower than the values  $[(8.44 \pm 0.03),^{39} 8.32^{42}$  eV] obtained from mass spectrometry by using the extrapolated voltage difference method. This suggests that  $AP([Mn(CO)_5]^+)$ , measured as 9.26<sup>39</sup> and 9.40 eV<sup>42</sup> by the same method, should also be reduced. On the other hand, the kinetically determined<sup>40</sup> value of  $D(Mn-Mn) = 154$  kJ mol<sup>-1</sup> requires that  $AP([Mn(CO)_5]^+)$  should be ca. 9.6 eV, which we regard as less likely. We are unable to reconcile these contradictions, so that in evaluating our results we have chosen a value of  $D(Mn-Mn) = 94$  kJ mol<sup>-1</sup> at 298 K in line with the results of mass spectrometry. Taking  $\Delta H_{sub}([Mn_2(CO)_{10}]) = (92.3 \pm 2.1)$  kJ mol<sup>-1</sup>, the choice corresponds to  $\Delta H_f^\circ([Mn(CO)_5], g) = -(745.5 \pm 2.5)$  kJ mol<sup>-1</sup>. The values of  $D(R-Mn(CO)_5)$  given in Table XX will require upward adjustment if  $D(Mn-Mn)$  should be closer to the kinetically determined value.

The values of  $D(R-Mn(CO)_5)$  decrease in passing along the series  $CF_3 \approx C_6H_5 > CH_3 > CH_2C_6H_5$  and follow the trend in the hydrocarbons  $RH$ , where  $D(R-H)$  falls substantially in passing from  $R = C_6H_5$  ( $(460 \pm 8)$  kJ mol<sup>-1</sup>) to  $R = CH_2C_6H_5$  ( $(360 \pm 4)$  kJ mol<sup>-1</sup>). The same trend is observed in  $D(R-CH_3)$ . However, whereas both  $D(R-H)$  and  $D(R-CH_3)$  are greater for  $R = C_6H_5$  than for  $R = CF_3$ , they are almost equal for  $R = Mn(CO)_5$ , which might be interpreted as a relative strengthening of the  $Mn-CF_3$  bond in  $[Mn(CO)_5CF_3]$ . A further indication of this is that the value of  $D([(CO)_5Mn-CF_3])$  exceeds  $D([(CO)_5Mn-CH_3])$  by more ( $19$  kJ mol<sup>-1</sup>) than the difference ( $6$  kJ mol<sup>-1</sup>) between  $D(H-CF_3)$  and  $D(H-CH_3)$ . This is consistent with many observations<sup>45</sup> that the replacement of H by F in  $\sigma$ -bonded transition-metal alkyls increases their thermal stability and decreases the metal-C(alkyl) bond length. Whereas  $D(X-COC_6H_5) \approx D(X-COCH_3)$  ( $X = H, CH_3$ ),  $D([(CO)_5Mn-COC_6H_5])$  is much less than  $D([(CO)_5Mn-COCH_3])$ , it would be interesting to know whether the  $Mn-C(sp^2)$  bond in the benzoyl complex is longer than that in the acetyl complex. The evidence available from the structures<sup>46</sup> of  $[Zr(\eta-$

$C_5H_5)_2(CH_3)(COCH_3)]$  ( $d(Zr-COMe) = 2.197$  (6) Å) and  $[Fe(\eta-C_5H_5)(CO)(PPh_3)(COC_6H_5)]$  ( $d(Fe-COPh) = 1.97$  Å) is ambiguous but does not appear to confirm this expectation. Recent studies of the oxidative addition of  $CH_3I$  and of  $CH_3COI$  to *trans*- $[IrCl(CO)(PMe_3)_2]$  by titration calorimetry suggest<sup>47</sup> that  $D(Ir-CH_3) \approx D(Ir-COCH_3)$ , a conclusion which does not agree with our own. A value of  $D(Ir-COCH_3) = (205 \pm 46)$  kJ mol<sup>-1</sup> has been obtained.<sup>48</sup>

The enthalpies of the carbonylation reaction (32) at 298 K can be derived from the values for  $\Delta H_f^\circ(c)$ . The values

$$[Mn(CO)_5R](c) + CO(g) \rightarrow [Mn(CO)_5COR](c) \quad (32)$$

of  $\Delta H_{32}$  change in the order  $R = C_6H_5$  ( $-(63 \pm 8)$  kJ mol<sup>-1</sup>)  $< R = CH_3$  ( $-(54 \pm 8)$  kJ mol<sup>-1</sup>)  $< R = CF_3$  ( $-(12 \pm 7)$  kJ mol<sup>-1</sup>). These reactions involve the loss of the translational contribution to the entropy of CO absorbed by reaction, and the overall entropy change for the process is probably not less than this ( $\Delta S_{trans} \approx 150$  JK<sup>-1</sup> mol<sup>-1</sup>). In this event, the Gibbs energy change  $\Delta G_{32}^\circ$  remains negative for  $R = C_6H_5$  and  $CH_3$  but is positive for  $R = CF_3$ . In practice,<sup>49</sup> the carbonylation of  $[Mn(CO)_5CH_3]$  is readily accomplished; in contrast,  $[Mn(CO)_5CF_3]$  resists direct carbonylation, even under high pressures of CO, and the decarbonylation of  $[(CO)_5Mn-COCF_3]$  is the preferred route to  $[(CO)_5MnCF_3]$ . Recent molecular orbital calculations have suggested<sup>50</sup> that the decrease in the rate of carbonylation of  $[Mn(CO)_5R]$  from  $R = CH_3$  to  $R = CF_3$  is not connected with a strengthening of the  $Mn-C(sp^3)$  bond but rather with a change in the charge distribution on the carbon atom which reduces the likelihood of nucleophilic attack.

The intervention of metal-formyl complexes as possible intermediates in metal-catalyzed reactions between CO and hydrogen to form hydrocarbons and oxohydrocarbons (the Fischer-Tropsch reaction) has received much study in the recent past.<sup>51</sup> These studies have proceeded from the premise that a possible initial step in the activation of CO is the insertion of CO into a M-H bond or, alternatively, a hydride migration from M-H onto a coordinated CO ligand<sup>52</sup> under the influence of added CO, in the manner of an alkyl migration process. When the known values (Table XX) of  $D([(CO)_5Mn-R])$  are included in a

(46) Facinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* 1976, 522. Semion, V. A.; Strutchkov, Y. T. *Zh. Strukt. Khim.* 1969, 10, 664.

(47) Yoneda, G.; Blake, D. M. *Inorg. Chem.* 1981, 20, 67.

(48) Yoneda, G.; Lin, S. M.; Wang, L. P.; Blake, D. M. *J. Am. Chem. Soc.* 1981, 103, 5768.

(49) Calderazzo, F. *Angew. Chem.* 1977, 89, 305.

(50) Saddeci, D.; Freund, H. J.; Hohlneicher, G. *J. Organomet. Chem.* 1980, 186, 63.

(51) Masters, C. *Adv. Organomet. Chem.* 1979, 17, 61. See also several articles in: *ACS Symp. Ser.* 1981, No. 152.

(52) Pearson, R. G.; Walker, H. W.; Mauermann, H.; Ford, P. C. *Inorg. Chem.* 1981, 20, 2741.

(42) Junk, G. A.; Svec, H. J. *J. Chem. Soc. A* 1970, 2102.

(43) Poř, A. *ACS Symp. Ser.* 1981, No. 155, 135.

(44) Higginson, B. R.; Lloyd, D. R.; Evans, S.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* 1975, 71, 1913.

(45) Bruce, M. I.; Wallis, R. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1981, 2205.

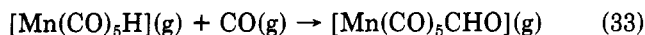


Table XXI. Bond Dissociation Enthalpy Contribution in the Ion  $D([\text{R-Mn}(\text{CO})_5]^+)$ 

complex	IP/kJ mol <sup>-1</sup>	$\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{R}]^+)/$ kJ mol <sup>-1</sup>	$D([\text{R-Mn}(\text{CO})_5]^+)/$ kJ mol <sup>-1</sup>	$\Delta D/\text{kJ mol}^{-1}$
$[\text{Mn}(\text{CO})_5\text{CF}_3]$	~855 <sup>a</sup>	~-531	~103	~69
$[\text{Mn}(\text{CO})_5\text{H}]$	(825 ± 8) <sup>b</sup>	(85 ± 13)	(173 ± 15)	(40 ± 18)
$[\text{Mn}(\text{CO})_5\text{Cl}]$	~811 <sup>c</sup>	~-107	~268	~26
$[\text{Mn}(\text{CO})_5\text{Br}]$	807 <sup>c</sup>	~-69	~221	~21
$[\text{Mn}(\text{CO})_5\text{CH}_3]$	(801 ± 8) <sup>b</sup>	(49 ± 9)	(137 ± 12)	(16 ± 13)
$[\text{Mn}(\text{CO})_5\text{I}]$	~780 <sup>a</sup>	~-54	~201	~-6
$[\text{Mn}_2(\text{CO})_{10}]$	(741 ± 1) <sup>d</sup>	-(837 ± 6)	135	-(38 ± 12)

<sup>a</sup> IP at peak maximum of first band in He I photoelectron spectrum<sup>44</sup> has been reduced by 30 kJ mol<sup>-1</sup> to correct to adiabatic IP. <sup>b</sup> Reference 56. <sup>c</sup> Unresolved first band in He I photoelectron spectrum<sup>44</sup> reduced by 45 kJ mol<sup>-1</sup> to allow for nonresolution and to correct to adiabatic IP. <sup>d</sup> This work.

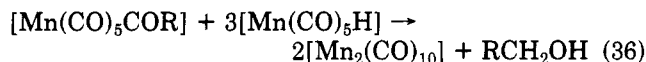
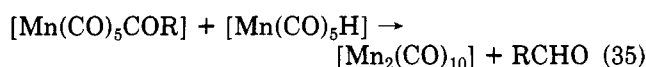
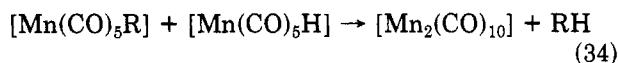
diagram representing the variation of  $D(\text{X-R})$  ( $\text{X} = \text{H}, \text{CH}_3$ ) with  $\Delta H_f^\circ(\text{R}, \text{g})$  ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5, \text{CHO},^{53} \text{COCH}_3, \text{COC}_6\text{H}_5$ ), an estimate of  $D([\text{Mn}(\text{CO})_5\text{Mn-CHO}])$  [ $\sim 115$  kJ mol<sup>-1</sup>] is obtained. Using this value, we estimate  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{CHO}, \text{g})] \approx -830$  kJ mol<sup>-1</sup> for the unknown formyl complex so that the enthalpy change for reaction 33 can be estimated,  $\Delta H_{33} \approx +20$  kJ mol<sup>-1</sup> which is made



yet less favorable when the entropy contribution of CO (45 kJ mol<sup>-1</sup> at 300 K) is included. This suggests that the production of a formyl intermediate in the Fischer-Tropsch reaction is unlikely to be significant. This constraint will be relaxed if the metal center is both coordinatively unsaturated and has good affinity for oxygen, thereby enabling the stabilization of the formyl ligand in the  $\eta^2$ -(C, O) form, as has been observed recently in the reaction of  $[\text{Th}(\eta\text{-C}_5\text{Me}_5)_2(\text{O}-t\text{-Bu})\text{H}]$  with CO in toluene solution.<sup>54</sup>

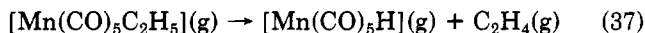
The values of  $D([\text{Mn}(\text{CO})_5\text{Mn-X}])$  for the monoatomic ligands  $\text{X} = \text{Cl}, \text{Br},$  and  $\text{I}$  parallel the related values of  $D(\text{X-CH}_3)$  and  $D(\text{X-H})$ , but  $D([\text{Mn}(\text{CO})_5\text{Mn-H}])$  is rather smaller than might have been predicted simply from this comparison.

The formation of C-H bonds as a result of binuclear reductive elimination reactions between  $[\text{Mn}(\text{CO})_4\text{L}(\text{CH}_2\text{C}_6\text{H}_4\text{-4-X})]$  and  $[\text{MnH}(\text{CO})_4\text{L}]$  has been described.<sup>55</sup> The enthalpy values in Table XX can be used to calculate values of the enthalpy change in reactions 34-36. In each

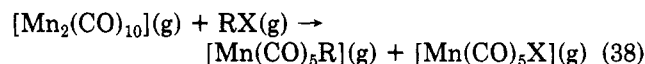


case the change is favorable to reaction; for example, in the case of  $\text{R} = \text{CH}_3$ ,  $\Delta H_{34} = -160$  kJ mol<sup>-1</sup>,  $\Delta H_{35} = -114$  kJ mol<sup>-1</sup>, and  $\Delta H_{36} = -288$  kJ mol<sup>-1</sup>, for gas-phase reactions.

Assuming that the enthalpy contribution of the Mn-C(sp<sup>3</sup>) bond in  $[\text{Mn}(\text{CO})_5\text{C}_2\text{H}_5]$  is the same (153 kJ mol<sup>-1</sup>) as in  $[\text{Mn}(\text{CO})_5\text{CH}_3]$ , we can estimate  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5\text{C}_2\text{H}_5, \text{g})] \approx -791$  kJ mol<sup>-1</sup>. With this value, the enthalpy change for the elimination reaction (37) is calculated,



culated,  $\Delta H_{37} \approx 103$  kJ mol<sup>-1</sup>.  $[\text{Mn}(\text{CO})_5\text{C}_2\text{H}_5]$  is stable with respect to thermal decomposition at room temperature<sup>27</sup> but decomposes above 330 K to give a variety of products including ethene. The enthalpy change in the formal oxidative addition reaction (38) is calculated to be



thermoneutral within the stated uncertainty limits, except for  $\text{CF}_3\text{I}$  ( $\Delta H_{38} = -45$  kJ mol<sup>-1</sup>) and  $\text{C}_6\text{H}_5\text{COBr}$  ( $\Delta H_{38} = +32$  kJ mol<sup>-1</sup>).

Values for the ionization potentials of  $[\text{Mn}(\text{CO})_5\text{R}]$  have been obtained from photoelectron spectra,<sup>44</sup> and some data are also available on the appearance potentials of  $[\text{Mn}(\text{CO})_5]^+$  from photoionization mass spectra,<sup>56</sup> which are (994 ± 10) kJ mol<sup>-1</sup> from  $[\text{Mn}(\text{CO})_5\text{H}]$  and (941 ± 5) kJ mol<sup>-1</sup> from  $[\text{Mn}(\text{CO})_5\text{CH}_3]$ . Coupled with the present  $\Delta H_f^\circ(\text{g})$  values, these lead to  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5]^+, \text{g}) = (36 \pm 14)$  kJ mol<sup>-1</sup> (from  $[\text{Mn}(\text{CO})_5\text{H}]$ ) and  $(42 \pm 7)$  kJ mol<sup>-1</sup> (from  $[\text{Mn}(\text{CO})_5\text{CH}_3]$ ). Choosing  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5]^+, \text{g}) \approx (40 \pm 8)$  kJ mol<sup>-1</sup>, the dissociation enthalpies  $D([\text{R-Mn}(\text{CO})_5]^+)$  in the molecular ions are as listed in Table XXI. The two values used in this paper  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5, \text{g})] = -(745.5 \pm 2.5)$  kJ mol<sup>-1</sup> and  $\Delta H_f^\circ([\text{Mn}(\text{CO})_5]^+, \text{g}) = (40 \pm 8)$  kJ mol<sup>-1</sup> require the adiabatic ionization potential of the free  $[\text{Mn}(\text{CO})_5]$  radical = (785.5 ± 9) kJ mol<sup>-1</sup>; this compares with a direct measurement by electron-impact mass spectrometry<sup>39</sup> of the vertical ionization potential, of (814 ± 10) kJ mol<sup>-1</sup>. The final column in Table XXI gives the difference  $\Delta D = D([\text{R-Mn}(\text{CO})_5]) - D([\text{R-Mn}(\text{CO})_5]^+)$  kJ mol<sup>-1</sup>; the values are generally positive and increase with the electron-acceptor character (electronegativity) of the group R. There is an apparent reversal of sign for  $\text{R} = \text{Mn}(\text{CO})_5$ , the calculated value in the ion of  $E([\text{Mn}(\text{CO})_5\text{Mn-Mn}(\text{CO})_5]^+)$  exceeding that in neutral  $[\text{Mn}_2(\text{CO})_{10}]$ . The value of  $\Delta D$  in this case is given directly by the difference  $\Delta D = \text{IP}([\text{Mn}_2(\text{CO})_{10}]) - \text{IP}([\text{Mn}(\text{CO})_5])$ , and an accurate measurement of the latter is required to establish the validity of the trend indicated in Table XXI.

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**Registry No.**  $[\text{Mn}_2(\text{CO})_{10}]$ , 10170-69-1;  $[\text{Mn}(\text{CO})_5\text{Br}]$ , 14516-54-2;  $[\text{Mn}(\text{CO})_5\text{I}]$ , 14879-42-6;  $[\text{Mn}(\text{CO})_5\text{H}]$ , 16972-33-1;  $[\text{Mn}(\text{CO})_5\text{CH}_3]$ , 13601-24-6;  $[\text{Mn}(\text{CO})_5\text{CF}_3]$ , 13601-14-4;  $[\text{Mn}(\text{CO})_5\text{C}_6\text{H}_5]$ , 13985-77-8;  $[\text{Mn}(\text{CO})_5\text{CH}_2\text{C}_6\text{H}_5]$ , 14049-86-6;  $[\text{Mn}(\text{CO})_5\text{COCH}_3]$ , 13963-91-2;  $[\text{Mn}(\text{CO})_5\text{COCF}_3]$ , 14099-62-8;  $[\text{Mn}(\text{CO})_5\text{COC}_6\text{H}_5]$ , 15612-92-7.

(53) Dyke, J. M.; Jonathan, N. B. H.; Morris, A.; Winter, M. J. *Mol. Phys.* **1980**, *39*, 629.

(54) Fagan, P. J.; Molloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959.

(55) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619.

(56) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 190.