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REACTION OF METAL CARBONYL HYDRIDES WITH DECACARBONYLDIMANGANESE ($Mn_2(CO)_{10}$): RADICAL REACTIONS INITIATED BY ROOM LIGHT

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Summary

We have investigated the room light initiated reactions of $HFeCp(CO)PPh_3$ or $HMoCp(CO)_2PPh_3$ with $Mn_2(CO)_{10}$. In the reaction with the iron hydride we have observed six products and in the reaction with molybdenum hydride we have observed eight products. The nature of the products strongly suggests reactions of seventeen-electron complexes. The number of products show that recombinations of the seventeen-electron species occur with very low activation barriers, showing very little selectivity.

Introduction

Reactions of transition metal hydrides are of considerable interest because of their role in homogeneous catalysis [1—5]. Recently hydrides have demonstrated new types of reactivity such as transfer of the hydride to an electrophile [6] and homolytic cleavage of the H—M bond [7,8]. Brown and coworkers showed that once generated, radical species could undergo chain reactions for substitution on the metal hydride [7,8].

$$HMn(CO)_5 + L \xrightarrow[h\nu]{Mn_2(CO)_{10}} HMn(CO)_4L + HMn(CO)_3L_2 \qquad (1)$$

These reactions were initiated by photolysis of small amounts of the dimers or by adventitious radicals. Photochemical cleavage of M—H bonds has been reported for $HMCp(CO)_3$ (M = Mo, W; Cp = η^5-C_5H_5) and $HCo(CO)_4$ [8,9]; evidence was recently summarized by Sweany [9]. Homolysis of H—M bonds of metal carbonyl hydrides may also be involved in the decomposition of hydrides to H_2 and the metal carbonyl dimer, although no mechanistic work has been done on this type of decomposition.

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One of the interesting features in reactions of radical species is in the possible selectivities of recombinations [10—15]. Brown has shown that reactions of a variety of seventeen-electron species, generated photochemically from the dimers, react at diffusion controlled rates [15]. This would indicate that the radical species recombine with a very low activation barrier and thus non-selectively. A very selective recombination has been suggested in mechanistic considerations of reactions of Group VII carbonyl dimers, although this mechanism has recently been called into question [10].

To examine this question of selectivity of radical reactions we have elected to investigate reactions of hydride complexes with metal carbonyl dimers with different metals where a number of products may be expected. We selected $Mn_2(CO)_{10}$ as the dimer because it has been often investigated and its products are well characterized. As hydride complexes we selected the triphenylphosphine species, $HFeCp(CO)PPh_3$ and $HMoCp(CO)_2PPh_3$. The triphenylphosphine stabilizes the hydride towards decomposition and provides another indicator since ligand scrambling occurs readily in seventeen-electron species. We have investigated the reactions of these hydrides with $Mn_2(CO)_{10}$ at room temperature in hexane.

Experimental

$Mn_2(CO)_{10}$ and $Cp_2Fe_2(CO)_4$ were purchased from Strem Chemicals and used without further purification. Hexane was refluxed over CaH_2 and distilled prior to use; toluene was refluxed over sodium-benzophenone and distilled prior to use in the reactions; benzene-d_6 was dried over CaH_2 and distilled prior to use.

Preparation of $HCpFe(CO)P(C_6H_5)_3$

Six mmol (3.5 g) of $CpFe(CO)P(C_6H_5)_3I$ [16] was dissolved in 100 ml of THF. The solution was cooled to 0°C and 0.19 g (30 mmol) of $LiAlH_4$ was added. After stirring for one minute, the reaction mixture was suction filtered through a fine porosity glass frit and taken to dryness under reduced pressure to give a brown oil. The brown oil was dissolved in 10 ml of toluene and chromatographed on a 2 × 10 alumina column. Vigorous reaction occurred between the brown solution and alumina, but a yellow solution was eluted with toluene. The yellow solution was concentrated and chromatographed again on a 2 × 20 cm alumina column. Elution of the column with toluene resulted in the development of a single yellow band, which was collected. The yellow band was concentrated and recrystallized in toluene/hexane (80/20 v/v) resulting in yellow crystals of $HCpFe(CO)PPh_3$ (0.6 g, 25%). An infrared spectrum in toluene exhibited a single carbonyl absorption at 1928 cm^{-1}. An NMR spectrum exhibited the hydride peak at δ —13.0 ppm ($J(^{31}P—H)$ 75 Hz) in benzene-d_6. Both IR and NMR agreed with literature values [17].

The preparation of $HMoCp(CO)_2PPh_3$ was effected by a similar sequence of reactions (from $CpMo(CO)_2PPh_3I$), as described previously [18]. Purification was accomplished by elution from alumina columns. The spectral parameters (infrared: 1941s, 1871(sh), 1864s cm^{-1}; NMR: —15.6 ppm, $J(^{31}P—H)$ 48 Hz) are in good agreement with those previously determined [18].

The reactions of $HMCp(CO)_nPPh_3$ ($M = Fe$, $n = 1$; $M = Mo$, $n = 2$) and

$Mn_2(CO)_{10}$ were accomplished under an argon atmosphere in an inert atmosphere glove box at room temperature or in a sealed NMR tube. The solvent was hexane, toluene or benzene-d_6 purified as described above. Reactions in the dark were accomplished in foil-wrapped flasks which were covered with black plastic.

Three products were isolated from solution in the reaction of $HFeCp(CO)PPh_3$ by separation on a 2 × 20 cm silica gel column with hexane/toluene mixtures ranging from 50/50 to 10/90. $Mn_2(CO)_{10}$ was eluted first, followed successively by $HMn(CO)_4PPh_3$, $Mn_2(CO)_8(PPh_3)_2$, and $Cp_2Fe_2(CO)_4$. These products were identified by their NMR and infrared spectra: $HMn(CO)_4PPh_3$: δ (2064m, 1985m, 1970s, 1958s, and −6.9 ppm (J(P—H) 34 Hz)) [19]; $Mn_2(CO)_8(PPh_3)_2$ (1980(sh), 1956vs) [13]; $Cp_2Fe_2(CO)_4$: (1993vs, 1952s, 1787vs cm^{-1}) [20]. Other products which were seen during the course of the reaction were identified by their infrared spectra. Infrared spectra in hexane at various times are shown in Fig. 1. The absorption at 2092 cm^{-1} is assigned to $Mn_2(CO)_9PPh_3$ [13]; the absorption at 2080 cm^{-1} to $Cp(CO)_2FeMn(CO)_5$ [21]; and the absorption at 1740 cm^{-1} to $Cp_2Fe_2(CO)_3PPh_3$ [22]. All of the remaining bands can be assigned to these species.

In the reaction of $HMoCp(CO)_2PPh_3$ with $Mn_2(CO)_{10}$ two products were isolated from the product mixture after reaction, again by separation on an alumina column with varying ratios of hexanes and toluene. $Mn_2(CO)_{10}$ was eluted first, followed by $Mn_2(CO)_8(PPh_3)_2$ and $Cp_2Mo_2(CO)_6$. These products were identified by their infrared spectra ($Mn_2(CO)_8(PPh_3)_2$ as described above, $Cp_2Mo_2(CO)_6$, 1959s and 1915s cm^{-1}). The remaining products were identified in solution by their infrared spectra. The primary absorptions used to assign products were as follows: $Mn_2(CO)_9PPh_3$, 2092 cm^{-1} [13]; $HMn(CO)_4PPh_3$, 2061 cm^{-1} [19]; $Cp_2Mo_2(CO)_4(PPh_3)_2$, 1853 and 1830 cm^{-1} [23]; $Cp(CO)_3$-

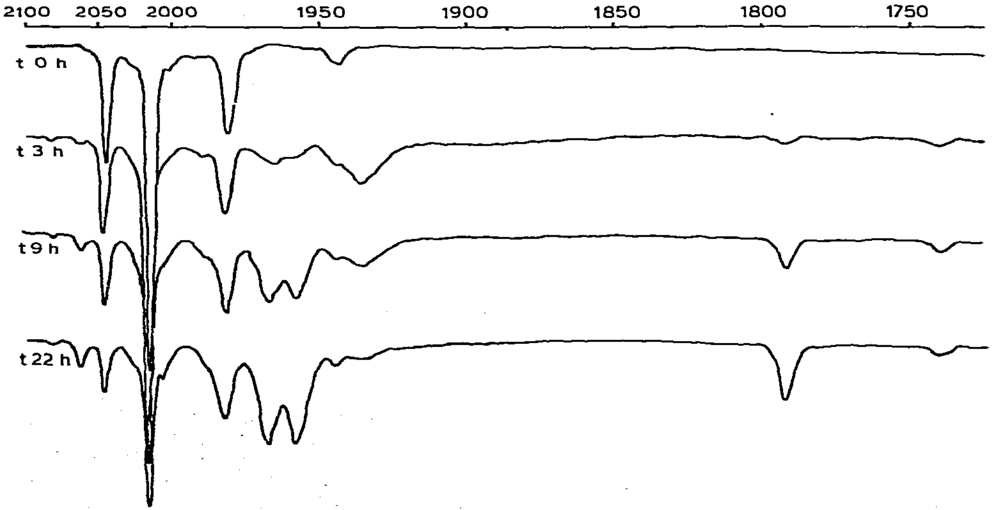

Fig. 1. Infrared spectra at various times during the reaction of $HFeCp(CO)PPh_3$ with $Mn_2(CO)_{10}$ in room light.

$MoMn(CO)_5$, 2081 and 1906 cm^{-1} [24]; $Cp_2Mo_2(CO)_5PPh_3$, 1900(s) [25]; $HMoCp(CO)_3$, 2030 and 1949 cm^{-1} [26].

Results

We have investigated the reaction of equimolar amounts of $HFeCp(CO)PPh_3$ and $Mn_2(CO)_{10}$ at room temperature under an argon atmosphere.

$$\begin{aligned} HFeCp(CO)PPh_3 + Mn_2(CO)_{10} \rightarrow {} & Cp_2Fe_2(CO)_3PPh_3 + Mn_2(CO)_9PPh_3 \\ & + Cp(CO)_2FeMn(CO)_5 + Cp_2Fe_2(CO)_4 \qquad (2) \\ & + HMn(CO)_4PPh_3 + Mn_2(CO)_8(PPh_3)_2 \end{aligned}$$

Three products ($Cp_2Fe_2(CO)_4$, $HMn(CO)_4PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$) were isolated and characterized after the reaction was complete (2 days). The other three products were identified by characteristic infrared absorptions. NMR spectra taken during the course of the reaction showed evidence for a trace of $HMn(CO)_5$ in addition to the predominant hydrides $HMn(CO)_4PPh_3$ and $HFeCp(CO)PPh_3$. With a ten fold excess of $Mn_2(CO)_{10}$ only $Cp(CO)_2FeMn(CO)_5$ and $Mn_2(CO)_9PPh_3$ were observed by infrared spectroscopy.

When light was excluded no reaction was observed between $HFeCp(CO)PPh_3$ and $Mn_2(CO)_{10}$ as shown by the infrared spectrum after 22 h. Exposure of this mixture to room light caused reaction to the products shown in reaction 2. Light was constantly required as exposure of $HFeCp(CO)PPh_3$ and $Mn_2(CO)_{10}$ to light for 1 h and then covering showed no further reaction in the dark. In the presence of *p*-dinitrobenzene only decomposition of the hydride was observed; the $Mn_2(CO)_{10}$ was unchanged.

The only product observed after 1 h is $Cp_2Fe_2(CO)_3PPh_3$. Over the next 2 h $Mn_2(CO)_9PPh_3$, $Cp(CO)_2FeMn(CO)_5$ and $Cp_2Fe_2(CO)_4$ appear. $Cp_2Fe_2(CO)_3PPh_3$, $Mn_2(CO)_9PPh_3$, $Cp(CO)_2FeMn(CO)_5$ and $HMn(CO)_5$ are never present in a large concentration (less than 10% yield) and disappear toward the end of the reaction. The products which can be separated after the reaction, $Cp_2Fe_2(CO)_4$, $HMn(CO)_4PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$ continue to grow in over 48 h.

The reaction of $HMoCp(CO)_2PPh_3$ with $Mn_2(CO)_{10}$ gives a similar range of products.

$$\begin{aligned} HMoCp(CO)_2PPh_3 + Mn_2(CO)_{10} \rightarrow {} & Mn_2(CO)_9PPh_3 + Cp(CO)_3MoMn(CO)_5 \\ & + Mn_2(CO)_8(PPh_3)_2 + HMn(CO)_4PPh_3 \qquad (3) \\ & + Cp_2Mo_2(CO)_4(PPh_3)_2 + HMoCp(CO)_3 \\ & + Cp_2Mo_2(CO)_5PPh_3 + Cp_2Mo_2(CO)_6 \end{aligned}$$

The product distribution between the two reactions is remarkably similar and involves the mixing of metal fragments and ligands between groups. Many of the molybdenum complexes are more stable than the iron analogues and are still present when the reaction is complete. The presence of more products at the end of the reaction makes separation more difficult and we have only been able to isolate two products in completely pure form, $Mn_2(CO)_8(PPh_3)_2$ and

$Cp_2Mo_2(CO)_6$. In this reaction there were additional infrared absorbances which could not be assigned to known products. We suspect that these are from substituted mixed-metal dimers and perhaps $Cp_2Mo_2(CO)_4$ [27]. In the absence of light no reaction is observed in this system either.

Discussion

Several pieces of evidence indicate radical character for reactions 2 and 3. The nature of the products indicates transfer of groups between the metal centers consistent with a radical reaction and very difficult to explain in terms of non-radical reactions. The necessity of light for the reaction to occur is typical of radical reactions of metal carbonyls. The failure to observe any products in the presence of *p*-dinitrobenzene could indicate a trapping of the radical before reaction can occur.

Radical reactions could be initiated by either H—M or Mn_2 bond homolysis in these systems. There is considerable literature precedent for both processes [9,11—14], and quite plausible schemes can be conceived for either initiating step. We favor homolysis of the Mn—Mn bond for the following reasons. (1) Storing $Mn_2(CO)_{10}$ in CCl_4 in room light leads to substantial conversion to $Mn(CO)_5Cl$ in a few hours. (2) Reactions of $HFeCp(CO)PPh_3$ and $HMoCp(CO)_2PPh_3$ with $Mn_2(CO)_{10}$ are very similar in nature. (3) This would be consistent with the previous observations of facile reactions of $HRe(CO)_5$ when initiated by a small amount of $^{\bullet}Re(CO)_5$ formed photochemically. Scheme 1 uses $Mn_2(CO)_{10}$ homolysis as the initiating step and illustrates the formation of the products by radical reactions, when M = Fe, $n = 1$ and when M = Mo, $n = 2$. This

SCHEME 1

(1) $Mn_2(CO)_{10} \xrightarrow{\text{room light}} 2\,^{\bullet}Mn(CO)_5$

(2) $^{\bullet}Mn(CO)_5 + HMCp(CO)_nPPh_3 \rightarrow HMn(CO)_5 + {}^{\bullet}MCp(CO)_nPPh_3$

$^{\bullet}Mn(CO)_5 + L \rightleftharpoons {}^{\bullet}Mn(CO)_4L + CO$

$^{\bullet}MCp(CO)_nPPh_3 + CO \rightleftharpoons {}^{\bullet}MCp(CO)_{n+1} + L$

(3) $^{\bullet}Mn(CO)_4L + RH \rightarrow HMn(CO)_4L + R^{\bullet}$

$^{\bullet}Mn(CO)_5 + {}^{\bullet}MCp(CO)_{n+1} \rightarrow (CO)_5MnMCp(CO)_{n+1}$

$^{\bullet}MCp(CO)_nPPh_3 + CO \rightleftharpoons {}^{\bullet}MCp(CO)_{n+1} + L$

$2\,^{\bullet}Mn(CO)_4L \rightarrow Mn_2(CO)_8L_2$

$^{\bullet}MCp(CO)_{n+1} + RH \rightarrow HMCp(CO)_{n+1} + R^{\bullet}$

$2\,^{\bullet}MCp(CO)_{n+1} + L \rightarrow$ substituted dimers

scheme is not meant to contain all of the reactions which occur, but to show how the observed products could be formed from known radical reactions.

Number 1 refers to the initiation step, number 2 to the formation of the radical species and number 3 to the radical recombinations. Certainly the initially formed products that disappear toward the end of the reaction must be undergoing further reactions. The source of free CO and $^{\bullet}$H are not indicated. The CO would arise from dissociation of the radical species and hydrogen would arise by abstraction from solvent or from a metal hydride [15].

We have observed nine of the possible products based on the radical species, $^{\bullet}$FeCp(CO)PPh$_3$, $^{\bullet}$FeCp(CO)$_2$, $^{\bullet}$Mn(CO)$_5$, $^{\bullet}$Mn(CO)$_4$PPh$_3$, and $^{\bullet}$H. The species which have not been observed in this reaction are either unstable or could be present in small amounts with infrared absorptions overlapping those of major components. Although infrared bands due to the hydride HFeCp(CO)$_2$ and HMn(CO)$_5$ could be obscured by those of Mn$_2$(CO)$_{10}$ and Cp$_2$Fe$_2$(CO)$_4$, the NMR spectra show only a trace of HMn(CO)$_5$ and no evidence of HFeCp(CO)$_2$. Attempts to prepare Cp$_2$Fe$_2$(CO)$_2$(PPh$_3$)$_2$ have been unsuccessful [17]. The substituted mixed metal dimers, Cp(CO)(PPh$_3$)FeMn(CO)$_5$, Cp(CO)$_2$FeMn(CO)$_4$-PPh$_3$ and Cp(CO)(PPh$_3$)FeMn(CO)$_4$PPh$_3$, have not been reported. Thus we have identified all previously prepared complexes possible from radical recombinations in this system with the exception of HFeCp(CO)$_2$. For the reaction of the possible radical species in the Mo system ($^{\bullet}$Me(CO)$_5$, $^{\bullet}$Mn(CO)$_4$PPh$_3$, $^{\bullet}$CpMo(CO)$_3$, $^{\bullet}$CpMo(CO)$_2$PPh$_3$, $^{\bullet}$H) we have observed ten of the possible products. Apparently the activation barrier for combination of these radicals is low, with very little selectivity seen in recombination reactions.

We have extended the known radical reactions to species of different metal centers and identified a large number of products from these reactions. We would suggest that great care needs to be exercised in studies of reactivity of metal hydrides, especially where a possible impurity is metal dimers.

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References

1 H.D. Kaesz, J. Organometal. Chem., 200 (1980) 145.
2 H.D. Kaesz and R.B. Saillant, Chem. Rev., 72 (1972) 231.
3 J. Halpern, J. Organometal. Chem., 200 (1980) 133.
4 G.L. Geoffroy and J.R. Lehman, Adv. Inorg. Radiochem., 20 (1977) 189.
5 A. Humphries and H.D. Kaesz, Prog. Inorg. Chem., 25 (1979) 145.
6 T. Bodnar, S.J. LaCroce and A.R. Cutler, J. Amer. Chem. Soc., 102 (1980) 3294.
7 B.H. Byers and T.L. Brown, J. Amer. Chem. Soc., 99 (1977) 2527.
8 N.W. Hoffman and T.L. Brown, Inorg. Chem., 17 (1978) 613.
9 R.L. Sweany, Inorg. Chem., 19 (1980) 3512.
10 D. Sonnenberger and J.D. Atwood, J. Am. Chem. Soc., 102 (1980) 3484 and ref. therein.
11 D.R. Kidd and T.L. Brown, J. Am. Chem. Soc., 100 (1978) 4095.
12 H.B. Abrahamson and M.S. Wrighton, J. Am. Chem. Soc., 99 (1977) 5510.
13 M.S. Wrighton and D.S. Ginley, J. Am. Chem. Soc., 97 (1975) 2065.
14 A.F. Hepp and M.S. Wrighton, private communications.
15 R.W. Wegman, R.J. Olson, D.R. Gard, L.R. Faulkner and T.L. Brown, J. Am. Chem. Soc., 103 (1981) 6089.
16 P.M. Treichel, R.L. Shubkin, K.M. Barnett and D. Reichard, Inorg. Chem., 5 (1966) 1177.
17 P. Kalck and R. Poilblanc, C.R. Acad. Sci., Ser. C, 274 (1972) 66.

18 A.R. Manning, J. Chem. Soc. A, (1966) 157.
19 W. Hieber, G. Faubhaber and S. Theubert, Z. Anorg. Chem., 314 (1963) 125.
20 A. Wong, M. Harris and J.D. Atwood, J. Am. Chem. Soc., 102 (1980) 4529.
21 R.B. King, P.M. Treichel and F.G.A. Stone, Chem. Ind., (1961) 747.
22 R.J. Haines and A.L. duPreez, Inorg. Chem., 8 (1969) 1459.
23 M.I. Bruce, B.L. Goodall, D.N. Sharrocks, F.G.A. Stone, J. Organomet. Chem., 39 (1972) 139.
24 T. Madach and H. Vahrenkamp, Chem. Ber., 113 (1980) 2675.
25 R.J. Haines, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc. A, (1968) 43.
26 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
27 There are infrared bands at 1891 and 1843 cm^{-1} as expected for $Cp_2Mo_2(CO)_4$ [28] but always as part of a mixture so we could not be certain that it was present.
28 R.C. Job and M.D. Curtis, Inorg. Chem., 12 (1973) 2510.