$^1H$ NMR of **5g**: $\delta$ 1.1 (s), 9 H, *t*-Bu; 1.5 (d), 6 H, $-CH(CH_3)_2$; 2.3 (m) 1 H, $-CH(CH_3)_2$; 6.5 (m), 2 H, $F_2SiCH{=}$. $^{19}F\{^1H\}$ NMR of **5g**: 130.6 (t), $=C(t\text{-}Bu)SiF_2$; 141.65 ppm (t), $=C(i\text{-}Pr)SiF_2$. Mass spectrum of **5g**/**5h**: very similar to that of **5g**. $^{19}\{^1H\}$ NMR of **5h** (obtained by comparing spectra): 139.5 (t), $=C(i\text{-}Pr)SiF_2$; 126.1 ppm (t), $=CHSiF_2$.

**Acknowledgment.** We thank the Chinese National Science Council for financial support of this work. C.-h.L. thanks the Nuclear Energy Research Institute for a research fellowship.

**Registry No.** **1**, 36091-97-1; **2a**, 109034-53-9; **2b**, 109034-54-0; **2c**, 109034-56-2; **2d**, 109034-57-3; **3a**, 109064-32-6; **3b**, 109034-55-1; **4e**, 109034-58-4; **5e**, 55499-35-9; **5f**, 55499-34-8; **5g**, 109034-59-5; **5h**, 109034-60-8; **7a**, 109034-51-7; **7b**, 109034-52-8; $Fe(CO)_5$, 13463-40-6; $F_2\overline{Si(t\text{-}Bu)C{=}C(H)SiF_2Fe}(CO)_4$, 78514-11-1; $Fe_3(CO)_{12}$, 17685-52-8; $F_2\overline{Si(t\text{-}Bu)C{=}C(H)SiF_2Mo}(CO)_5$, 75311-40-9; $Mo(CO)_6$, 13939-06-5; $t\text{-}BuC{\equiv}CH$, 917-92-0; 1,3-butadiene, 106-99-0; 2,3-dimethyl-1,3-butadiene, 513-81-5; isoprene, 78-79-5.

---

# Formation of Metal–Metal Bonds by Ion-Pair Annihilation. Dimanganese Carbonyls from Manganate(–I) Anions and Manganese(I) Cations

K. Y. Lee, D. J. Kuchynka, and J. K. Kochi*

*Department of Chemistry, University of Houston, University Park, Houston, Texas 77004*

*Received February 17, 1987*

The coupling of the anionic $Mn(CO)_5^-$ and the cationic $Mn(CO)_6^+$ occurs upon mixing to afford the dimeric $Mn_2(CO)_{10}$ in essentially quantitative yields. Dimanganese decacarbonyl is formed with equal facility from the coupling of $Mn(CO)_5^-$ with $Mn(CO)_5(py)^+$ and $Mn(CO)_5(NCMe)^+$. By way of contrast, the annihilation of $Mn(CO)_4PPh_3^-$ with $Mn(CO)_6^+$ yields a pair of homo dimers $Mn_2(CO)_{10}$ and $Mn_2(CO)_8(PPh_3)_2$ together with the cross dimer $Mn_2(CO)_9PPh_3$. Extensive scrambling of the carbonylmanganese moieties also obtains with $Mn(CO)_4P(OPh)_3^-$ and $Mn(CO)_5PPh_3^+$, as indicated by the production of $Mn_2(CO)_8[P(OPh)_3]_2$, $Mn_2(CO)_8[P(OPh)_3](PPh_3)$, and $Mn_2(CO)_8(PPh_3)_2$ in more or less statistical amounts. These diverse Mn–Mn couplings can be accounted for by a generalized formulation (Scheme VI), in which the carbonylmanganese anions $Mn(CO)_4P^-$ and the cations $Mn(CO)_5L^+$ undergo an initial electron transfer to produce $Mn(CO)_4P^\bullet$ and $Mn(CO)_5L^\bullet$, respectively. The behaviors of these 17- and 19-electron radicals coincide with those independently generated in a previous study of the anodic oxidation of $Mn(CO)_4P^-$ and the cathodic reduction of $Mn(CO)_5L^+$, respectively. The facile associative ligand substitution of 17-electron carbonylmanganese radicals by added phosphines provides compelling evidence for the interception of $Mn(CO)_4P^\bullet$ and its interconversion with 19-electron species in the course of ion-pair annihilation. The reactivity trend for the various ion pairs qualitatively parallels the driving force for electron transfer based on the oxidation and reduction potentials of $Mn(CO)_4P^-$ and $Mn(CO)_5L^+$, respectively, in accord with the radical-pair mechanism in Scheme VI.

## Introduction

A wide variety of organometallic dimers are now known.[1,2] The formation of the metal–metal bonds in dimeric metal carbonyls commonly derives from various reductive procedures including the use of carbon monoxide, metals, alkylmetals, etc. as reagents.[3] The oxidation of carbonylmetalate anions is also known to lead to carbonylmetal dimers.[4] Heterobimetallic carbonyls result from the interaction of carbonylmetalates with different types of metal halides and homo dimers.[5,6] The latter can be generally classified as nucleophilic substitution processes, although mechanistic studies of such metal–metal bond formations are generally lacking.

The heterolytic coupling of carbonylmetal cations and anions is indicated in an earlier report of the treatment of tetracarbonylcobaltate(–I) with hexacarbonylrhenium(I) to afford the mixed carbonyl,[7,8] i.e., eq 1. Similarly the

$$Co(CO)_4^- + Re(CO)_6^+ \rightarrow ReCo(CO)_9 + CO \qquad (1)$$

---

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley CA, 1980. (c) Lukehart, C. M. *Fundametal Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985.

(2) Compare also: (a) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155. (b) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207.

(3) (a) Podall, H. E.; Dunn, J. H.; Shapiro, H. *J. Am. Chem. Soc.* **1960**, *82*, 1325. (b) Hieber, W.; Fuchs, H. *Z. Anorg. Allg. Chem.* **1941**, *248*, 256. (c) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133. (d) Hieber, W.; Schulten, H.; Marin, R. *Z. Anorg. Allg. Chem.* **1939**, *240*, 261. (e) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211. (f) Ungurenasu, C.; Palie, M. *J. Chem. Soc., Chem. Commun.* **1975**, 388.

(4) (a) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 193. (b) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239. (c) Armstead, J. A.; Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1982**, *236*, 213. (d) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117.

(5) (a) Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5129. (b) Pandey, V. N. *Inorg. Chim. Acta* **1977**, *23*, L26. (c) Fontana, S.; Orama, O.; Fischer, E. O.; Schubert, U.; Kreissl, F. R. *J. Organomet. Chem.* **1978**, *149*, C57. (d) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 113. (e) Roberts, D. A.; Mercer, W. C.; Zahurak, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 910. (f) Bennett, M. A.; Patmore, D. J. *Inorg. Chem.* **1971**, *10*, 2387. (g) Anders, U.; Graham, W. A. G. *J. Am. Chem. Soc.* **1967**, *89*, 539. (h) Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1818. (i) Fischer, E. O.; Lindner, T. L.; Kreissl, F. R.; Braunstein, P. *Chem. Ber.* **1977**, *110*, 3139. (j) Michels, G. D.; Svec, H. J. *Inorg. Chem.* **1981**, *20*, 3445. (k) Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Chem. Commun.* **1982**, 1001. (l) Compare also: Hriljac, J. A.; Swepston, P. N.; Shriver, D. *Organometallics* **1985**, *4*, 158.

(6) (a) Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5124. (b) See also: Morse, D. L.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *125*, 71.

0276-7333/87/2306-1886$01.50/0

**Table I. Products and Stoichiometry from the Coupling of $Mn(CO)_5^-$ and $Mn(CO)_5L^+$ [a]**

| | $Mn(CO)_5L^+$ L (mmol) | $Mn_2(CO)_{10}$, mmol (%) | $Mn_2(CO)_9L$, mmol (%) | $Mn_2(CO)_8L_2$, mmol (%) | $HMn(CO)_4L$, mmol (%) | time,[b] min | material balance |
|---|---|---|---|---|---|---|---|
| I | CO (0.05) | 0.040 (80) | | ... | ... | <5 | 80 |
| IIa | $CH_3CN$ (0.05) | 0.044 (88) | | ... | ... | <5 | 88 |
| IIb | py (0.05) | 0.042 (84) | | ... | ... | <5 | 84 |
| IIIa | $PPh_3$ (0.05) | 0.033 (66) | | 0.007 (14) | 0.008 (8) | <5 | 88 |
| IIIb | $P(p\text{-tol})_3$ (0.05) | 0.028 (56) | | 0.007 (14) | 0.015 (15) | <5 | 85 |
| IIIc | $PPh_2Et$ (0.05) | 0.023 (46) | tr | 0.006 (16) | 0.018 (18) | 30 | 76 |
| IIId | $PPhEt_2$ (0.05) | 0.019 (38) | tr | 0.006 (12) | 0.022 (22) | 200 | 72 |
| IIIe | $PEt_3$ (0.05) | 0.014 (28) | *c* (10) | 0.006 (12) | 0.017 (17) | 300 | 67 |
| IIIf | $PPh_2Me$ (0.05) | 0.018 (36) | tr | 0.004 (8) | 0.017 (17) | 5 | 61 |
| IIIg | $PPhMe_2$ (0.05) | 0.020 (40) | *c* (5) | 0.010 (20) | 0.016 (16) | 200 | 81 |

[a] In 10 mL of THF with $5 \times 10^{-3}$ M $NaMn(CO)_5$ and $5 \times 10^{-3}$ M $Mn(CO)_5L^+PF_6^-$ (or $BF_4^-$) at 22 °C. [b] Approximate time required for complete disappearance of ions. [c] Estimated, based on severe overlap of CO bands. tr = trace (<1%).

treatment of $Co(CO)_4^-$ with the phenanthroline-substituted tetracarbonylmanganese(I) cation leads to the substituted heterobimetallic carbonyl,[9] viz., eq 2. It is noteworthy that

$$Co(CO)_4^- + (\eta^2\text{-phen})Mn(CO)_4^+ \rightarrow (\eta^2\text{-phen})MnCo(CO)_7 + CO \quad (2)$$

coupling of metal centers in eq 2 is equivalent to the microscopic reverse of the well-known base-induced disproportionation of metal carbonyls,[10] e.g., eq 3, where B = phosphorus-, nitrogen-, and oxygen-centered bases.[11]

$$Co_2(CO)_8 + 2B \rightarrow [Co(CO)_4^-][Co(CO)_3B_2^+] + CO \quad (3)$$

In the course of our recent electrochemical redox studies of metal carbonyls,[12] we observed the highly selective coupling of the carbonylmanganese anion and cation, i.e., eq 4. Furthermore in the reduction of substituted-carbonylmanganese cations, cyclic voltammetry established

$$Mn(CO)_5^- + Mn(CO)_6^+ \rightarrow Mn_2(CO)_{10} + CO \quad (4)$$

that the anion $Mn(CO)_5^-$ formed at the cathode in the presence of the cationic precursor $Mn(CO)_5L^+$ afforded both $Mn_2(CO)_{10}$ and $Mn_2(CO)_8L_2$—the relative amounts of each varying considerably with the nature of L = MeCN, pyridine, phosphine, etc. The unusual selectivities prompted us to examine the coupling processes in detail, especially with regard to the products and stoichiometry. We focus in this study on the formation of manganese–manganese bonds from various substituted-carbonylmanganese cations and anions, i.e., eq 5, with an emphasis placed on phosphorus and nitrogen ligands.

$$Mn(CO)_5L^+ + Mn(CO)_4P^- \rightarrow Mn_2(CO)_8(L)(P) + CO \quad (5)$$

## Results

**Synthesis of Carbonylmanganese Cations and Anions.** For purposes of our study, we arbitrarily classified the carbonylmanganese cations $(OC)_5MnL^+$ in eq 5 into three groups: I, L = CO; II, L = the nitrogen-centered ligands acetonitrile and pyridine; III, L = phosphorus(III) ligand consisting of a series of aryl- and alkylphosphines with different base strengths[13] and steric properties (cone angles).[14] Each of the carbonylmanganese cations was prepared as a pure crystalline ($BF_4^-$ or $PF_6^-$) salt that was readily characterized by its distinctive carbonyl stretching bands ($\nu_{CO}$) in the IR spectrum. Thus the parent hexacarbonylmanganese(I) cation I was obtained as colorless crystals ($\nu_{CO}$ = 2097 cm$^{-1}$) from $Na^+Mn(CO)_5^-$ and ethyl chloroformate followed by cleavage with boron trifluoride.[15] The acetonitrile derivative $(MeCN)Mn(CO)_5^+$ (IIa) was obtained as colorless crystals ($\nu_{CO}$ = 2163, 2075, 2051 cm$^{-1}$) from the oxidative cleavage of $Mn_2(CO)_{10}$ with nitrosonium hexafluorophosphate in acetonitrile.[16] It was converted to the yellow pyridine analogue IIb ($\nu_{CO}$ = 2155, 2066, 2043 cm$^{-1}$) by treatment with 4 equiv of pyridine in refluxing chloroform for 15 h. The series of phosphine derivatives IIIa–g ($\nu_{CO} \simeq$ 2140, 2090, 2050 cm$^{-1}$) were prepared also from IIa by a slow ligand substitution with 1.0–1.3 equiv of the appropriate phosphine in acetone.[12,16,17]

Three different types of carbonylmanganate(−I) anions were used to treat each of the carbonylmanganese(I) cations. The parent carbonylmanganate $Mn(CO)_5^-$ (A, $\nu_{CO}$ = 1998, 1864 cm$^{-1}$) was prepared as the crystalline sodium salt by reductive cleavage of $Mn_2(CO)_{10}$ with sodioamalgam.[18] Likewise, the triphenyl phosphite derivative $Mn(CO)_4[P(OPh)_3]^-$ (B, $\nu_{CO}$ = 1964, 1850 cm$^{-1}$) and the triphenylphosphine analogue $Mn(CO)_4PPh_3^-$ (C, $\nu_{CO}$ = 1945, 1827 cm$^{-1}$) were prepared with the same reductive procedure from $Mn_2(CO)_8[P(OPh)_3]_2$ and $Mn_2(CO)_8(PPh_3)_2$,[19] respectively, as described in the Experimental Section.

**Coupling of Anionic Carbonylmanganates(−I) and Carbonylmanganese(I) Cations.** The composition of the reaction mixture derived from the ion-pair interaction of $Mn(CO)_5L^+$ and $Mn(CO)_4P^-$ in eq 5 differed according to the nature of the ligands L and P. In order to facilitate

---

(7) Kruck, T.; Hofler, M. *Angew. Chem., Int. Eng. Ed.* **1964**, *3*, 701.

(8) See also (a) Joshi, K. K.; Pauson, P. L. *Z. Naturforsch, B: Anorg. Chem. Org. Chem., Biochem., Biophys., Biol.* **1962**, *17B*, 565. (b) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Kolomnokov, I. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 194. (c) Szabo, P.; Fekete L.; Bor, G.; Nagy-Magos, Z.; Marko, L. *J. Organomet. Chem.* **1968**, *12*, 245.

(9) Kruck, T.; Hofler, M. *Chem. Ber.* **1964**, *97*, 2289.

(10) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217.

(11) (a) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q.; Pitts, R. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1189. (b) Hieber, W.; Schropp, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1960**, *15*, 271. (c) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528. (d) Hudson, A.; Lappert, M. F.; Nicholson, B. K. *J. Organomet. Chem.* **1975**, *92*, C11. (e) Hudson, A.; Lappert, M. F.; Macquitty, J. J.; Nicholson, B. K.; Zainal, H.; Luckhurst, G. R.; Zannoni, C.; Bratt, S. W.; Symons, M. C. R. *J. Organomet. Chem.* **1976**, *110*, C5. (f) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032. (g) Stiegman, A. E.; Goldman, A. S.; Philbin, C. E. Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 2976.

(12) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087.

(13) (a) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. (b) Henderson, W. A., Jr.; Streuli, W. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791. (c) See also: Zizelman, P. M.; Amatore, C. Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771.

(14) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(15) Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.

(16) Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* 1975, *14*, 1579.

(17) Reimann, R. H.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1976**, 2109.

(18) Wrighton, M. S.; Faltynek, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 2701.

(19) Osborne, A. G.; Stiddard, M. H. B. *J. Chem. Soc.* **1964**, 634.

**Table II. Products and Stoichiometry for the Coupling of $Mn(CO)_4[P(OPh)_3]^-$ and $Mn(CO)_5L^+$ [a]**

| $Mn(CO)_5L^+$ L (mmol) | $Mn_2(CO)_{10}$, mmol (%) | $Mn_2(CO)_8P_2$,[b] mmol (%) | $Mn_2(CO)_8PL$, mmol (%) | material balance |
|---|---|---|---|---|
| CO (0.05) | 0.020 (40) | 0.014 (28) | ... | 68[c] |
| py (0.05) | 0.020 (40) | 0.013 (26) | ... | 88[d] |
| $CH_3CN$ (0.05) | 0.010 (20) | 0.008 (16) | ... | 82[e] |
| $PPh_3$ (0.05) | 0.011 (22)[f] | 0.010 (20) | 0.012 (24) | 66[c] |
| $P(p\text{-tol})_3$ (0.05) | 0.021 (42)[f] | 0.012 (24) | 0.016 (32) | 98[c,g] |
| $PPh_2Et$ (0.05) | 0.022 (44)[f] | 0.010 (20) | 0.012 (24) | 88[c] |
| $PPhEt_2$ (0.05) | 0.010 (20)[f] | 0.006 (12) | 0.019 (38) | 70[c,g] |
| $PEt_3$ (0.05) | 0.018 (36)[f] | 0.009 (18) | 0.015 (30) | 84[c,g] |
| $PPh_2Me$ (0.05) | 0.017 (34)[f] | 0.009 (18) | 0.016 (32) | 84[c,g] |
| $PPhMe_2$ (0.05) | 0.022 (44)[f] | 0.008 (16) | 0.017 (34) | 94[c,g] |

[a] In 10 mL of THF with $5 \times 10^{-3}$ M $NaMn(CO)_4[P(OPh)_3]$ and $5 \times 10^{-3}$ M $Mn(CO)_5L^+PF_6^-$ (or $BF_4^-$) at 22 °C. All reactions complete <5 min. [b] $P = P(OPh)_3$. [c] $HMn(CO)_4P(OPh)_3$ detected, but not quantified. [d] Includes ~20% $Mn_2(CO)_9P$. [e] Includes ~40% $Mn_2(CO)_9P$. [f] $Mn_2(CO)_8L_2$. [g] $HMn(CO)_4L$ not quantified.

the descriptions of the product mixtures, the interactions of the carbonylmanganates A–C with each of the cations will be described separately.

**A. Pentacarbonylmanganate(−I)** and hexacarbonylmanganese(I) reacted upon mixing (<5 min) in tetrahydrofuran solutions and afforded dimanganese decacarbonyl as the sole carbonyl product. Essentially the same results were obtained in THF solution with the acetonitrile and pyridine derivatives IIa and IIb, respectively, as shown in Table I, i.e., eq 6, where L = CO, MeCN,

$$Mn(CO)_5^- + Mn(CO)_5L^+ \rightarrow Mn_2(CO)_{10} + L \quad (6)$$

and pyridine. When pentacarbonylmanganate(−I) was treated with the triarylphosphine-substituted cations IIIa and IIIb, high yields of $Mn_2(CO)_{10}$ were formed together with minor amounts of the bis-substituted dimer $Mn_2(CO)_8L_2$[19] and the substituted hydride $HMn(CO)_4L$,[20] i.e., eq 7, where L = phosphines and the numbers in parentheses

$$Mn(CO)_5^- + Mn(CO)_5L^+ \rightarrow \underset{(60\%)}{Mn_2(CO)} + \underset{(14\%)}{Mn_2(CO)_8L} + \underset{(10\%)}{HMn(CO)_4L} \quad (7)$$

indicate averaged yields. This somewhat complex product mixture was readily analyzed by quantitative IR spectroscopy (± 15%) using calibration curves constructed from the characteristic $\nu_{CO}$ stretching bands of the authentic components. The analysis was confirmed by chromatographic separation of the components (see Experimental Section). On this basis, the overall material balance in excess of 80% was considered to represent quantitative conversions of the carbonylmanganese anion and the various cations. No other carbonyl-containing manganese product could be discerned from the IR spectra of the products by spectral subtraction of the components listed in Table I. Treatment of pentacarbonylmanganate with the alkyl- and aralkylphosphines derivatives IIIa–g also afforded variable amounts of $Mn_2(CO)_{10}$ and the analogous carbonylmanganese products $Mn_2(CO)_8L_2$ and $HMn(CO)_4L$. In addition, small but distinctive amounts of the monosubstituted dimanganese carbonyl $Mn_2(CO)_9L$ were detected. Furthermore, the coupling processes of $Mn(CO)_5^-$ with IIIa–g often proceeded at significantly attenuated rates, as qualitatively indicated by the reaction times listed in column 6, Table I. The material balance in Table I indicates that all of the phosphine (L) included in $Mn(CO)_5L^+$ was not retained in the carbonylmanganese products. The examination of the $^{31}P$ NMR spectrum of the reaction mixture indicated that the deficit was present as free phosphine.

**B. Tetracarbonyl(triphenyl phosphite)manganate(−I)** and the cationic hexacarbonylmanganese(I) rapidly yielded two manganese dimers $Mn_2(CO)_{10}$ and $Mn_2(CO)_8[P(OPh)_3]_2$ in a roughly 4:3 ratio, i.e., eq 8, where

$$Mn(CO)_4P^- + Mn(CO)_6^+ \rightarrow [\underset{(40\%)}{Mn_2(CO)_{10}} + \underset{(30\%)}{Mn_2(CO)_8P_2}] + CO \quad (8)$$

$P = P(OPh)_3$ in Table II. When the acetonitrile and pyridine-substituted cations IIa and IIb were employed, the same pair of dimanganese carbonyls was obtained upon mixing, together with significant amounts of the monosubstituted analogue, i.e., eq 9, where $P = P(OPh)_3$ and

$$Mn(CO)_4P^- + Mn(CO)_5L^+ \rightarrow [\underset{(30\%)}{Mn_2(CO)_{10}} + \underset{(30\%)}{Mn_2(CO)_9P} + \underset{(20\%)}{Mn_2(CO)_8P_2}] + L \quad (9)$$

L = MeCN and py. The absence of any other carbonyl-containing product in the reaction mixture indicated that the nitrogen ligands (MeCN and py) were rapidly replaced, as given by the approximate stoichiometry presented in eq 9. In marked contrast, the reaction of the phosphine-substituted cations IIIa–g with the carbonylmanganate B afforded no $Mn_2(CO)_{10}$ or $Mn_2(CO)_9P$—the most important products being the other dimanganese carbonyls, i.e., eq 10. In addition, minor amounts of the manganese

$$Mn(CO)_4P^- + Mn(CO)_5L^+ \rightarrow \underset{(20\%)}{Mn_2(CO)_8P_2} + \underset{(30\%)}{Mn(CO)_8L_2} + \underset{(20\%)}{Mn_2(CO)_8(L)(P)} \quad (10)$$

hydrides $HMn(CO)_4L$ and $HMn(CO)_4P$ were observed (see Table II). With $Mn(CO)_5PEt_3^+$ and $Mn(CO)_5PEt_2Ph^+$, the IR spectrum of the solution taken immediately (~5 min) after mixing with $Mn(CO)_4P(OPh)_3^-$ showed the presence (~20%) of the reactant ion pair, the complete disappearance of which required approximately an hour.

**C. Tetracarbonyl(triphenylphosphine)manganate(−I)** reacted upon mixing with hexacarbonylmanganese(I) and its acetonitrile and pyridine derivatives IIa and IIb to produce three dimanganese carbonyls, i.e., eq 11, where $P = PPh_3$ and L = CO, MeCN, and py. The

$$Mn(CO)_4P^- + Mn(CO)_5L^+ \rightarrow [\underset{(30\%)}{Mn_2(CO)_{10}} + \underset{(20\%)}{Mn_2(CO)_9P} + \underset{(40\%)}{Mn_2(CO)_8P_2}] + L \quad (11)$$

complete replacement of acetonitrile and pyridine in IIa and IIb, respectively, according to eq 11 was supported by the singular absence of other carbonyl-containing products (see Table III). However with the phosphine-substituted cations IIIa–g, the ligand L was completely retained to afford a mixture of the homo- and cross-coupled dimers, similar to that described in eq 10, where $P = PPh_3$ and L = triaryl- and aralkylphosphines. Of the phosphine-sub-

---

(20) (a) Gladysz, J. A.; Tam, W.; Williams, G. M.; Johnson, D. L.; Parker, D. W. *Inorg. Chem.* **1979**, *18*, 1163. (b) Atwood, J. D.; Ruszczyk, R. J.; Huang, B.-L. *J. Organomet. Chem.* **1986**, *299*, 205.

**Table III. Products and Stoichiometry for the Coupling of $Mn(CO)_4PPh_3^-$ and $Mn(CO)_5L^+$**[a]

| $Mn(CO)_5L^+$ L (mmol) | $Mn_2(CO)_{10}$, mmol (%) | $Mn_2(CO)_9P$,[b] mmol (%) | $Mn_2(CO)_8PL$,[b] mmol (%) | $Mn_2(CO)_8P_2$,[b] mmol (%) | material balance |
|---|---|---|---|---|---|
| CO (0.05) | 0.016 (32) | 0.010 (20) | ... | 0.015 (30) | 82[d] |
| $CH_3CN$ (0.05) | 0.011 (22) | 0.009 (18) | ... | 0.026 (52) | 92[d] |
| py (0.05) | 0.014 (28) | 0.007 (14) | ... | 0.029 (58) | 100[d] |
| py[e] (0.05) | 0.014 (28) | 0.006 (12) | ... | 0.027 (54) | 94[d] |
| $PPh_3$ (0.05) | ... | ... | 0.039 (78) | ... | 78[d] |
| $PPh_3$[f] (0.05) | ... | ... | 0.043 (86) | ... | 86[d] |
| $PPh_2Et$[g] (0.10) | ... | 0.018[k] (18) | 0.046 (46) | 0.026 (26) | 90[h] |
| $PPhEt_2$[g] (0.10) | ... | 0.019[k] (19) | 0.028 (28) | 0.034 (34) | 81[h,m] |
| $PEt_3$[g] (0.10) | ... | 0.005[k] (5) | 0.012 (12) | 0.008 (8) | 63[j] |
| $PPh_2Me$[g] (0.10) | ... | 0.033[k] (33) | 0.035 (35) | 0.016 (16) | 84[h] |
| $PPhMe_2$[g] (0.10) | ... | 0.022[k] (22) | 0.046 (46) | 0.019 (19) | 87[h,m] |

[a] In 10 mL of THF with $5 \times 10^{-3}$ M $NaMn(CO)_4PPh_3$ and $5 \times 10^{-3}$ M $Mn(CO)_5L^+PF_6^-$ (or $BF_4^-$) at 22 °C unless indicated otherwise. All reactions complete within 5 min unless indicated otherwise. [b] P = $PPh_3$. [c] Isolated yield, unless indicated otherwise. [d] By IR analysis. [e] Carried out in the dark. [f] Contains 0.3 M TBAP. [g] Contains $1 \times 10^{-2}$ M $NaMn(CO)_4PPh_3$ and $1 \times 10^{-2}$ M $Mn(CO)_5L^+PF_6^-$. [h] Contains $HMn(CO)_4L$ and $HMn(CO)_4P$, not quantified. [j] Contains 26% $HMn(CO)_4P$ and 12% $HMn(CO)_4L$. [k] $Mn_2(CO)_8L_2$. [m] After ~60 min.

**Table IV. Effect of Added Phosphine on Ion Pair Annhilation**[a]

| added $PPh_3$, mmol | $Mn_2(CO)_{10}$, mmol (%) | $Mn_2(CO)_9P$, mmol (%) | $Mn_2(CO)_8P_2$, mmol (%) | $HMn(CO)_4P$, mmol (%) | material balance |
|---|---|---|---|---|---|
| 0[b] | 0.044 (88) | ... | ... | ... | 88 |
| 0.1[b] | 0.035 (70) | ... | 0.004 (8) | 0.008 (8) | 86 |
| 0.3[b] | 0.032 (64) | ... | 0.007 (14) | 0.012 (12) | 90 |
| 0.5[b] | 0.021 (42) | *d* | 0.009 (18) | 0.020 (20) | 80 |
| 0[c] | 0.011 (22) | 0.009 (18) | 0.026 (52) | | 92 |
| 0.05[c] | 0.008 (16) | 0.010 (20) | 0.027 (54) | | 90 |
| 0.15[c] | 0.006 (12) | 0.009 (18) | 0.032 (64) | | 94 |
| 0.25[c] | 0.003 (6) | 0.008 (16) | 0.033 (66) | *f* | 88 |
| 0.10[e] | 0 | 0 | 0.020 (40)[h] | 0.040 (40)[j] | *g* |
| 0.10[k] | 0 | 0 | 0.035 (70)[m] | 0.030 (30)[n] | |

[a] Conditions as stated in Tables I and III. P = $PPh_3$, unless indicated otherwise. [b] $NaMn(CO)_5$ and $Mn(CO)_5(NCMe)^+PF_6^-$. [c] $NaMn(CO)_4PPh_3$ and $Mn(CO)_5(NCMe)^+PF_6^-$. [d] Traces observed. [e] $NaMn(CO)_5$ and $Mn(CO)_5PEt_3^+PF_6^-$ with added $PEt_3$. [f] $HMn(CO)_4PPh_3$ detected, but not quantified. [g] Relative yield, not quantified. [h] $Mn_2(CO)_8(PEt_3)_2$. [j] $HMn(CO)_4PEt_3$ (20%) and $HMn(CO)_3(PEt_3)_2$ (20%). [k] $NaMn(CO)_5$ and $Mn(CO)_5PPh_3^+PF_6^-$ with added $PEt_3$. [m] Mixture of $Mn_2(CO)_8(PPh_3)_2$ (38%), $Mn_2(CO)_8(PPh_3)(PEt_3)$ (14%), and $Mn_2(CO)_8(PEt_3)_2$ (18%). [n] $HMn(CO)_4PPh_3$ and $HMn(CO)_4PEt_3$.

stituted cations, $Mn(CO)_5PEt_3^+$ was somewhat unusual in that it also afforded significant amounts of the hydrides $HMn(CO)_4PEt_3$ and $HMn(CO)_4PPh_3$.

**Effect of Added Phosphine on the Ion-Pair Couplings.** All of the anionic carbonylmanganates(−I) and carbonylmanganese(I) cations examined in this study were substitution stable. Thus separate solutions of these ions in acetonitrile or tetrahydrofuran remained unchanged in the presence of various amounts of added phosphine—certainly for periods far exceeding the time required for the ion-pair coupling (vide supra) to proceed to completion. Accordingly we examined the effect of added phosphine on the course of dimanganese formation.

The results in Table IV show three important changes accompanying the presence of triphenylphosphine on the ion-pair coupling of pentacarbonylmanganate A and the acetonitrile-substituted cation IIa, as represented in eq 6. First, with increasing amounts of $PPh_3$, the yield of $Mn_2(CO)_{10}$ dropped precipitously, as indicated by the trend in column 2, Table IV. The deficit was made by a pair of new products $Mn_2(CO)_8(PPh_3)_2$ in column 4 and $HMn(CO)_4PPh_3$ in column 5 (Table IV) (eq 12). Small amounts of the mono substituted dimer $Mn_2(CO)_9PPh_3$ was observed only at the highest concentrations of added $PPh_3$.

$$Mn(CO)_5^- + Mn(CO)_5(NCMe)^+ \xrightarrow{PPh_3} Mn_2(CO)_8(PPh_3)_2 + HMn(CO)_4PPh_3, \text{ etc.} \quad (12)$$

The effect of added triphenylphosphine on the ion-pair coupling of the $PPh_3$-substituted anion C and the MeCN-substituted cation IIa represented in eq 11 was more subtle. Thus the increasing amounts of added $PPh_3$ led to a gradual diminution in $Mn_2(CO)_{10}$ yield, which was solely made up by an increase in the yield of $Mn_2(CO)_8(PPh_3)_2$. The amount of the monosubstituted $Mn_2(CO)_9PPh_3$ remained relatively invariant. Hydridomanganese carbonyl $HMn(CO)_4PPh_3$ was found only at the highest concentrations of added triphenylphosphine.

Added phosphine also affected the ion-pair reaction of the phosphine-substituted cations. For example, when $Mn(CO)_5PEt_3^+$ was treated with pentacarbonylmanganate (compare entry 8, Table I) in the presence of 2 equiv of added triethylphosphine, the formation of $Mn_2(CO)_{10}$ was quenched with a concomitant increase in the yield of $Mn_2(CO)_8(PEt_3)_2$ to 40%, i.e., eq 13, together with $HMn(CO)_4PEt_3$ (20%) and $HMn(CO)_3(PEt_3)_2$ (20%).

$$Mn(CO)_5^- + Mn(CO)_5PEt_3^+ \xrightarrow{PEt_3} Mn_2(CO)_8(PEt_3)_2 + 2CO \quad (13)$$

**Effect of Solvent and Added Salt on the Ion-Pair Coupling.** Acetonitrile and tetrahydrofuran represent aprotic media of different properties, especially as evaluated by most measures of solvent polarity.[21] The large solvent effect on the ion-pair coupling of the pentacarbonylmanganate anion A was indicated by the more than 100-fold difference which separated its reactivity with hexacarbonylmanganese(I) cation in tetrahydrofuran and in acetonitrile (compare entries 1 and 2, Table V). The prolonged reaction times in the more polar acetonitrile can be related to the stabilization of the separate ions. The latter is consistent with the decreased reactivity of the ions in tetrahydrofuran containing 0.3 M tetra-*n*-butylammonium perchlorates (see entries 3 and 9, Table V).

---

[21] (a) Kosower, E. M. *Introduction to Physical Organic Chemistry*; Wiley: New York, **1968**. (b) Reichardt, C. *Justus Liebigs Ann. Chem.* **1971**, *752*, 64.

**Table V. Solvent and Salt Effects on the Ion-Pair Coupling of Pentacarbonylmanganate(−I) with Various Carbonylmanganese (I) Cations**[a]

| $Mn(CO)_5L^+$ L | solv | salt,[b] M | time,[c] min | products |
|---|---|---|---|---|
| CO | THF | 0 | <5 | $Mn_2(CO)_{10}$[d] |
| CO | MeCN | 0 | >1000 | $Mn_2(CO)_{10}$[e] |
| CO | THF | 0.3 | ~90 | $Mn_2(CO)_{10}$[e] |
| CO | MeCN | 0.2 | >2000 | $Mn_2(CO)_{10}$[e] |
| $CH_3CN$ | THF | 0 | <5 | $Mn_2(CO)_{10}$[d] |
| $CH_3CN$ | MeCN | 0 | ~500 | $Mn_2(CO)_{10}$[e] |
| $CH_3CN$ | THF | 0.3 | ~30 | $Mn_2(CO)_{10}$[e] |
| py | THF | 0 | <5 | $Mn_2(CO)_{10}$[d] |
| py | THF | 0.3 | ~30 | $Mn_2(CO)_{10}$[e] |
| $PEt_3$ | THF | 0 | $\sim 10^2$ | $Mn_2(CO)_{10}$,<br>$Mn_2(CO)_8(PEt_3)_2$[d] |
| $PEt_3$ | THF | 0.3 | $>10^3$ | $Mn_2(CO)_8(PEt_3)_2$[f] |

[a] $NaMn(CO)_5$ (1.2 M, 5 mL) added to 5 mL of $1 \times 10^{-2}$ M $Mn(CO)_5L^+BF_4^-$. [b] Tetra-*n*-butylammonium perchlorate. [c] Required for disappearance of ions (<5 = upon mixing). [d] See Table I. [e] Only product observed. [f] Plus $HMn(CO)_4PEt_3$.

**Table VI. Cyclic Voltammetric Potentials for Carbonylmetal Cations and Anions**[a]

| $Mn(CO)_5L^+$[b] | THF[c] | MeCN[c] |
|---|---|---|
| $Mn(CO)_6^+BF_4^-$ | [f] | −1.27 |
| $Mn(CO)_5(py)^+BF_4^-$ | −0.81 | −1.12 |
| $Mn(CO)_5[CH_3CN]^+PF_6^-$ | −0.84 | −1.19 |
| $Mn(CO)_5(PPh_3)^+PF_6^-$ | −1.05 | −1.29 |
| $Mn(CO)_5[P(p\text{-tol})_3]^+PF_6^-$ | −1.19 | −1.34 |
| $Mn(CO)_5(PPh_2Et)^+PF_6^-$ | −1.24 | −1.39 |
| $Mn(CO)_5(PPhEt_2)^+PF_6^-$ | −1.32 | −1.55 |
| $Mn(CO)_5(PEt_3)^+PF_6^-$ | −1.36 | −1.67 |
| $Mn(CO)_5(PPh_2Me)^+PF_6^-$ | −1.16 | −1.41 |
| $Mn(CO)_5(PPhMe_2)^+PF_6^-$ | −1.34 | −1.54 |
| $Mn(CO)_2(\eta^2\text{-DPPE})_2^+Cl^-$ | −1.84 | |
| $NaMn(CO)_5$[b] | THF[d] | MeCN[d] |
| $NaMn(CO)_5$ | −0.03 | −0.11 |
| $NaMn(CO)_4[P(OPh)_3]$ | −0.11 | |
| $NaMn(CO)_4(PPh_3)$ | −0.52 | −0.50 |
| $NaMn(CO)_4(\eta^1\text{-DPPE})$[e] | −0.48 | |

[a] In either THF containing 0.3 M TBAP or MeCN containing 0.1 M TEAP at scan rates of 500 mV $s^{-1}$ at 22 °C (see ref 12). [b] $5 \times 10^{-3}$ M. [c] Irreversible cathodic peak potential ($E_p^{red.}$) in V vs. SCE. [d] Irreversible anodic peak potential ($E_p^{ox.}$) in V vs. SCE. [e] Prepared in situ by cathodic (2e) reduction of $Mn(CO)_3(DPPE)Br$ (see Experimental Section). [f] Insoluble.

**Electrochemical Properties of Anionic Carbonylmanganates(−I) and Carbonylmanganese(I) Cations.** The energetics of the one-electron oxidation of the anionic pentacarbonylmanganates(−I) and reduction of carbonylmanganese(I) cations were examined by cyclic voltammetry in either acetonitrile solution containing 0.1 M tetraethylammonium or tetrahydrofuran containing 0.3 M tetra-*n*-butylammonium perchlorate (TBAP).

The initial *negative* scan cyclic voltammogram of hexacarbonylmanganese(I) in acetonitrile showed a one-electron cathodic wave with a peak potential $E_p^{red.} = -1.27$ V vs. SCE at 500 mV $s^{-1}$ by comparison with a ferrocene standard (eq 14).[22] The anodic wave on the return scan

$$Mn^I(CO)_6^+ + e \rightleftharpoons Mn^0(CO)_6^{\bullet} \qquad (14)$$

was not observed until the CV scan rate was increased to $v > 70\,000$ V $s^{-1}$ using a Pt microelectrode.[23] Accordingly the reversible $E_{1/2} = -1.0$ V was taken as the average of the cathodic and anodic peak potentials.[24] The cyclic voltammograms of the other carbonylmetal cations showed only a single cathodic wave, the accompanying anodic wave being absent even at the very fastest sweep rates. The irreversible peak potentials $E_p^{red.}$ listed in Table VI for the cations I–III were obtained at a standard sweep rate of 500 mV $s^{-1}$ in acetonitrile and in tetrahydrofuran.

The initial *positive* scan cyclic voltammogram of the $PPh_3$-substituted carbonylmanganate(−I) C was reversible only at sweep rates $v > 1500$ V $s^{-1}$ (eq 15). The reversible

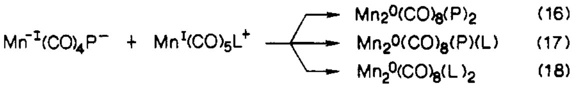
$$Mn^{I-}(CO)_4PPh_3^- \rightleftharpoons Mn^0(CO)_4PPh_3^{\bullet} + e \qquad (15)$$

$E_{1/2} = -0.33$ V vs. SCE measured for $Mn(CO)_4PPh_3^-$ in acetonitrile could not be obtained for either the parent carbonylmanganate(−I) $Mn(CO)_5^-$ or the phosphite analogue B owing to the irreversible cyclic voltammograms. Accordingly, the irreversible anodic peak potentials $E_p^{ox.}$ were measured at a standard sweep rate of $v = 500$ mV $s^{-1}$ (Table VI).

## Discussion

The ion-pair interaction of an anionic carbonylmanganate with a carbonylmanganese cation to afford various dimanganese carbonyls formally represents an annihilation of −1 and +1 oxidation states to a pair of metal(0). As such the material balance for the coupling of manganese centers can be represented from among the three possible combinations of ligand attachments, viz., Scheme I.

**Scheme I**



The most direct transformation of an ion pair is included in the cross-coupled combination in eq 17. The corresponding stoichiometry may be expressed in eq 6 when P = CO and L = CO, MeCN, or pyridine (see entries 1–3 in Table I). On the other hand, the interactions of the other ion pairs can lead to the homo-coupled products $Mn_2(CO)_8(P)_2$ and $Mn_2(CO)_8(L)_2$. For example, when P = CO and L = phosphine, the primary dimanganese carbonyls are the homo-coupled $Mn_2(CO)_{10}$ and $Mn_2(CO)_8(L)_2$ with only minor amounts of the cross-coupled $Mn_2(CO)_9L$ (see entries 4–7, Table I). Moreover, when P and L are both phosphines, all three combinations, viz., the homo-coupled $Mn_2(CO)_8P_2$ and $Mn_2(CO)_8(L)_2$ as well as the cross-coupled $Mn_2(CO)_8(P)(L)$, are obtained (see entries 4–10, Table II, and entries 7–11, Table III).

In order to account for this apparent ligand-dependent selectivity in the ion pair couplings, let us classify them in terms of the relative amounts of each combination (i.e., eq 16, 17, or 18) which is formed. In doing so however we take cognizance of only the major changes in the product compositions listed in Tables I–III, owing to the limited quantification of all the products, especially in complex mixtures (vide supra). Nonetheless, the general trends in the product variation with changes in the ligands P and L are instructive. Two clear-cut categories emerge as extremes from the data in Tables I–III—namely those in which the carbonylmanganese ions labeled with ligands P and L either (A) maintain their original identity or (B) they are randomly scrambled, as described individually below.

**(A) The cross-coupled combination of carbonylmanganese moieties** given by the stoichiometry in eq 19

$$Mn(CO)_5^- + Mn(CO)_5L^+ \rightarrow Mn_2(CO)_{10} + L \qquad (19)$$

---

[22] Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

[23] Based on unpublished results by D. Kuchynka. See also Howell et al.[24]

[24] Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

corresponds to the replacement of the ligand L in the cation by a carbonylmanganese group. The extent to which the latter is an electron-rich anion then represents a nucleophilic substitution at a cationic manganese center. Such a transformation obtains in eq 5 and 6 when L is CO and a nitrogen-centered ligand such as pyridine and acetonitrile, respectively.[25] However, the situation is somewhat ambiguous since the dimanganese decacarbonyl can also derive from a pair of $Mn(CO)_5^-$ anions (via oxidation) and/or a pair of $Mn(CO)_5L^+$ cations (via reductive loss of L).

**(B) The homo-coupled combination of carbonylmanganese moieties** given by the stoichiometry in eq 20

$$\mathrm{Mn(CO)_4P^- + Mn(CO)_5L^+ \rightarrow} \atop \mathrm{[\underset{(25\%)}{Mn_2(CO)_8P_2} + \underset{(25\%)}{Mn_2(CO)_8L_2} + \underset{(50\%)}{Mn_2(CO)_8(P)(L)}] + CO} \qquad (20)$$

represents the complete loss of anionic and cationic identities in the ion-pair precursor and the subsequent statistical reassemblage of the carbonylmanganese moieties as dimers. Such a randomization is unambiguously represented in eq 10 owing to the retention of either P or L (or both) in the dimanganese products. The same basic stoichiometry obtains in eq 8 and 9, but in a somewhat less obvious manner owing to the ligand loss of either CO or L.

The statistical mixture of manganese dimers as exemplified in eq 20 does provide an unusual bit of insight as to how the manganese–manganese bond can be formed by ion-pair annihilation, as described below.

**Formation of the Manganese–Manganese Bond via Radical Coupling.** The electron balance for the ion-pair annihilation leading to the homo-coupled products $Mn_2(CO)_8(P)_2$ and $Mn_2(CO)_8(L)_2$ formally requires the oxidation of the anionic $Mn(CO)_4P^-$ and the reduction of the cationic $Mn(CO)_5L^+$, respectively. As such, the most direct pathway for the formation of these dimeric products is via the well-known coupling of carbonylmanganese radicals,[27,28] i.e., Scheme II. These radicals are the direct products of

**Scheme II**

$$\mathrm{Mn(CO)_4P^- \xrightarrow{-e} Mn(CO)_4P^\bullet \rightarrow {}^1/_2Mn_2(CO)_8P_2} \qquad (21a,b)$$

$$\mathrm{Mn(CO)_5L^+ \xrightarrow{+e} Mn(CO)_5L^\bullet \xrightarrow{-CO} {}^1/_2Mn_2(CO)_8L_2} \qquad (22a,b)$$

electron transfer within the ion pair, i.e., eq 23. Furthermore if the CO loss from $Mn(CO)_5L^\bullet$ were rapid in eq 22b, the electron transfer in eq 23 would be tantamount

$$\mathrm{Mn(CO)_4P^- + Mn(CO)_5L^+ \rightarrow Mn(CO)_4P^\bullet + Mn(CO)_5L^\bullet} \qquad (23)$$

to the simultaneous production of a pair of similar radicals, i.e.

$$\mathrm{Mn(CO)_4P^- + Mn(CO)_5L^+ \xrightarrow{-CO} Mn(CO)_4P^\bullet + Mn(CO)_4L^\bullet}$$

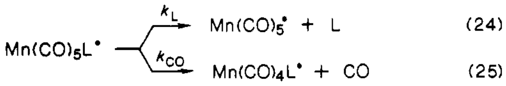
which would afford a more or less random mixture of dimanganese carbonyls. Accordingly, the homo-coupled combination found in eq 20 points to an electron-transfer mechanism for the ion-pair annihilation leading to the manganese–manganese couplings. By the same token, the cross-coupling combination observed in eq 5 and 6 seems to disfavor the same carbonylmanganese radicals as intermediates.

In order to resolve this conundrum, we recognize that the two carbonylmanganese radicals arising directly from the electron transfer in eq 23 are inherently different.

**Mechanistic Distinction between 19- and 17-Electron Carbonylmanganese Radicals.** The carbonylmanganese radical $Mn(CO)_5L^\bullet$ is a supersaturated 19-electron species, whereas $Mn(CO)_4P^\bullet$ an unsaturated 17-electron species.[12] The difference in the coordinative saturation in these two types of carbonylmanganese radicals immediately serves as a point of differentiation which is modulated by the rate of ligand loss from the 19-electron species. Accordingly it is worthwhile to review the properties and behavior of 19- and 17-electron carbonylmanganese radicals when they are separately generated by independent methods.

**A. The 19-electron radical $Mn(CO)_5L^\bullet$** is a transient species which is conveniently produced from the cathodic reduction of the carbonylmanganese(I) cations.[12] A previous study showed that $Mn(CO)_5L^\bullet$ undergoes two basic transformations, namely, (a) ligand dissociation and (b) hydrogen abstraction, the competition from which is highly dependent on the nature of ligand L in the following way.

(a) Ligand dissociation of the 19-electron $Mn(CO)_5L^\bullet$ is rapid and can involve the loss of either L or CO to produce the 17-electron carbonylmanganese radicals,[12] i.e., eq 24 and 25. In the case of the nitrogen-substituted radicals



$$\mathrm{Mn(CO)_5L^\bullet \xrightarrow{k_L} Mn(CO)_5^\bullet + L} \qquad (24)$$
$$\mathrm{Mn(CO)_5L^\bullet \xrightarrow{k_{CO}} Mn(CO)_4L^\bullet + CO} \qquad (25)$$

$Mn(CO)_5(NCMe)^\bullet$ and $Mn(CO)_5(py)^\bullet$, the loss of CO is not competitive with the expulsion of either MeCN or py since $Mn_2(CO)_{10}$ is obtained as the sole dimer. This selectivity is in accord with the expected difference in leaving group abilities of CO relative to MeCN and py. On the other hand, for the phosphine derivatives of $Mn(CO)_5L^\bullet$ there is a competition between the loss of carbon monoxide and phosphine. Moreover the logarithm of the relative rate constants $k_L/k_{CO}$ in eq 24 and 25 shows a linear correlation with the p$K_a$ value for the phosphine ligand.[12] It is noteworthy that the ratio $k_L/k_{CO} = 6.7$ for L = $PPh_3$ is more than a factor of 20 larger than $k_L/k_{CO} = 0.3$ for the more basic $PEt_3$.

(b) Hydrogen abstraction by $Mn(CO)_5L^\bullet$ from solvent (SH) yields the hydridomanganese complexes $HMn(CO)_4L$ when followed by the rapid extrusion of carbon monoxide,[29,30] i.e., Competition from this homolytic process

$$\mathrm{Mn(CO)_5L^\bullet \underset{(SH)}{\xrightarrow{k_H}} Mn(CO)_4(CHO)L \xrightarrow{-CO} HMn(CO)_4L} \qquad (26)$$

---

[25] Note that the known $Mn_2(CO)_9(NCMe)$ and $Mn_2(CO_9)(py)$[26] are not observed.

[26] $Mn_2(CO)_9(CH_3CN)$ and $Mn_2(CO)_9(py)$ are known. See: Koelle, U. *J. Organomet. Chem.* 1978, *155*, 53.

[27] (a) Hughey, J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* 1977, *125*, C49. (b) Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* 1981, *103*, 6089. (c) Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.* 1984, *23*, 3748. (d) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* 1983, *105*, 6249. (e) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536. (f) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* 1978, *100*, 7259.

[28] See also: Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

[29] (a) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* 1984, *3*, 802. (b) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* 1984, *272*, C49. (c) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* 1986, *5*, 926. (d) See also Hanckel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* 1986, *25*, 1852.

is most severe with L = phosphines. For the more labile 19-electron radicals derived from L = CO, MeCN, and py, the rate constant $k_L$ in eq 24 appears to be sufficiently greater than $k_H$ in eq 26 to obviate this competition, and hydride manganese carbonyls are not important products.

**B. The 17-electron radical $Mn(CO)_4P^\bullet$** can be independently generated by the anodic oxidation of the carbonylmanganate anion (Table VI). The ease of oxidation of $Mn(CO)_4P^-$ follows the σ-donor properties of the ligands in the order: P = $PPh_3$ ≫ $P(OPh)_3$ > CO; and it is an indication of the reactivity of the resulting radical $Mn(CO)_4P^\bullet$, as reflected in the rates of self-dimerization (eq 27).[27] For example, the second-order rate constant for

$$2Mn(CO)_4P^\bullet \xrightarrow{k_d} Mn_2(CO)_8P_2 \qquad (27)$$

$Mn(CO)_5^\bullet$ is $k_d = 9 \times 10^8\ M^{-1}\ s^{-1}$, and for $Mn(CO)_4PPh_3^\bullet$ it is roughly 2 orders of magnitude slower ($k_d = 1 \times 10^7\ M^{-1}\ s^{-1}$).[27,31] These 17-electron species are also labile and undergo rapid ligand substitution by an associative mechanism,[31,32] e.g., eq 28, where $k_s = 1.7 \times 10^7\ M^{-1}\ s^{-1}$.[31a]

$$Mn(CO)_5^\bullet + PPh_3 \xrightarrow{k_s} Mn(CO)_4PPh_3^\bullet + CO \qquad (28)$$

The 19-electron intermediate in eq 28 is the same as that in eq 23 when L = phosphine. Thus the presence of added phosphine during the ion-pair annihilation would serve to equilibrate all carbonylmanganese radicals to a common species, as observed in eq 12 and 13.

With this background established for the properties and behavior of relative 19- and 17-electron carbonylmanganese radicals, let us now reconsider the distribution among the diverse products obtained from the various ion-pair annihilations.

**Radical-Pair Interactions of Transient 19- and 17-Electron Carbonylmanganese Species.** Several pathways are conceivable for the formation of $Mn_2(CO)_{10}$ in high yields from $Mn(CO)_5^-$ and $Mn(CO)_5(NCMe)^+$ in Table I. On one hand, the most economical route for this ion-pair annihilation involves cross-coupling accompanied by the displacement of MeCN, i.e., eq 29. On the other

$$Mn(CO)_5^- + Mn(CO)_5(NCMe)^+ \rightarrow Mn_2(CO)_{10} + MeCN \qquad (29)$$

hand, a prior electron-transfer (eq 23) involves a multistep process in which the 19- and 17-electron radical pair are involved in ligand loss (eq 24) and dimerization (eq 27), i.e., Scheme III. The marked effect of added triphenylphosphine strongly supports the latter mechanism. Thus the presence of $PPh_3$ effectively diverts the course of reaction from $Mn_2(CO)_{10}$ to a pair of new products $Mn_2(CO)_8(PPh_3)_2$ and $HMn(CO)_4PPh_3$ without materially affecting the rate (see Table IV). Both of the products are readily attributed to the efficient interception of the carbonylmanganese radical, i.e., Scheme IV (as described in eq 28 and 26), followed by rapid dimerization (eq 27). Essentially the same results obtain when the ion-pair annihilation of $Mn(CO)_4PPh_3^-/Mn(CO)_5(NCMe)^+$ is carried out with added $PPh_3$, and $Mn(CO)_5^-/Mn(CO)_5PEt_3^+$ with added $PEt_3$ (eq 13). At this juncture, it is important to re-emphasize that the control experiments establish both the precursor carbonylmanganate(-I) anion and carbonylmanganese(I) cation to be substitution stable, and no ligand exchange of the type described above can occur within the time span of these experiments.

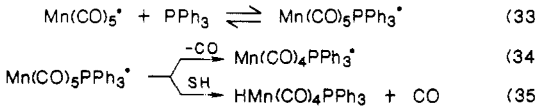
**Scheme III**

$$Mn(CO)_5^- + Mn(CO)_5(NCMe)^+ \rightarrow Mn(CO)_5^\bullet + Mn(CO)_5(NCMe)^\bullet \qquad (30)$$

$$Mn(CO)_5(NCMe)^\bullet \xrightarrow{\text{fast}} Mn(CO)_5^\bullet + MeCN \qquad (31)$$

$$2Mn(CO)_5^\bullet \xrightarrow{\text{fast}} Mn_2(CO)_{10} \qquad (32)$$

**Scheme IV**



The principal byproduct of the ion-pair coupling of $Mn(CO)_4P^-/Mn(CO)_5L^+$ is the hydridomanganese carbonyl $HMn(CO)_4L$, which most commonly arises when L = phosphines. On the other hand when L = CO, MeCN, or py, the corresponding hydride is absent. These results accord with hydride formation occurring via the 19-electron radical $Mn(CO)_5L^\bullet$, as described in eq 26. Furthermore, hydrogen atom transfer to phosphorus-substituted radicals with L = phosphine should occur more readily than that with L = CO, MeCN, or py owing to the dissociation rate constant $k_L > k_{CO}$ in eq 24 and 25. It is possible that the small amounts of $HMn(CO)_4P$ observed in some cases (see Table II, entries 4 and 6) arise by protonation of the carbonylmanganate anion by adventitious moisture[33] or by multiple-ligand substitutions of the 17-electron radical, i.e., Scheme V. Indeed, the ion-pair annihilation of $Mn(CO)_5^-/Mn(CO)_5PEt_3^+$ carried out in the presence of 2 equiv of $PEt_3$ afforded $Mn_2(CO)_8(PEt_3)_2$, $HMn(CO)_4PEt_3$, and the bis-substituted hydride $HMn(CO)_3(PEt_3)_2$ as the principal products, with no evidence of either $Mn_2(CO)_{10}$ or $Mn_2(CO)_9PEt_3$. These results accord with efficient interception of $Mn(CO)_5^\bullet$ (compare eq 33–35). Moreover, the appearance of $HMn(CO)_3(PEt_3)_2$ indicates the facility with which further homolytic substitution occurs,[32d,34] i.e., eq 38. According to the electron-transfer formulation, the

$$Mn(CO)_4PEt_3^\bullet + PEt_3 \xrightarrow{-CO} Mn(CO)_3(PEt_3)_2^\bullet \text{ etc.} \qquad (38)$$

relative amounts of products are largely determined by the

**Scheme V**

$$Mn(CO)_4P^\bullet + L \rightarrow Mn(CO)_4L^\bullet + P \qquad (36)$$

$$Mn(CO)_5^\bullet + P \rightarrow Mn(CO)_5P^\bullet \text{ etc.} \qquad (37)$$

---

[30] It is also possible that some of the manganese hydrides are formed by a direct hydrogen transfer to the 17-electron species. Though 17-electron radicals of the type $Mn(CO)_3P_2^\bullet$ undergo hydrogen transfer, the rates are very slow even with active donors such as tin hydrides.[34b] The homolytic reactivity of the type $Mn(CO)_4P^\bullet$ has not been examined, but the related $Re(CO)_4P^\bullet$ only reacts with $Bu_3SnH$ present in large excess.[29d] Finally, the product studies in Tables I–IV show that the cations (not the anions) are the principal precursors to the manganese hydrides.

[31] For three recent summaries see: (a) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700. (b) Turaki, N. N.; Huggins, J. M. *Organometallics 1986*, *5*, 1703. (c) See Meyer et al.[28] and related references therein.

[32] (a) Fox, A.; Malito, J.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (b) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065. (c) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095. (d) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007. (e) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527. (f) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613. (g) Absi-Halabi, M.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2982. (h) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032.

[33] Zotti, G.; Zeechin, S.; Pilloni, G. *J. Organomet. Chem.* **1983**, *246*, 61.

[34] Compare: (a) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103. (b) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496. (c) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *J. Organomet. Chem.* submitted.

[35] The rates of cross combination ($k_d'$) are unknown, and must also be taken into account.

**Scheme VI**

$$Mn(CO)_4P^- + Mn(CO)_5L^+ \longrightarrow [Mn(CO)_4P^\bullet, Mn(CO)_5L^\bullet] \quad (39)$$

$$[Mn(CO)_4P^\bullet, Mn(CO)_5L^\bullet] \xrightarrow{\text{collapse}} Mn_2(CO)_8(P)(L) + CO \quad (40)$$

$$[Mn(CO)_4P^\bullet, Mn(CO)_5L^\bullet] \xrightarrow{\text{diffuse}} Mn(CO)_4P^\bullet + Mn(CO)_5L^\bullet \quad (41)$$

$$Mn(CO)_5L^\bullet \xrightarrow{k_L, k_{CO}} Mn(CO)_4X^\bullet + L(CO) \quad (42)$$

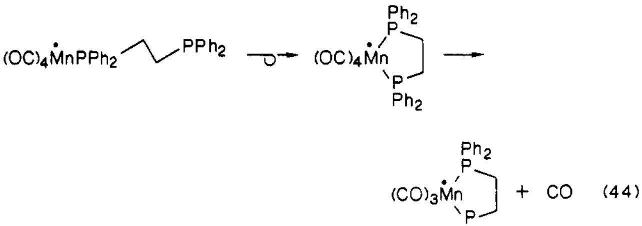
$$2Mn(CO)_4X^\bullet \xrightarrow{k_d} Mn_2(CO)_8X_2 \quad (43)$$

$$X = CO, P, L$$

magnitudes of $k_L$, $k_{CO}$, and $k_H$ since they regulate the steady-state concentration of the 19-electron radical. The extent to which $k_d$ for the coupling of the 17-electron radical is dependent on X = CO, P, and L[27c] also affects the distribution among the various dimanganese carbonyls. The availability of free phosphine is responsible for raising the steady-state concentration of the 19-electron species by the microscopic reverse of eq 24. This results in increased hydride (eq 26) and phosphine incorporation into the dimanganese carbonyls (eq 36 and 38). Most importantly, the diversion of $Mn(CO)_5^-$ and $Mn(CO)_5(NCMe)^+$ by added $PPh_3$ (Table IV) demonstrates that a substantial portion, if not all, of the ion-pair annihilation occurs via scavengable radicals according to Schemes III and IV.

**Mechanism of Mn–Mn Bond Formation by Ion-Pair Annihilation.** Taken together, the foregoing analyses show that the diverse products derived from the ion-pair annihilations in Tables I–IV can be completely accounted for by the known behavior of 19- and 17-electron carbonylmanganese radicals.[12,28–34] Accordingly, the initiation by electron-transfer is included in the generalized formulation shown in Scheme VI for Mn–Mn bond formation. The first-order rate constants $k_L$ and $k_{CO}$ represent the ligand dissociation from the 19-electron radical, and $k_d$ is the second-order rate constant for the couplings of pairs of 17-electron radicals.

According to Scheme VI, electron transfer is the first step (eq 39) in the annihilation of the carbonylmanganese cations by anions. The nonstatistical distribution among the homo-coupled and cross-coupled dimers in Scheme I derive primarily from the competition between cage collapse (eq 40) and diffusive separation (eq 41) of the initially formed radical pair.[36] The extent to which cage collapse occurs faster than diffusive separation will determine the amounts of cross-coupled products obtained.[35] Alternatively, the efficiency with which added phosphines divert the products to $Mn_2(CO)_8P_2$ (Table IV) reflects the extent to which 17-electron carbonylmanganese radicals have escaped and consequently are subject to ligand substitution (eq 28).[38] In the same way the trapping of 19-electron $Mn(CO)_5L^\bullet$ by hydrogen transfer reflects cage escape. Indeed the multiple substitution of phosphine in the hydride products (see eq 38) suggests that the 17-electron carbonylmanganese species are longer lived than their 19-electron precursors. A further indication of this difference is shown in the carbonylmanganate $Mn(CO)_4(\eta^1\text{-DPPE})^-$ in which the corresponding 17-electron radical will be susceptible to intramolecular trapping, i.e., eq 44.



The facile annihilation of $Mn(CO)_4(\eta^1\text{-DPPE})^-$ by an equivalent amount of either $Mn(CO)_5(NCMe)^+$ or $Mn(CO)_5(py)^+$ afforded three principal products, viz., $Mn_2(CO)_{10}$ (30%), $Mn_2(CO)_9(\eta^1\text{-DPPE})$ (15%), and $HMn(CO)_3(\eta^2\text{-DPPE})$ (35%). The formation of the chelated $HMn(CO)_3(\eta^2\text{-DPPE})$ is consistent with the trapping of the 19-electron intermediate in eq 44, as indicated by the mechanism for hydride formation in eq 26. The observation of the $\eta^1$ dimanganese carbonyl $Mn_2(CO)_9(\eta^1\text{-DPPE})$ suggests that the cross-coupling either involves a concerted process[39] or a cage collapse in eq 40 which is faster than intramolecular trapping (eq 44). Be that as it may, from a purely operational point of view, there are two pathways for the formation of Mn–Mn carbonyls by ion-pair annihilation, namely, (i) a process in which pairs of carbonylmanganese radicals behave more or less independently as discrete species as a result of diffusive separation and (ii) a minor pathway in which the cation and anion more or less maintain their identity either by the cage collapse of the radical pair (eq 40) or by concerted action.[39]

**Driving Force for the Formation of Mn–Mn Bonds by Ion-Pair Annihilation.** Since the radical-pair mechanism in Scheme VI commences with an electron-transfer initiation, a critical part of the driving force for Mn–Mn bond formation is the oxidation/reduction of the anion/cation pair.[41] As such, the energetics for the production of the 19- and 17-electron carbonylmanganese radical pair derives from the reversible electrode potentials for $Mn(CO)_5L^+$ and $Mn(CO)_4P^-$.

(a) For the *reduction* of the parent cation $Mn(CO)_6^+$ in eq 14, a value of $E_{1/2} \cong -1.0$ V vs. SCE is obtained from the partially reversible cyclic voltammogram at very high sweep rates.[23] Although we are unable to measure directly the reversible electrode potentials for the other carbonylmanganese(I) cations, they can be reliably estimated from the peak potentials listed in Table VI by an additive correction of ~0.3 V.[42] The wide span in potentials indicates a large ligand dependence on the ease of reduction of $Mn(CO)_5L^+$ in the order L = py > MeCN > CO > $PPh_3$

---

[36] Such a cross coupling may occur specifically at a carbonyl ligand followed by a facile migratory de-insertion of carbon monoxide,[37] e.g., $[Mn(CO)_4P^\bullet, Mn(CO)_5L^\bullet] \rightarrow [P(CO)_4MnCOMn(CO)_4L] \xrightarrow{-CO} Mn_2(CO)_8(P)(L)$. Experimentally, a process involving a very rapid cage combination would be difficult to distinguish from a concerted mechanism for ion-pair annihilation.

[37] Compare: de Boer, E. J. M.; de With, J.; Meijboom, N.; Orpen, A. G. *Organometallics* **1985**, *4*, 259.

[38] The relative insensitivity of the cross-coupled $Mn_2(CO)_9PPh_3$ with added $PPh_3$ in Table IV may reflect the cage collapse, as described in ref 36.

[39] A concerted process may involve nucleophilic addition of $Mn(CO)_4P^-$ to a coordinated carbonyl ligand in $Mn(CO)_5L^+$ followed by migratory CO loss (compare ref 36). The electrophilic character of the cationic carbonyls is indicated by their relative large $\nu_{CO}$ stretching force constants.[40]

[40] (a) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919. Darensbourg, M. Y.; Darensbourg, D. J.; Drew, D.; Conder, H. L. *J. Organomet. Chem.* **1974**, *74*, C33. (c) Compare also: Darensbourg, M. Y.; Hanckel, J. M. *Organometallics* **1982**, *1*, 82. Darensbourg, M. Y.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3127. Dobson, G. R.; Paxson, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5925. Brink, R. W.; Angelici, R. J. *Inorg. Chem.* **1973**, *12*, 1062. Angelici, R. J.; Brink, R. W. *Inorg. Chem.* **1973**, *12*, 1067. Raab, K.; Nagel, U.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1983**, *38*, 1466.

[41] The total driving force includes a contribution from the Mn–Mn bond energy.

[42] Calculated from the difference $E_{1/2} - E_p^{\text{red.}}$ for $Mn(CO)_6^+$ in Table VI. For the electrochemical basis for this type of correction, see ref 43.

[43] (a) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102* 4790. (b) See also: Klingler, R. J.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 1731 and references therein.

$> PPh_2Et > PPhEt_2 > PEt_3 \gg \eta^2$-DPPE.

(b) For the *oxidation* of the anionic $Mn(CO)_4PPh_3^-$ in eq 15, $E_{1/2} \cong -0.33$ V vs. SCE. The reversible potentials for the other carbonylmanganates can be estimated from the peak potentials in Table VI by an additive correction of $\sim$0.2 V.[44] The ligand effect on the ease of oxidation is opposite to that in the cation in the order L = $PPh_3 \gg P(OPh)_3 > CO$.[45]

On this basis, the driving force for electron transfer will be the most favorable for the ion pair $Mn(CO)_4PPh_3^-/Mn(CO)_5(py)^+$ with $\Delta E \approx 0.5$ V and the least favorable for $Mn(CO)_5^-/Mn(CO)_2(DPPE)_2^+$ with $\Delta E \approx 1.6$ V.[46,47] Indeed the latter is an unreactive ion pair, and it can be readily isolated as a simple salt from THF solution, i.e., eq 45, owing to the insolubility of $NaBF_4$. Although we

$$Na^+Mn(CO)_5^- + Mn(CO)_2(DPPE)_2^+BF_4^- \rightarrow [Mn(CO)_5^-Mn(CO)_2(DPPE)_2^+] + NaBF_4 \quad (45)$$

have not yet measured the reaction rates quantitatively, the ion-pair reactivities in Tables I–III qualitatively follow the trend in the driving forces.[48] Thus we find the ion pairs $Mn(CO)_4PPh_3^-/Mn(CO)_5py^+$ and $Mn(CO)_4PPh_3^-/Mn(CO)_5(NCMe)^+$ in Table III to be the most reactive in this study. At the other extreme, the couplings of the parent anion $Mn(CO)_5^-$ with the phosphine-substituted cations in Table I require the longest times. Since $\Delta E \approx 1.2$ V for $Mn(CO)_5^-/Mn(CO)_5PEt_3^+$, it appears that the threshold in the driving force for ion-pair annihilation lies somewhere between 1.2 and 1.6 V in THF solution. If the rate of electron transfer in eq 39 is taken in the outer-sphere context of Marcus theory,[49] two other factors must also be considered. Thus the interaction of oppositely charged ions will be aided considerably by the electrostatics.[50] Indeed such a positive work term accords with the strong solvent dependence and the negative salt effect described in Table V. The contribution from the reorganization energies of $Mn(CO)_4P^-$ and $Mn(CO)_5L^+$ cannot be evaluated at this juncture. However these large highly polarizable, 5- and 6-coordinate ions are likely to show only minor differences in basic structural change.[51] If so, the driving force $\Delta E$ will be the dominant factor in determining the ease with which ion pairs are annihilated to form metal–metal bonds.

## Summary and Conclusion

The carbonylmanganese(I) cation $Mn(CO)_6^+$ and the carbonylmanganate(−I) $Mn(CO)_5^-$ react upon mixing in THF solution to afford high yields of dimanganese decacarbonyl. Similarly the substituted cations $Mn(CO)_5L^+$ with L = py, MeCN, and aryl- and alkylphosphines and the substituted anions $Mn(CO)_4P^-$ with P = $PPh_3$ and $P(OPh)_3$ lead to mixtures of dimanganese carbonyls labeled with the P and L tracers. The extensive (if not complete) scrambling of the carbonylmanganese moieties during ion-pair annihilation is ascribed to the 17- and 19-electron radicals $Mn(CO)_4L^\bullet$ and $Mn(CO)_5P^\bullet$, respectively, as the reactive intermediates. This conclusion is strongly supported by the known behavior of both types of radicals when they are independently generated by the anodic oxidation of $Mn(CO)_4P^-$ and the cathodic reduction of $Mn(CO)_5L^+$. The reversible addition of ligands to 17-electron radicals provides a ready means for interconversion with their 19-electron counterparts. Thus the effect of added phosphine in altering the course of Mn–Mn coupling via ligand substitution (eq 28) and the formation of the hydrido byproducts $HMn(CO)_4L$ via hydrogen transfer (eq 26) provide compelling evidence for carbonylmanganese radicals since neither the cation nor the anion is susceptible to additives on the time scale of the coupling experiments. These experiments also rule out any type of concerted displacement mechanism as a dominant route in the formation of $Mn_2(CO)_{10}$ from ion pairs such as $Mn(CO)_5^-/Mn(CO)_5(NCMe)^+$ or $Mn(CO)_5^-/Mn(CO)_5(py)^+$ in which the carbonylmanganese moieties are not labeled.[52] The participation of specific cross-coupling is included in the unified mechanism as a minor pathway stemming from cage collapse (eq 40) of radicals immediately following an initial electron transfer. The latter is consistent with the reactivity trends for carbonylmanganese ion pairs which qualitatively parallel the differences $\Delta E$ in the oxidation and reduction potentials of $Mn(CO)_4P^-$ and $Mn(CO)_5L^+$.

**Table VII. Carbonyl Stretching Frequencies for Mn–Mn Dimers**[a]

| | $\nu_{CO}$, cm$^{-1}$ |
|---|---|
| $[Mn(CO)_5]_2$ | 2045 (m), 2009 (s), 1982 (w) |
| $[Mn(CO)_4PPh_3]_2$ | 1983 (vw), 1954 (s) |
| $[Mn(CO)_4P(OPh)_3]_2$ | 2002 (vw), 1979 (s) |
| $[Mn(CO)_4PEt_3]_2$ | 1970 (vw), 1944 (s) |
| $[Mn(CO)_4PMe_2Ph]_2$ | 1972 (vw), 1947 (s) |
| $Mn_2(CO)_9PPh_3$ | 2090 (w), 2010 (m), 1991 (s), 1970 (w), 1934 (m) |
| $Mn_2(CO)_9P(OPh)_3$ | 2097 (w), 2020 (m), 1997 (vs), 1975 (w), 1953 (m) |
| $Mn_2(CO)_9(\eta^1$-DPPE) | 2089 (w), 2010 (m), 1991 (s), 1970 (w), 1934 (w) |

[a] In THF solution.

## Experimental Section

**Materials.** Triphenylphosphine (Matheson, Coleman and Bell) and tri-*p*-tolylphosphine (M and T) were recrystallized from ethanol prior to use. All the other phosphines were prepared from either trichlorophosphine (Mallinckrodt), dichlorophenylphosphine (Pressure Chemical), or chlorodiphenylphosphine (Aldrich) with the appropriate Grignard or organolithium reagent.[53] Dimanganese decacarbonyl (Strem) was resublimed prior to use; $Mn_2(CO)_8(PPh_3)_2$, $Mn_2(CO)_8[P(OPh)_3]_2$, $Mn_2(CO)_8(PEt_3)_2$, and $Mn_2(CO)_8(PPhMe_2)_2$ were prepared either by refluxing a solution of $Mn_2(CO)_{10}$ and 2 equivalents of the corresponding phosphine in *n*-butyl alcohol for 24 h[16] or by irradiating a solution

---

(44) Calculated from the difference $E_{1/2} - E_p^{ox.}$ for $Mn(CO)_4PPh_3^-$ in Table VI.[43]

(45) See also: Richmond, M. G.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 656.

(46) (a) Osborne, A. G.; Stiddard, M. H. B. *J. Chem. Soc.* **1965**, 700. (b) Snow, M. R.; Stiddard, M. H. B. *J. Chem. Soc. A.* **1966**, 777.

(47) The driving force for electron transfer between $Mn(CO)_4PPh_3^-$ and $Mn(CO)_6^+$ is endergonic by 0.67 V or 15 kcal mmol$^{-1}$, obtained simply as the difference $\Delta E$ of the redox potentials in eq 14 and 15.

(48) For similar observations in other systems, see: (a) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121. (b) Dessy, R. E.; Pohl, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 2005. See also ref 6 and 4d.

(49) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966; **1957**, *26*, 867; **1965**, *43*, 679. For a review, see: Cannon, R. D. *Electron Transfer Mechanisms*; Butterworths: London, **1980**.

(50) For the strong ion pairing of carbonylmetal ions in solvents such as THF, see: (a) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chim. Acta* **1971**, *5*, 247. (b) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R. *J. Organomet. Chem.* **1980**, *202*, C68. (c) Darensbourg, M. Y.; Hanckel, J. M. *J. Organomet. Chem.* **1981**, *217*, C9. (d) Drew, D.; Darensbourg, M. Y.; Darensbourg, D. J. *J. Organomet. Chem.* **1975**, *85*, 73. (e) Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics* **1984**, *3*, 871.

(51) The strong steric inhibition is shown by the slow reaction between $Mn(CO)_4PPh_3^-$ and $Mn(CO)_5P(o\text{-anisyl})_3^+$ which yields a mixture of Mn–Mn dimers [including $Mn_2(CO)_{10}$] as well as $Mn(CO)_5^-$ (unpublished results).

(52) Unfortunately, isotopic $Mn^{55}$ is not readily available for independent labeling studies on the parent ion pair.

(53) See ref 13c.

**Table VIII. Carbonyl Stretching Frequencies of Carbonylmanganese Cations $Mn(CO)_5L^{+a}$**

| L | $\nu_{CO}$, cm$^{-1}$ |
|---|---|
| $PPh_3$ | 2144 (w), 2073 (sh), 2055 (s) |
| $P(p\text{-tol})_3$ | 2143 (w), 2090 (sh), 2053 (s) |
| $PPh_2Et$ | 2143 (w), 2091 (sh), 2052 (s) |
| $PPhEt_2$ | 2142 (s), 2088 (sh), 2050 (s) |
| $PEt_3$ | 2141 (w), 2083 (sh), 2049 (s) |
| $PPh_2Me$ | 2144 (w), 2093 (sh), 2053 (s) |
| $PPhMe_2$ | 2143 (w), 2091 (sh), 2053 (s) |
| py | 2155 (w), 2066 (s), 2043 (m) |
| $CH_3CN$ | 2163 (w), 2075 (s), 2051 (m) |
| CO | 2097 |

[a] In acetonitrile solution as $PF_6^-$ salt, except for L = CO as $BF_4^-$ salt.

**Table IX. Carbonyl Stretching Frequencies of Carbonylmanganates $Mn(CO)_4P^{-a}$**

| P | solv | $\nu_{CO}$, cm$^{-1}$ |
|---|---|---|
| CO | THF | 1898 (s), 1872 (sh), 1864 (s), 1831 (w) |
| | $CH_3CN$ | 1902 (m), 1965 (s) |
| $PPh_3$ | THF | 1945 (m), 1854 (w), 1827 (s), 1777 (w) |
| $P(OPh)_3$ | THF | 1964 (m), 1877 (w), 1850 (s), 1801 (w) |
| ($\eta^1$-DPPE) | THF | 1942 (m), 1853 (w), 1822 (s), 1772 (w) |

[a] As the sodium salt.

of $Mn_2(CO)_{10}$ and the phosphine in cyclohexane with a 450-W medium-pressure Hg lamp (Hanovia) for 6–18 hours.[17,19] The products were collected and recrystallized from a mixture of benzene and hexane at 0 °C. The carbonyl stretching frequencies in the IR spectra are listed in Table VII. $Mn_2(CO)_9PPh_3$ was prepared as previously described[54,55] and purified by chromatography on a foil-wrapped silica gel column with a 1:2 v/v mixture of toluene and hexane as the eluent.[54] $Mn_2(CO)_9P(OPh)_3$ was similarly prepared by photolysis of $Mn_2(CO)_{10}$ in the presence of 1 equiv of $P(OPh)_3$. It was separated on a foil-wrapped silica gel column with hexane as the eluent. UV: (cyclohexane) $\lambda_{max}$ 352, 414 nm (lit.[56] 351, 415 nm). The carbonylmanganese(I) cations $Mn(CO)_6^+BF_4^-$,[15] $Mn(CO)_5(CH_3CN)^+PF_6^-$,[12,16] and $Mn(CO)_5(py)^+PF_6^-$,[12,16] and all the phosphine analogues $Mn(CO)_5P^+PF_6^-$ were generally prepared as described in the literature. Thus $Mn(CO)_5(CH_3CN)^+PF_6^-$ [12,16] was prepared by the cleavage of $Mn_2(CO)_{10}$ by $NOPF_6$ in acetonitrile. This derivative was used as the starting material for the preparation of $Mn(CO)_5P^+PF_6^-$ and $Mn(CO)_5(py)^+PF_6^-$. Typically $Mn(CO)_5(CH_3CN)^+PF_6^-$ was dissolved in acetone together with 1.1 equiv of phosphine, and the mixture was stirred at room temperature in the dark for 24 h under argon. Purification was effected by recrystallization from a mixture of acetone and ethyl ether. The carbonyl stretching frequencies are listed in Table VIII. The carbonylmanganese(−I) anions $Mn(CO)_5^-$,[15] $Mn(CO)_4PPh_3^-$,[12] and $Mn(CO)_3P(OPh)_3^-$ were prepared from $Mn_2(CO)_{10}$, $Mn_2(CO)_8(PPh_3)_2$, and $Mn_2(CO)_8[P(OPh)_3]_2$, respectively, by sodium amalgam reduction. Thus sodioamalgam from 0.11 g of sodium in 1 mL of mercury was used immediately by treatment with $Mn_2(CO)_8L_2$ in either THF or acetonitrile for 1–2 h under argon. Excess mercury and amalgam were removed, and the mixture was filtered through Celite under an argon atmosphere. The complete conversion of the dimer to the anion was monitored by IR analysis (Table IX).

Tetrahydrofuran was purified by distillation from sodiobenzophenone and stored in a Schlenk flask under an argon atmosphere. Acetonitrile (Fisher) was stirred over potassium permanganate for 12 h at room temperature, and the mixture was refluxed for an additional hour. After filtration, the clear liquid was treated with diethylenetriamine. Phosphorus pentoxide was added, and the mixture was refluxed for 5 h. Fractionation under argon afforded pure acetonitrile which was stored under argon in a Schlenk flask.

All manipulations were carried out under an argon atmosphere with the aid of standard Schlenk line techniques. $^1H$ and $^{31}P$ NMR spectra were recorded on a JEOL FX 90Q FT spectrometer operating at 89.55 and 36.23 MHz, respectively. IR spectra were obtained with NaCl cells (0.1 mm) using a Nicolet 10 DX FT spectrometer with 4 cm$^{-1}$ resolution, unless indicated otherwise.

**Ion-Pair Couplings. General Procedure.** The coupling reaction between carbonylmanganese cations and anions was carried out by using the techniques previously described.[12] Typically a $1 \times 10^{-2}$ M solution of cation was made up in 5 mL of THF under an argon atmosphere. A separate $1 \times 10^{-2}$ M solution of anion was made up in THF. A 5-mL aliquot was added to the cation solution with the aid of a hypodermic syringe under an argon atmosphere. The course of the coupling was monitored by periodically extracting a sample for IR analysis until the starting material was completely consumed. The products of coupling were identified by spectral comparisons with those of authentic samples or relative to those reported in the literature. They were quantified by comparison with calibration curves constructed from the IR absorbance vs. concentration of the unique band. The Mn–Mn dimers were quantified by the principal carbonyl bands ($\nu$(CO)): for $Mn_2(CO)_{10}$, 2009 cm$^{-1}$; $Mn_2(CO)_8(PPh_3)_2$, 1954 cm$^{-1}$; $Mn_2(CO)_8[P(OPh)_3]_2$, 1979 cm$^{-1}$; $Mn_2(CO)_8(PEt_3)$, 1944 cm$^{-1}$; $Mn_2(CO)_8(PMe_2Ph)_2$, 1947 cm$^{-1}$; $Mn_2(CO)_9PPh_3$, 1991 cm$^{-1}$; $Mn_2(CO)_9P(OPh)_3$, 1997 cm$^{-1}$ (Table VII). In every case the calibration curve was linear (correction coefficient > 0.999). The manganese hydride was identified and quantified by its characteristic high-energy band.

The ion-pair couplings in Tables I–III are listed individually below, so as to emphasize their distinctive behavior.

**$Mn(CO)_5^-$.** The addition of 5 mL of $1 \times 10^{-2}$ M $NaMn(CO)_5$ in THF to 5 mL of $1 \times 10^{-2}$ Mn $Mn(CO)_5L^+PF_6^-$ ($BF_4^-$) in THF under argon resulted in the formation of mainly $Mn_2(CO)_{10}$. When L = CO, $CH_3CN$, py, $PPh_3$, $P(p\text{-tol})_3$, or $PPh_2Me$, the IR spectrum recorded within 5 min showed no cation and anion absorptions, and it was unchanged even after several hours. The couplings of the other cations were slower and showed variable reaction times (Table I). The complete disappearance of cation and anion was monitored by IR analysis at periodic intervals. $Mn_2(CO)_{10}$ and $Mn_2(CO)_8L_2$ were identified by their principal IR bands: $Mn_2(CO)_{10}$, 2009.0 cm$^{-1}$; $Mn_2(CO)_8(PPh_3)_2$, 1954 cm$^{-1}$; $Mn_2(CO)_8[P(p\text{-tol})_3]_2$, 1953 cm$^{-1}$;[12] $Mn_2(CO)_8(PPh_2Et)_2$, 1950 cm$^{-1}$;[12] $Mn_2(CO)_8(PPhEt_2)_2$, 1947 (cm$^{-1}$;[12] $Mn_2(CO)_8(PEt_3)_2$, 1945 cm$^{-1}$; $Mn_2(CO)_8(PPh_2Me)_2$, 1952 cm$^{-1}$;[12] $Mn_2(CO)_8(PPhMe_2)_2$, 1948.0 cm$^{-1}$. $Mn_2(CO)_{10}$ was quantified with the aid of the correlation curve for the absorbance at 2009.0 cm$^{-1}$ vs. concentration. $Mn_2(CO)_8(PPh_3)_2$, $Mn_2(CO)_8(PEt_3)_2$, and $Mn_2(CO)_8(PPhMe_2)_2$ were quantified with similar correlation curves obtained from authentic samples. For the analysis of the other dimers, the correlation was based on the curve for the analogous dimer: $Mn_2(CO)_8(PPh_3)_2$ for $Mn_2(CO)_8P(p\text{-tol})_3$ and $Mn_2(CO)_8(PPh_2Et)$, $Mn_2(CO)_8(PEt_3)_2$ for $Mn_2(CO)_8(PEt_2Ph)_2$, and $Mn_2(CO)_8PPhMe_2$ for $Mn_2(CO)_8PPh_2Me$. The manganese hydrides were analyzed by using their highest energy carbonyl band. For quantification, the correlation curve from $HMn(CO)_4PPh_3$ was used ($\nu$(CO)): for $HMn(CO)_4PPh_3$, 2060 cm$^{-1}$;[12] $HMn(CO)_4P(p\text{-tol})_3$, 2058 cm$^{-1}$;[12] $HMn(CO)_4PPh_2Et$, 2059 cm$^{-1}$;[12] $HMn(CO)_4PPhEt_2$, 2057 cm$^{-1}$;[12] $HMn(CO)_4PEt_3$, 2055 cm$^{-1}$;[12] $HMn(CO)_4PPh_2Me$, 2061 cm$^{-1}$;[12] $HMn(CO)_4PPhMe_2$, 2058 cm$^{-1}$,[12] [compare $\nu_{CO}$ for $HMn(CO)_5$, 2118.0 cm$^{-1}$]. The manganese hydrides were also identified by $^1H$ NMR analysis in $C_6D_6$ as solvent: $HMn(CO)_4PPh_3$, −6.88 ppm (d, $J_{PH}$ = 34.4 Hz); $HMn(CO)_4P(p\text{-tol})_3$, −6.80 ppm (d, $J_{PH}$ = 26.9 Hz);[12] $HMn(CO)_4PPh_2Et$, −7.28 ppm (d, $J_{PH}$ = 36.5 Hz);[12] $HMn(CO)_4PPhEt_2$, −7.79 ppm (d, $J_{PH}$ = 38.8 Hz);[12] $HMn(CO)_4PEt_3$, −7.88 ppm ($J_{PH}$ = 37.4 Hz);[12] $HMn(CO)_4PMePh_2$, −7.33 ppm ($J_{PH}$ = 39.1 Hz);[12] $HMn(CO)_4PMe_2Ph$, −7.67 ppm (d, $J_{PH}$ = 39.1 Hz).[12] When L = $PPh_2Et$, $PPhEt_2$, and $PPh_2Me$ the small amounts of $Mn_2(CO)_9L$ were not distinguished by IR analysis. They were detected in trace amounts by TLC with a 1:4 mixture of THF and hexane as the eluent ($R_f$): for $Mn_2(CO)_9PPh_2Et$, 0.46; $Mn_2(CO)_9PPhEt_2$, 0.48; $Mn_2(CO)_9PPh_2Me$, 0.43. When L was $PEt_3$ or $PPhMe_2$ the spectral subtraction of $Mn_2(CO)_{10}$ and $Mn_2(CO)_8L_2$ revealed the IR spectrum of $Mn_2(CO)_9L$ which had the same pattern as that for $Mn_2(CO)_9PPh_3$ with the principal band at 1990 cm$^{-1}$. Due to the severe overlap with the other products, quantitative analysis was effected by TLC using a 4:1

---

(54) Fawcett, J. P.; Poë, A. J.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *61*, 315.

(55) Wawersik, H.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1966**, 366.

(56) Jackson, R. A.; Poë, A. *Inorg. Chem.* **1978**, *17*, 997.

mixture of hexane and THF as the eluent ($R_f$): for $Mn_2(CO)_9PEt_3$, 0.5; $Mn_2(CO)_9PPhMe_2$, 0.47. The effect of added ligand was studied in the coupling with $Mn(CO)_5PEt_3^+$ in which 5 mL of $1 \times 10^{-2}$ Mn $NaMn(CO)_5$ in THF was added under argon to 5 mL of $1 \times 10^{-2}$ M $Mn(CO)_5Et_3P^+$ in THF with 15 μL (0.1 mmol) of triethylphosphine. The reaction was complete within 2 h. The products were $Mn_2(CO)_8(PEt_3)_2$ (40%), $HMn(CO)_4PEt_3$ (20%), and $HMn(CO)_3(PEt_3)_2$ (20%). $HMn(CO)_3(PEt_3)_2$ was identified by its low-energy band at 1894 $cm^{-1}$. Compare $HMn(CO)_3(PPh_3)_2$, 1917 $cm^{-1}$,[12] and $HMn(CO)_3[(n\text{-}Bu)_3P]_2$, 1891 $cm^{-1}$.

**$Mn(CO)_4[P(OPh)_3]^-$.** A 5-mL aliquot of $1 \times 10^{-2}$ M $Mn(CO)_4P(OPh)_3^-Na^+$ in THF was added to 5 mL of $1 \times 10^{-2}$ M $Mn(CO)_5L^+PF_6^-$ ($BF_4^-$). The couplings were complete within 5 min, except when L = $PEt_3$ and $PEt_2Ph$ which required ~60 min for completion. When L = CO, pyridine, or $CH_3CN$, products were $Mn_2(CO)_{10}$, $Mn_2(CO)_9P(OPh)_3$, and $Mn_2(CO)_8[P(OPh)_3]_2$. Quantification of these products was achieved by spectral substration from the IR spectrum of the reaction mixture. The amount of each dimer was calculated from the correlation curves using their principal carbonyl bands. When L = $PPh_3$ and $PPh_2Et$, $HMn(CO)_4P(OPh)_3$[20b] was detected by its high-energy band at $\nu_{CO}$ = 2077 $cm^{-1}$. When L = $P(p\text{-tol})_3$, $PPhEt_2$, $PPhMe_2$, or $PEt_3$, $HMn(CO)_4L$ was observed in addition to $HMn(CO)_4P(OPh)_3$ but were not quantified. When L = phosphines, three strong carbonyl absorptions were observed. Two of them were ascribed to $Mn_2(CO)_8[P(OPh)_3]_2$ and $Mn_2(CO)_8L_2$ by their principal bands. The other absorption was intermediate between those of the two symmetrical dimers. TLC [4:1 v/v hexane/THF] also showed a strong band between those of the two dimers ($R_f$): for $Mn_2(CO)_8(PPh_3)_2$, 0.28; $Mn_2(CO)_8(PPh_3)[P(OPh)_3]$, 0.30; $Mn_2(CO)_8[P(OPh)_3]_2$, 0.37. When L = $PPh_3$, the spectral substaction of $Mn_2(CO)_8(PPh_3)_2$ and $Mn_2(CO)_8[P(OPh)_3]_2$ from the IR spectrum of the reaction mixture yielded a residual spectrum which was reminiscent of $Mn_2(CO)_8P_2$ with $D_{4d}$ symmetry, containing one very weak and one very strong band [$\nu_{CO}$ 1969 (vs) and 1990 $cm^{-1}$(vw)]. The same type of spectrum was obtained from the photoreaction of $Mn_2(CO)_8(PPh_3)_2$ and $Mn_2(CO)_8[P(OPh)_3]_2$ using 11 mg ($1.25 \times 10^{-5}$ mol) of $Mn_2(CO)_8(PPh_3)_2$ and 12 mg ($1.25 \times 10^{-5}$ mol) of $Mn_2(CO)_8[P(OPh)_3]_2$ dissolved in 5 mL of THF in a Schlenk tube under argon. After this solution was irradiated with the 450-W Hanovia lamp for 30 min, it showed three strong carbonyl bands at 1979, 1969, and 1954 $cm^{-1}$, which yielded a mixture of $Mn_2(CO)_8(PPh_3)_2$–$Mn_2(CO)_8(PPh_3)[P(OPh)_3]$–$Mn_2(CO)_8[P(OPh)_3]_2$ in a relative ratio of 1.1:1.2:1.0. This spectrum was well correlated with the mixture of coupling products from $Mn(CO)_4P(OPh)_3^-$ and $Mn(CO)_5PPh_3^+$. In order to isolate the mixed dimer, we photolyzed a solution containing 21.5 mg ($2.5 \times 10^{-5}$ mol) of $Mn_2(CO)_8(PPh_3)_2$ and 47.7 mg ($5 \times 10^{-5}$ mol) of $Mn_2(CO)_8[P(OPh)_3]_2$ in 5 mL of THF under the conditions as described above. The cross dimer was separated by TLC using a 4:1 v/v mixture of hexane and THF in the dark; $\nu_{CO}$ for $Mn_2(CO)_8(PPh_3)[P(OPh)_3]$ in THF: 1969.4 (vs) and 1990.7 (vw) $cm^{-1}$ at 1 $cm^{-1}$ spectral resolution. Anal. Calcd for $C_{44}H_{30}Mn_2O_{11}P_2$: C, 58.30; H, 3.34. Found: C, 58.00; H, 3.68. The related cross dimers $Mn_2(CO)_8[P(OPh)_2]L$ were obtained by a similar procedure, and the principal carbonyl bands were as follows ($\nu_{Co}$ (THF)): L = $P(p\text{-}CH_3C_6H_4)_3$, 1968 $cm^{-1}$; L = $PPh_2Et$, 1968 $cm^{-1}$; L = $PPhEt_2$, 1966 $cm^{-1}$; L = $PEt_3$, 1966 $cm^{-1}$; L = $PPh_2Me$, 1966 $cm^{-1}$; L = $PPhMe_2$, 1963 $cm^{-1}$.

**$Mn(CO)_4PPh_3^-$.** The highly air-sensitive $Mn(CO)_4PPh_3^-$ was generated by the sodioamalgam reduction of $Mn_2(CO)_8(PPh_3)_2$ in THF under an argon atmosphere. A 5-mL aliquot of $1 \times 10^{-2}$ M $Mn(CO)_4PPh_3^-$ was added to 5 mL of $1 \times 10^{-2}$ M $Mn(CO)_5L^+$ in THF. The ensuing reactions were all very rapid with L = CO, py, and MeCN, and complete within the time the initial IR spectrum was recorded. The products always consisted of a mixture of $Mn_2(CO)_{10}$, $Mn_2(CO)_9PPh_3$, and $Mn_2(CO)_8(PPh_3)_2$. These $Mn_2$ dimers were quantified with the aid of correlation curves based on the principal carbonyl bands. When L = $PPh_3$, the coupling reaction was complete within 5 min and yielded $Mn_2(CO)_8(PPh_3)_2$ as the major product, together with traces of $Mn(CO)_5^-$. The reaction was unaffected by the presence of 0.3 M TBAP. Furthermore when $Mn(CO)_4PPh_3^-$ and $Mn(CO)_5PPh_3^+$ were mixed at -78 °C, the same coupling occurred within the time required for the initial IR spectrum. In a control experiment, it was found that $5 \times 10^{-3}$ M $Mn(CO)_4PPh_3^-$ reacted with an equimolar amount of $Mn_2(CO)_9PPh_3$ to yield $Mn_2(CO)_8(PPh_3)_2$ and $Mn(CO)_5^-$ in 30% conversion within 5 min. After 90 min, only $Mn(CO)_5^-$, $Mn_2(CO)_8(PPh_3)_2$, and residual $Mn_2(CO)_9PPh_3$ were observed in the IR spectrum. The other phosphine-substituted cations reacted with $Mn(CO)_4PPh_3^-$ in a similar manner, the coupling being complete upon mixing. The IR spectrum of the reaction mixture consisted of a single intense band together with a weak one. The prinicpal band was not resolved into those of the component dimers at a spectral resolution of 1 $cm^{-1}$. Accordingly, the mixture was chromatographed on silica gel with a 4:1 v/v mixture of hexane and THF as the eluent and consistently separated into three components given individually below. **$Mn(CO)_5PPh_2Et^+$.** $Mn_2(CO)_8(PPh_3)_2$: 11.2 mg ($R_f$ 0.28; $\nu_{CO}$ = 1954.0 (vs), 1981.1 (vw) $cm^{-1}$. $Mn_2(CO)_8(PPh_3)(PPh_2Et)$: 18.6 mg ($R_f$ 0.30); mp 106–108 °C dec; $\nu_{CO}$ = 1952.1 (vs), 1981.0 (vw) $cm^{-1}$. Anal. Calcd for $C_{40}H_{30}Mn_2O_8P_2$: C, 59.28; H, 3.73. Found: C, 60.48; H, 4.20. $Mn_2(CO)_8(PPh_2Et)_2$: 13.7 mg ($R_f$ 0.32); $\nu_{CO}$ = 1952.1 (vs) 1981.0 (vw) $cm^{-1}$. **$Mn(CO)_5PPhEt_2^+$.** $Mn_2(CO)_8(PPh_3)_2$: 14.6 mg ($R_f$ 0.28); $\nu_{CO}$ = 1954.0 (vs), 1981 (vs) $cm^{-1}$. $Mn_2(CO)_8(PPh_2)(PPhEt_2)$: 10.7 mg ($R_f$ 0.33); mp 119–125 °C dec; $\nu_{CO}$ = 1950.2 (vs), 1979.1 (vs) $cm^{-1}$. Anal. Calcd for $C_{36}H_{30}Mn_2O_8P_2$: C, 56.71; H, 3.97. Found: C, 55.87; H, 4.33. $Mn_2(CO)_8(PPhEt_2)_2$: 6.3 mg ($R_f$ 0.39); $\nu_{CO}$ = 1946.3 (vs), 1977 (vs) $cm^{-1}$. **$Mn(CO)_5PEt_3^+$.** $Mn_2(CO)_8(PPh_3)_2$: 3.4 mg, ($R_f$ 0.28); $\nu_{CO}$ = 1954.0 (vs), 1981.1 (vw) $cm^{-1}$; $^{31}P$ NMR ($C_6D_6$) 75.67(s) ppm. $Mn_2(CO)_8(PPh_3)(PEt_3)$: 4.3 mg ($R_f$ 0.37); mp 128–132 °C dec; $\nu_{CO}$ = 1950.2 (vs), 1975.2 $cm^{-1}$ (vw) $cm^{-1}$; $^{31}P$ NMR ($C_6D_6$) 75.3 (s), 58.0 (s) ppm. $Mn_2(CO)_8(PEt_3)_2$ (vide infra) ($R_f$ 0.47): $\nu_{CO}$ = 1944.4 (vs), 1969.5 (vw) $cm^{-1}$; $^{31}P$ NMR ($C_6D_6$) 58.50 (s) ppm. The TLC band for $Mn_2(CO)_8(PEt_3)_2$ was contaminated with $HMn(CO)_4PPh_3$, the concentration of which was estimated by $^1H$ NMR analysis with *p*-dimethoxybenzene as the internal standard. The cross-coupled dimer $Mn_2(CO)_8(PPh_3)(PEt_3)$ [Anal. Calcd for $C_{32}H_{30}Mn_2O_8P_2$: C, 53.8; H, 4.23. Found: C, 52.7; H, 4.61] was also identical with the product obtained from the photolysis of a mixture of $Mn_2(CO)_8(PPh_3)_2$ and $Mn_2(CO)_8(PEt_3)_2$. **$Mn(CO)_5PPh_2Me^+$.** $Mn_2(CO)_8(PPh_3)_2$: 6.7 mg ($R_f$ 0.28); $\nu_{CO}$ = 1954.0 (vs), 1981.0 (vw) $cm^{-1}$. $Mn_2(CO)_8(PPh_3)(PPh_2Me)$: 14.0 mg ($R_f$ 0.31); mp 117–120 °C dec; $\nu_{CO}$ = 1952.1 (vs), 1979.1 (vw) $cm^{-1}$. $Mn_2(CO)_8(PPh_2Me)_2$: 12.1 mg ($R_f$ 0.34); $\nu_{CO}$ = 1950.2 (vs), 1979.1 (vw), $cm^{-1}$. **$Mn(CO)_5PPhMe_2^+$.** $Mn_2(CO)_8(PPh_3)_2$: 8.2 mg ($R_f$ 0.28); $\nu_{C}O$ = 1954.0 (vs), 1981.0 (vw) $cm^{-1}$. $Mn_2(CO)_8PPh_3(PPhMe_2)$: 16.9 mg ($R_f$ 0.34); mp 116–123 °C dec; $\nu_{CO}$ = 1952.0 (vs), 1978.4 (vw) $cm^{-1}$. $Mn_2(CO)_8(PPhMe_2)_2$: 6.7 mg ($R_f$ 0.42); $\nu_{CO}$ = 1948.2 (vs), 1979.0 (vw) $cm^{-1}$. When L = P ($p\text{-}CH_3C_6H_4)_3$, three spots with $R_f$ 2.8–3.1 were distinctly visible but were too overlapped for effective separation. The addition of 0.1 mmol of $PEt_3$ to the coupling of $5 \times 10^{-3}$ M $Mn(CO)_4PPh_3^-$ and $5 \times 10^{-3}$ M $Mn(CO)_5PEt_3^+$ in THF had no effect on the products as determined by either IR or TLC analysis. Furthermore the addition of 0.1 mmol of $P(OMe)_3$ under comparable conditions afforded a mixture which had essentially the same IR spectrum as that from $Mn(CO)_4PPh_3^-$ and $Mn(CO)_5PEt_3^+$, with the exception of a shoulder at 1960–1970 $cm^{-1}$. The $^1H$ NMR spectrum showed three hydrides: $HMn(CO)_4PPh_3$, δ -6.88 (*d*, $J_{PH}$ 34.4 Hz), $HMn(CO)_4PEt_3$, δ -7.88 (d, $J_{PH}$ = 37.4 Hz), and an unidentified species, δ -6.66 (d, $J_{PH}$ = 31.5 Hz). Compare $HMn(CO)_4P(OMe)_3$, δ -7.8 (d, $J_{PH}$ = 50 Hz).[20b]

**Ion-Pair Coupling with $Mn(CO)_4(\eta^1\text{-DPPE})^-$.** The highly air-sensitive $Mn(CO)_4(\eta^1\text{-DPPE})^-Na^+$ was prepared by the reduction of $Mn(CO)_3(\eta^2\text{-DPPE})Br$[57] with excess sodioamalgam under an atmosphere of CO. Excess amalgam was removed by filtration through Celite under an argon atmosphere, and the solvent (with CO) was removed in vacuo. Fresh THF was added to make up a $1 \times 10^{-2}$ M solution of $Mn(CO)_4(\eta^1\text{-DPPE})^-$, the IR spectrum of which was almost identical with that of $Mn(CO)_4PPh_3^-$. Upon the treatment of this solution with an equivalent amount of $Mn(CO)_5(py)^+$ or $Mn(CO)_5(NCMe)^+$, an immediate reaction ensued to produce $Mn_2(CO)_{10}$ (~30%), $HMn(CO)_3(\eta^2\text{-DPPE})$ (~35%), and $Mn_2(CO)_9(\eta^1\text{-DPPE})$ (~15%). The IR spectrum of $Mn_2(CO)_9(\eta^1\text{-DPPE})$ was very similar to that of $Mn_2(CO)_9PPh_3$. The IR spectrum of $HMn(CO)_3(\eta^2$-

---

[57] (a) Colton, R.; McCormick, M. J. *Aust. J. Chem.* **1976**, *29*, 1657. See also: (b) Angelici, R. J.; Basolo, F.; Poë, A. J. *J. Am. Chem. Soc.* **1963**, *85*, 2115.

DPPE) with $\nu_{CO}$ = 1994.9 (m) and 1906.1 (m) cm$^{-1}$ was identical with that reported earlier.[58]

**Acknowledgment.** We thank the National Science Foundation and Robert A. Welch Foundation for financial support.

**Registry No.** I·($BF_4$), 15557-71-8; IIa·($PF_6$), 37504-44-2; IIb($BF_4$), 96412-38-3; IIIa·($PF_6$), 54039-57-5; IIIb·($PF_6$), 54039-59-7; IIIc·($PF_6$), 104350-97-2; IIId·($PF_6$), 104350-98-3; IIIe·($PF_6$), 68166-17-6; IIIf·($PF_6$), 104350-99-4; IIIg·($PF_6$), 54039-52-0; $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(cO)_9(PPh_3)$, 14592-26-8; $Mn_2(CO)_9P(OPh)_3$, 24476-72-0; $Mn_2(CO)_9PPh_2Me$, 61943-58-6; $Mn_2(CO)_9PEt_3$, 109335-73-1; $Mn_2(CO)_9PPhMe_2$, 50540-29-9; $Mn_2(CO)_9(\eta'$-DPPE), 109335-87-7; $Mn_2(CO)_8(PPh_3)_2$, 10170-70-4; $Mn_2(CO)_8[P(OPh)_3]_2$, 15529-62-1; $Mn_2(CO)_8(PEt_3)_2$, 15529-60-9; $Mn_2(CO)_8(PMe_2Ph)_2$, 55029-78-2; $Mn_2(CO)_8[P(p\text{-tol})_3]_2$, 63588-37-4; $Mn_2(CO)_8(PPh_2Et)_2$, 15444-76-5; $Mn_2(CO)_8(PPhEt_2)_2$, 15444-75-4; $Mn_2(CO)_8(PPh_2Me)_2$, 63393-52-2; $Mn_2(CO)_8(PPh_3)[P(OPh)_3]$, 109335-75-3; $Mn_2(CO)_8[P(OPh)_3]P(p\text{-}CH_3C_6H_4)_3$, 109335-76-4; $Mn_2(CO)_8[P(OPh)_3]PPh_2Et$, 109335-77-5; $Mn_2(CO)_8[P(OPh)_3]PPhEt_2$, 109335-78-6; $Mn_2(CO)_8[P(OPh)_3]PEt_3$, 109335-79-7; $Mn_2(CO)_8[P(OPh)_3]PPh_2Me$, 109335-80-0; $Mn_2(CO)_8[P(OPh)_3]PPhMe_2$, 109335-81-1; $Mn_2(CO)_8(PPh_3)(PPh_2Et)$, 109335-82-2; $Mn_2(CO)_8(PPh_3)(PPhEt_2)$, 109335-83-3; $Mn_2(CO)_8(PPh_3)(PEt_3)$, 109335-84-4; $Mn_2(CO)_8(PPh_3)(PPh_2Me)$, 109335-85-5; $Mn_2(CO)_8(PPh_3)(PPhMe_2)$, 109363-36-2; Mn(CO)6·, 104350-83-6; $NaMn(CO)_5$, 13859-41-1; $HMn(CO)_4PPh_3$, 16925-29-4; $HMn(CO)_4P(p\text{-tol})_3$, 104419-62-7; $HMn(CO)_4PPh_2Et$, 92816-72-3; $HMn(CO)_4PPhEt_2$, 104350-79-0; $HMn(CO)_4PEt_3$, 68199-71-3; $HMn(CO)_4PPh_2Me$, 104350-80-3; $HMn(CO)_4PPhMe_2$, 104419-63-8; $Mn(CO)_4P(OPh)_3^-Na^+$, 59778-90-4; $M(CO)_4PPh_3^-$, 53418-18-1; $Mn(CO)_4(\eta^1$-DPPE)$^-Na^+$, 109335-86-6; $Mn(CO)_4(PPh_3)$·, 14971-47-2; $HMn(CO)_3(PEt_3)_2$, 109335-74-2; $HMn(CO)_3(\eta^2$-DPPE), 36352-75-7; $Mn(CO)_3(\eta^2$-DPPE)Br, 37523-64-1; $Mn(CO)_2(\eta^2$-DPPE)$_2^+Cl^-$, 14239-02-2; Mn, 7439-96-5.

---

[58] Darensbourg, D. J.; Froelich, J. A. *Inorg. Chem.* **1978**, *17*, 3300.

---

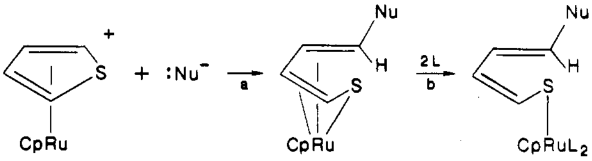
# Model Studies of Thiophene Hydrodesulfurization Using ($\eta$-Thiophene)Ru($\eta$-$C_5H_5$)$^+$: Reactions Leading to C–S Bond Cleavage

George H. Spies and Robert J. Angelici*

*Department of Chemistry and Ames Laboratory,[1] Iowa State University, Ames, Iowa 50011*

*Received November 10, 1986*

As models for the adsorption and reactions of thiophenes on hydrodesulfurization (HDS) catalysts, the thiophene $\pi$-complexes ($\eta$-thiophene)RuCp$^+$, where the thiophene is thiophene, 2-methylthiophene, or 2,5-dimethylthiophene and Cp = $\eta$-$C_5H_5$, have been prepared by reactions of these thiophenes with $CpRu(NCMe)_3^+$ or with $CpRu(PPh_3)_2Cl$ and $AgBF_4$. Nucleophilic (Nu = $MeO^-$, $MeS^-$, $EtS^-$, $i$-$PrS^-$, and $CH(CO_2Me)_2^-$) addition (step a) to a carbon adjacent to the S in the thiophene and 2-methylthiophene $\pi$-ligands results in cleavage of a C–S bond to give the product with a butadienethiolate ligand coordinated through the sulfur and all four unsaturated carbon atoms. Upon reaction (step b) with phosphines (L), the two olefins are displaced leaving the butadienethiolate ligand coordinated only via the sulfur in the product $CpRu(L)_2$(*cis*,*trans*-SC(R)=CHCH=CH(Nu)). Step a provides a basis for understanding how C–S bond cleavage might occur in the catalytic HDS of thiophene on heterogeneous catalysts.



## Introduction

An understanding of the catalytic hydrodesulfurization (HDS) of organosulfur compounds in petroleum is a formidable problem of continuing interest.[2] Despite decades of research primarily focused on the reactions of individual sulfur-containing compounds over industrially relevant catalysts,[3] most fundamental aspects of these important reactions have yet to be established. Several mechanistic proposals for the desulfurization of organosulfur compounds such as thiophene, benzothiophene, and dibenzothiophene have been suggested; however, there is little

---

[1] Ames Laboratory is 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 Office of Basic Energy Sciences, Chemical Sciences Division.

[2] (a) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (b) Mitchell, P. C. H. *Catalysis* (*London*) **1977**, *1*, 204. (c) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245.

[3] (a) Moldavskii, B. L.; Prokoptshuk, N. J. *J. Appl. Chem. USSR* (*Engl. Transl.*) **1932**, *5*, 619. (b) Moldavskii, B. L.; Kumari, Z. I. *J. Gen. Chem. USSR* (*Engl. Transl.* **1934**, *4*, 298. (c) Griffith, R. H.; March, J. D. F.; Newling, W. B. S. *Proc. R. Soc. London, Ser. A* **1949**, *197*, 194. (d) Kirsch, F. W.; Heinemann, H.; Stevenson, D. H. *Ind. Eng. Chem.* **1957**, *49*, 646. (e) Komarewsky, V. I.; Knaggs, E. A. *Ind. Eng. Chem.* **1951**, *43*, 1415. (f) Owens, P. J.; Amberg, C. H. *Can. J. Chem.* **1962**, *40*, 941, 947. (g) Desikan, P.; Amberg, C. H. *Ibid.* **1963**, *41*, 1966. (h) *Ibid.* **1964**, *42*, 843. (i) Kolboe, S.; Amberg, C. H. *Ibid.* **1966**, *44*, 2623. (j) Kolboe, S. *Ibid.* **1969**, *47*, 352. (k) Zdrazil, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1484. (l) Cowley, S. W. Ph.D. Thesis, Southern Illinois University, Carbondale, 1975.

0276-7333/87/2306-1897\$01.50/0