Coordination Chemistry Reviews, 63 (1985) 217–240
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PHOTOCHEMICAL DISPROPORTIONATION OF METAL–METAL BONDED CARBONYL DIMERS

ALBERT E. STIEGMAN and DAVID R. TYLER *

Department of Chemistry, Columbia University, New York, New York 10027 (U.S.A.)

(Received 14 June 1984)

CONTENTS

A. INTRODUCTION

Organometallic carbonyl compounds containing a single metal–metal bond are known to undergo a variety of photochemical reactions [1]. Typical among these are halogen atom extraction reactions (eqns. 1 and 2) [2]

$$Cp_2Mo_2(CO)_6 + CCl_4 \xrightarrow{h\nu} 2\ CpMo(CO)_3Cl + (CCl_3) \quad (1)$$

$$Re_2(CO)_{10} + C_6H_5CH_2Cl \xrightarrow{h\nu} 2\ Re(CO)_5Cl + (CH_2C_6H_5) \quad (2)$$

---

* Author for correspondence.

0010-8545/85/$08.40

and substitution reactions (eqns. 3 and 4) [3]

$$Mn_2(CO)_{10} + 2\ P(C_6H_5)_3 \overset{h\nu}{\rightarrow} Mn_2(CO)_8(P(C_6H_5)_3)_2 + 2\ CO \qquad (3)$$

$$Cp_2Mo_2(CO)_6 + P(\text{t-butyl})_3 \overset{h\nu}{\rightarrow} Cp_2Mo_2(CO)_5(P(\text{t-butyl})_3) + CO \qquad (4)$$

These types of reactions have been thoroughly studied and their mechanisms are thought to be well understood [4].

A class of reactions which poses a number of interesting mechanistic questions and one that is only now beginning to be understood is the photochemical disproportionation of these dimers. These reactions, which involve a formal change in the metal atom oxidation states of ±1, can be formulated in the following general fashion

$$L_nM{-}ML_n \underset{L'}{\overset{h\nu}{\rightarrow}} ML_n^- + ML_mL'^{+}_{(n-m+1)} \qquad (5)$$

where L and L′ are ligands. Examples of these reactions are the disproportionation of $Cp_2Mo_2(CO)_6$ by certain phosphines [5],

$$Cp_2Mo_2(CO)_6 + 2\ PR_3 \overset{h\nu}{\rightarrow} CpMo(CO)_2(PR_3)_2^+ + CpMo(CO)_3^- + CO \qquad (6)$$

and the reaction of $Mn_2(CO)_{10}$ with amines [6],

$$Mn_2(CO)_{10} + 3\ NR_3 \overset{h\nu}{\rightarrow} Mn(CO)_3(NR_3)_3^+ + Mn(CO)_5^- + 2\ CO \qquad (7)$$

The disproportionation reactions occur both thermally and photochemically with a variety of metal–metal bonded dimers.

The disproportionation reactions are of fundamental interest to the photochemist because they are examples of photoinduced electron transfer reactions. Conceivably, the primary photoprocess in these reactions may even be the elusive heterolytic cleavage process (eqn. 8).

$$L_nM{-}ML_n \overset{h\nu}{\rightarrow} L_nM^+ + ML_n^- \qquad (8)$$

Simple theoretical arguments show that this process should occur with metal–metal bonded dimers yet it has never been observed. Because ionic products are formed, the disproportionation reactions are the best systems in which to observe a heterolytic metal–metal bond cleavage. In addition, many of the disproportionation reactions are thought to involve organometallic radical intermediates. Studies of the disproportionation reactions are contributing to the burgeoning chemistry (substitution, electron transfer, and otherwise) of these important species.

This review surveys the known photochemical disproportionation reactions and critically analyzes the mechanisms proposed for these reactions.

B. ELECTRONIC STRUCTURE OF THE DIMER COMPLEXES

The electronic structures of the metal–metal bonded carbonyl dimers have been previously discussed at length and need only be summarized here [1,7]. The electronic spectra of these compounds are all similar in that there are two characteristic transitions in the visible or near ultraviolet region of the spectrum [1]; all of the complexes exhibit a weak band (or in some cases several weak bands, e.g. $Co_2(CO)_8$) at lowest energy and a more intense band to higher energy. Based on spectroscopic arguments and a molecular orbital calculation, Levenson, Gray, and Ceasar [7] assigned the lowest energy absorption band to a $d\pi \rightarrow \sigma^*$ transition and the intense higher energy band to the $\sigma \rightarrow \sigma^*$ (metal–metal bonding to metal–metal antibonding) transition in the $Mn_2(CO)_{10}$ complex. Similar assignments are usually assumed for the analogous bands in the other dimer complexes, but Caspar and Meyer have pointed out that these assignments are probably not correct for complexes with bridging CO ligands or with cyclopentadienyl ligands [8]. It is generally accepted that either $d\pi \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$ excitation, both of which promote an electron into the antibonding orbital of the metal–metal bond, will rupture the bond and fragment the molecule. Furthermore, the dissociation is usually assumed to be homolytic, so two 17-valence electron metal radical fragments are formed. Indeed, flash photolysis [9], low-temperature matrix isolation [10], and EPR spin-trapping [11] experiments have shown homolytic metal–metal bond cleavage to occur readily with most of the dimers. For example, the metal–metal bonds in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ can cleave homolytically upon irradiation to form $Mn(CO)_5$ and $Re(CO)_5$, respectively [1]. Also, the cyclopentadienyl carbonyl dimers, $Cp_2M_2(CO)_6$ (M = Cr, Mo, W) and $Cp_2Fe_2(CO)_4$ can photolyze to form radicals of the form $CpM(CO)_3$ and $CpFe(CO)_2$, respectively [1].

It is the electron-deficient 17-electron radical fragments which account for most of the observed photochemistry. For example, the reaction with halocarbons to produce the halogen atom abstraction product has been shown to proceed predominantly by the mechanism in Scheme 1 [3,12].

$$Mn_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} 2\ Mn(CO)_5$$

$$Mn(CO)_5 + CCl_4 \rightarrow Mn(CO)_5Cl + CCl_3$$

Scheme 1

In addition, because of their lability [13], the 17-electron radical fragments are implicated in the substitution reactions of the metal–metal bonded dimer (Scheme 2) [14].

$$\mathrm{Mn_2(CO)_{10}} \overset{h\nu}{\rightleftharpoons} 2\ \mathrm{Mn(CO)_5}$$

$$\mathrm{Mn(CO)_5} + \mathrm{L} \rightarrow \mathrm{Mn(CO)_4L} + \mathrm{CO}$$

$$\mathrm{Mn(CO)_5} + \mathrm{Mn(CO)_4L} \rightarrow \mathrm{Mn_2(CO)_9L}$$

$$2\ \mathrm{Mn(CO)_4L} \rightarrow \mathrm{Mn_2(CO)_8L_2}$$

Scheme 2

While the photochemical production of radicals is easily demonstrated and explained, a closer look at the potential energy surfaces for these dimers gives additional insight into the possibility of other primary photochemical processes [15]. Figure 1 shows the potential energy surfaces for the σ^2 and $\sigma^1\sigma^{*1}$ electronic configurations of the molecule. Note that the lowest energy $\sigma^1\sigma^{*1}$ singlet excited state is an ionic state whose dissociation products are ions. It is, in fact, the lower-lying triplet state which dissociates into radical fragments. Thus, the homolytic cleavage photochemical pathway must result from a facile intersystem crossing from the excited singlet to the triplet state (or perhaps to the $d\pi\sigma^*$ state). From this argument it is clear that direct heterolysis of the metal–metal bond is theoretically possible provided the dissociation limit of the singlet state can be reached. Direct heterolysis is a

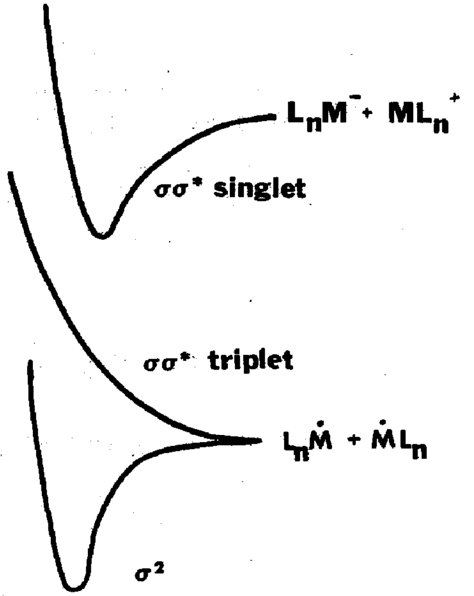

Fig. 1. Proposed relationship of the potential energy surfaces for the σ^2, $\sigma\sigma^*$ (triplet), and $\sigma\sigma^*$ (singlet) states of metal–metal bonded complexes. The σ^2 and $\sigma\sigma^*$ (triplet) states correlate to two 17-electron fragments at infinite separation of the metals. The $\sigma\sigma^*$ (singlet) state correlates to ionic species at infinite separation.

particularly appealing photochemical pathway to propose in disproportionation reactions given the ionic nature of the products.

C. A GENERAL SURVEY OF DISPROPORTIONATION

(i) $Mn_2(CO)_{10}$

In 1960, Hieber reported that $Mn_2(CO)_{10}$ reacted with pyridine according to eqn. (9) [16]. He later showed that the disproportionation reaction was general for many monodentate and bidentate nitrogen bases [17]. It was further observed that these reactions proceeded photochemically [6] as well as thermally (eqn. 9).

$$Mn_2(CO)_{10} \xrightarrow[B]{\Delta \text{ or } h\nu} Mn(B)_6^{2+} + Mn(CO)_5^- \tag{9}$$

B = pyridine, picoline, ethylenediamine, piperidine

Interestingly, disproportionation of $Mn_2(CO)_{10}$ with ammonia [18] and n-butylamine [17] resulted in the formation of a manganese(I) species (eqn. 10) instead of the manganese(II) species usually observed.

$$Mn_2(CO)_{10} \xrightarrow[B]{\Delta \text{ or } h\nu} Mn(CO)_n(B)_{6-n}^+ + Mn(CO)_5^- \tag{10}$$

$B = NH_3$, $n = 3$; $B = NH_2(\text{n-butyl})$, $n = 5$

Why the cations obtained in reactions (9) and (10) should be different was to remain a puzzle for over 20 years. Not until 1981 were McCullen and Brown able to show that disproportionation of $Mn_2(CO)_{10}$ in pyridine initially gave $Mn(CO)_5^-$ and the Mn(I) complex $Mn(CO)_3(py)_3^+$ (eqn. 10) [19]. They showed that the Mn(II) cation observed by Hieber resulted from a secondary disproportionation of the $Mn(CO)_3(py)_3^+$ complex (eqn. 11).

$$3\ Mn(CO)_3(B)_3^+ + 3\ B \xrightarrow{h\nu} Mn(CO)_5^- + 2\ Mn(B)_6^{2+} \tag{11}$$

The results with pyridine can presumably be extended to other amine ligands.

Another very important contribution of McCullen and Brown was to recognize that disproportionation is a ligand effect and not a solvent effect [19]. Thus, in the examples above the amines are acting as ligands (Lewis bases). Originally, the bulk solvent properties such as polarizability were thought to be important factors in determining whether disproportionation occurred [17].

Hieber also reported that bidentate ligands such as *o*-phenanthroline and bipyridine reacted to produce monosubstituted dimers, $Mn_2(CO)_8(N_2)$ (N_2 = bpy, *o*-phen), when the ligand was present in low concentrations [16].

Although disproportionation was never reported with *o*-phenanthroline, the $Mn_2(CO)_8(bpy)$ complex was shown to disproportionate in the presence of additional bipyridine in polar solvents. While it has since been shown that the nature of the solvent does not effect the disproportionation reaction, Hieber's result established that in certain cases substitution products form concomitantly with the disproportionation products. In addition, his results established that the substituted dimers will also disproportionate if additional ligand is present.

In 1973, it was reported that irradiation of $Mn_2(CO)_{10}$ in non-amine donor solvents such as THF and acetonitrile produced an EPR signal [20]. Further investigations [19,21] showed that the signal was attributable to a high spin d^5 manganese(II) complex (formulated as $Mn(S)_6^{2+}$, S = solvent). Infrared spectroscopy established the presence of the $Mn(CO)_5^-$ anion [22] in the solutions and the disproportionation reactions of $Mn_2(CO)_{10}$ were thus extended to Lewis bases other than amines.

In general, the manganese dimer undergoes facile disproportionation by a number of Lewis bases by both thermal and photochemical means. Two notable exceptions that do not yield disproportionation are phosphines and phosphites. Phosphines and phosphites photochemically substitute the dimer producing a variety of mono-, di-, and trisubstituted products but no disproportionation occurs [3,23]. While there are several reports in the literature [24] of phosphine-induced disproportionation, in all cases the reactions were carried out in donor solvents and any disproportionation can be attributed to use of these solvents.

(ii) $Re_2(CO)_{10}$ and $Tc_2(CO)_{10}$

The rhenium and technetium analogs of $Mn_2(CO)_{10}$ are not as well studied as the manganese complex. It is known that $Re_2(CO)_{10}$ does not yield $Re(CO)_5^-$ upon irradiation in acetonitrile [25]; however, Cox and coworkers [6] did observe $Re(CO)_5^-$ when $Re_2(CO)_{10}$ was irradiated in pyridine and DMF. The cationic species formed in these reactions were not reported. Disproportionation has not been observed (and apparently not even attempted) with $Tc_2(CO)_{10}$.

(iii) $Co_2(CO)_8$

Of the pure metal carbonyls, dicobaltoctacarbonyl shows the most extensive thermal and photochemical activity in the presence of Lewis bases. The molecule is generally more reactive than manganese decacarbonyl but undergoes much the same substitution and disproportionation chemistry.

Hieber first reported the thermal disproportionation of $Co_2(CO)_8$ in the reaction with ammonia (eqn. 12) [26]. Wender, Sternberg, and coworkers [27] studied this reaction in detail and found it to be general for a variety of ligands including amines, alcohols, and water, as well as bidentate ligands such as ethylenediamine and *o*-phenanthroline (eqn. 12).

$$Co_2(CO)_8 \xrightarrow[B]{\Delta} Co(B)_6^{2+} + Co(CO)_4^- \tag{12}$$

$B = NH_3, (CH_3)_2NH, CH_3OH, C_5H_5N$, and H_2O

Unlike $Mn_2(CO)_{10}$, the disproportionation of $Co_2(CO)_8$ proceeds rapidly with phosphines. However, the disproportionation products are different from those of the amines in that cobalt(I) species, $Co(CO)_3(L)_2^+$ (L = phosphine) are the resulting cations; no cobalt(II) complex analogous to $Co(B)_6^{2+}$ is formed (eqn. 13) [28],

$$Co_2(CO)_8 \xrightarrow[PR_3]{\Delta} Co(CO)_3(PR_3)_2^+ + Co(CO)_4^- \tag{13}$$

This result appears analogous to the $Mn_2(CO)_{10}$ case just discussed, in which weaker bases, such as ammonia and NH_2(n-butyl), yielded a Mn(I) species while stronger bases gave an Mn(II) product. As with the Mn(I) species it seems logical to propose that the Co(I) species further disproportionate to give Co(II) and Co(I-) species. Interestingly, Sternberg and coworkers reported the isolation of a cobalt(I) species from the reaction of $Co_2(CO)_8$ with piperdine at low temperature [27]. (Tucci and Gwynn reported an analogous compound for the reaction of $Co_2(CO)_8$ with alcohols [28c].) Sternberg further postulated that the Co(I) complex was the initial disproportionation product and the Co(II) was forming in a secondary reaction.

The Co(I) species isolated by Sternberg was formulated as $Co(CO)_4L^+$. This complex is different from the species $Co(CO)_3L_2^+$ observed with phosphines. Nearly 30 years later, Brown pointed out that the $Co(CO)_4(amine)^+$ complexes reported by Sternberg were not well characterized and he discounted their actual formation [29]. However, as will be discussed in the mechanistic section, it is not unreasonable that $Co(CO)_4(amine)^+$ would result from the initial disproportionation of $Co_2(CO)_8$ with strong electron donors. In the photochemical disproportionation reactions of $Cp_2Mo_2(CO)_6$, Stiegman and Tyler detected a product distribution analogous to that proposed above for $Co_2(CO)_8$ [30]. That is, with weaker donors such as phosphines, the product is $CpMo(CO)_2(PR_3)_2^+$, while with strong donors such as acetonitrile or acetone, $CpMo(CO)_3L^+$ is produced (eqns. 14 and 15).

$$Cp_2Mo_2(CO)_6 + 2\ PR_3 \xrightarrow{h\nu} CpMo(CO)_2(PR_3)_2^+ + CpMo(CO)_3^- + CO \tag{14}$$

$$Cp_2Mo_2(CO)_6 + L \xrightarrow{h\nu} CpMo(CO)_3(L)^+ + CpMo(CO)_3^- \qquad (15)$$

$L = CH_3CN, (CH_3)_2CO$, DMSO

It is reasonable to suggest that $Co_2(CO)_8$ has a similar dependence in the initial disproportionation (compare eqns. 13 and 16).

$$Co_2(CO)_8 \xrightarrow[L]{\Delta \text{ or } h\nu} Co(CO)_4L^+ + Co(CO)_4^- \qquad (16)$$

L = amines, alcohols

(iv) Cyclopentadienyl metal carbonyl dimers

Another class of dimers that undergoes disproportionation reactions is the cyclopentadienyl carbonyl dimers: $Cp_2M_2(CO)_6$ (M = Cr, Mo, W; $Cp = \eta^5\text{-}C_5H_5$), $Cp_2Fe_2(CO)_4$, and $Cp_2Ni_2(CO)_2$. These dimers are highly colored (generally purple to black) with the $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ transitions in the visible region of the spectrum [31]. They differ in their molecular structures in that the iron and nickel dimers possess a pair of bridging carbonyl ligands while the Cr, Mo, and W complexes have only terminally bonded carbonyl ligands [32].

Using triphenylphosphine as the ligand, Haines, Nyholm, and Stiddard were the first to establish that photochemical disproportionation of the $Cp_2M_2(CO)_6$ dimers occurs (eqn. 17) [5,33]. Haines subsequently reported the rapid thermal disproportionation of the molybdenum or tungsten dimer in the presence of a number of phosphines and phosphites (eqn. 17) [34].

$$Cp_2Mo_2(CO)_6 + 2\ PR_3 \xrightarrow{\Delta} CpMo(CO)_2(PR_3)_2^+ + CpMo(CO)_3^- \qquad (17)$$

King et al. later reported analogous reactions with bidentate phosphines and arsines [35]. In his initial study, Haines reported that the thermal reaction of the $Cp_2Mo_2(CO)_6$ complex with phosphines resulted in disproportionation while irradiation of the dimer with the same ligands produced the disubstituted product, $Cp_2Mo_2(CO)_4(PR_3)_2$ [34]. Recent work has shown this not to be true [36]. In the absence of light these dimers were found to be inert to thermal disproportionation by phosphites and phosphines, i.e. the observed disproportionation is always photochemical. It was also shown that both the monosubstituted and disubstituted dimers form photochemically in conjunction with the ionic products. The types and amounts of the various products are dependent on a number of ligand factors, including steric bulk, electron donating ability, and concentration [36].

Meyer and coworkers reported the photochemical disproportionation of $Cp_2Mo_2(CO)_6$ in the presence of halides and thiocyanate in acetonitrile or acetone solution (eqn. 18) [37].

$$Cp_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu} CpMo(CO)_3X + CpMo(CO)_3^- \quad (18)$$

$X = Cl, Br, I, SCN$

They also observed that the quantum yield for the reaction did not depend on the concentration of the halide. The independence of the quantum yield on halide concentration has been recently attributed to a solvent-induced disproportionation [38].

Although no net reaction of the $Cp_2Mo_2(CO)_6$ complex occurs with acetone or CH_3CN at room temperature, a reaction does occur at −78°C (eqn. 19).

$$Cp_2Mo_2(CO)_6 + S \xrightarrow[-78]{h\nu} CpMo(CO)_3S^+ + CpMo(CO)_3^- \quad (19)$$

S = acetone or CH_3CN

It was proposed that the reaction is not observed at room temperature because the thermal back reaction is fast [30]. A net reaction does occur when halide is present because the halide traps the cation as it is formed and thus prevents the back reaction (eqn. 20).

$$CpMo(CO)_3S^+ + X^- \rightarrow CpMo(CO)_3X + S \quad (20)$$

Complete details are discussed in the mechanistic section.

Cox and coworkers reported the disproportionation of $Cp_2Mo_2(CO)_6$ in DMSO, DMF, and pyridine [6], $CpMo(CO)_3^-$ was the anionic product in all cases. The cationic products were not discussed but from the published infrared data in the CO stretching region it is apparent that DMSO and DMF act similarly to acetone and acetonitrile in producing the monosubstituted cations, $CpMo(CO)_3(DMSO)^+$ and $CpMo(CO)_3(DMF)^+$. For the reaction in pyridine, the reported cation peaks, 2335 cm^{-1} and 1953 cm^{-1}, do not correspond to either the monosubstituted cation, $CpMo(CO)_3(py)^+$ ($\nu(C\equiv O) = 2065$, 2000, and 1974 cm^{-1}) or the disubstituted cation, $CpMo(CO)_2(py)_2^+$ ($\nu(C\equiv O) = 1997$ and 1880 cm^{-1}) [39]. Recent work with amines has shown that the stoichiometry is correct for disproportionation (i.e. the disappearance of 1 mole of $Cp_2Mo_2(CO)_6$ leads to the appearance of 1 mole of $CpMo(CO)_3^-$) but the nature of the cation has not yet been determined. The exact nature of the photochemical disproportionation reaction with amines remains somewhat uncertain.

In general, the $Cp_2M_2(CO)_6$ ($M = Cr$, Mo, W) complexes disproportionate with a range of Lewis bases from phosphines and phosphites to ketones and nitriles. The secondary disproportionation reactions of the cationic products such as observed with $Mn_2(CO)_{10}$ and proposed for

$Co_2(CO)_8$ are not observed with these dimers. As mentioned above, the cationic products vary from $CpMo(CO)_2L_2^+$ in the case of phosphines and phosphites to $CpMo(CO)_3L^+$ with stronger electron donor ligands such as DMSO and acetonitrile.

The cyclopentadienyl dicarbonyl dimer of iron has been well-studied photochemically and has been found to substitute with amines and donor solvents as well as with phosphines and phosphites [40]. The only reported disproportionation occurs thermally in the reaction with the bidentate phosphine 1,2-bis(dimethylphosphino)ethane (PP).

$$Cp_2Fe_2(CO)_4 + PP \xrightarrow{h\nu} CpFe(CO)(PP)^+ + CpFe(CO)_2^- \qquad (21)$$

The extent to which the reaction will proceed photochemically has not been investigated. Recent work suggests that dppe (1,2-bis(diphenylphosphine)ethane) will photochemically disproportionate the iron dimer, but the reaction appears to be inefficient with a relatively low quantum yield [39,41].

The photochemistry of the ruthenium analog, $Cp_2Ru_2(CO)_4$, has not been extensively studied. Wrighton and coworkers showed that homolysis of the metal–metal bond occurs upon irradiation and that the photochemically produced radicals will abstract halogen atoms from chlorocarbons [31], but no photochemical disproportionation reactions have been reported.

The final cyclopentadienyl dimer to be discussed is that of nickel, $Cp_2Ni_2(CO)_2$. Ellgen thoroughly studied the thermal reaction of $Cp_2Ni_2(CO)_2$ with a variety of Lewis bases, including mono- and bi-dentate phosphines, arsines, and CO [42]. He reported that the general disproportionation first observed by King for tris(dimethylamino)phosphine also held for these ligands (eqn. 22) [43].

$$Cp_2Ni_2(CO)_2 + 2\ L \xrightarrow{\Delta} Ni(CO)_2L_2 + Cp_2Ni \qquad (22)$$

L = phosphines, arsines, or CO

This reaction is notably different from that associated with the molybdenum and iron dimers in that it involves displacement of the cyclopentadienyl ligand instead of CO. Ellgen reported that exclusion of light did not affect the reaction rate. Thus, if there is a photochemical component to the reaction it is dominated by the thermal reaction. There have been no photochemical studies reported of reactions of this dimer with nucleophiles.

In summary, the disproportionation reactions of metal–metal bonded carbonyl dimers are induced by a range of Lewis bases including phosphites, phosphines, amines, nitriles, and oxygen donors. The ability of a particular ligand to disproportionate a dimer varies from dimer to dimer. In other words, a given ligand (or class of ligands) may disproportionate one dimer but not another. As will be seen in the next section, the overall ligand effect on the disproportionation reactions is complex, but it can be traced to two basic ligand properties: electron donating ability and steric bulk. In most of the cases studied the disproportionation reactions have been shown to proceed photochemically as well as thermally. For some dimers, photochemical experiments have yet to be performed. It is also possible that, as in the case of $Cp_2Mo_2(CO)_6$ with phosphines, some of the reported thermal reactions will prove to be photochemically initiated.

D. MECHANISTIC ASPECTS

(i) Early mechanistic proposals

Early mechanistic studies on the disproportionation reactions of metal–metal bonded carbonyl dimers were generally quite speculative because little definitive evidence was available. Hieber et al., who initially observed the thermal disproportionation of $Mn_2(CO)_{10}$ in neat pyridine, postulated that the disproportionation reactions were solvent effects; they suggested that polar solvent molecules induced a dipole in the metal–metal bond [17]. It was proposed that base attack on this dipolar intermediate produced ionic products. The idea of a solvent induced dipole was carried over to explain the photochemical disproportionation of these dimers; it was proposed that excitation of this dipolar species resulted in heterolysis [6]. Later work on these reactions showed that they occurred in nonpolar solvents with relatively small ligand concentrations, thus discounting the possibility that the disproportionation reactions were the result of a polar solvent effect [19].

(ii) Energy dependence

Disproportionation reactions occur, generally, when metal–metal bonded complexes are irradiated in the region of the spectrum resulting in metal–metal bond homolysis. As will be reviewed, recent mechanisms have been proposed that adequately explain the observed photochemistry without postulating direct heterolysis. Tyler and coworkers, however, reported a strong energy dependence for the disproportionation of $Cp_2Mo_2(CO)_6$ in the presence of phosphines [44]. The energy dependence suggests that two photochemical pathways are in operation: a low energy mechanism involving metal–metal bond homolysis and a high energy mechanism involving some other primary photoprocess. Energy-dependent disproportionation reactions have not been reported for the other classes of dimer molecules.

$$\mathrm{Cl_3SnCo(CO)_4 + B \overset{K}{\rightleftharpoons} Cl_3(B)SnCo(CO)_4} \tag{1}$$

$$\mathrm{Cl_3(B)SnCo(CO)_4 \xrightarrow[\text{or } h\nu]{k_1} Cl_3SnB + Co(CO)_4} \tag{2}$$

$$\mathrm{Co(CO)_4 + B \xrightarrow{k_2} Co(CO)_3B + CO} \tag{3}$$

$$\mathrm{Co(CO)_3B + Cl_3(B)SnCo(CO)_4 \xrightarrow{k_{31}} Co(CO)_3B^+ + Cl_3(B)SnCo(CO)_4^-} \tag{4}$$

$$\mathrm{Co(CO)_3B + Cl_3SnCo(CO)_4 \xrightarrow{k_{32}} Co(CO)_3B^+ + Cl_3SnCo(CO)_4^-} \tag{5}$$

$$\mathrm{Cl_3(B)SnCo(CO)_4^- \xrightarrow{k_{41}} Co(CO)_4 + SnCl_3^- + B} \tag{6}$$

$$\mathrm{Cl_3SnCo(CO)_4^- \xrightarrow{k_{43}} Co(CO)_4 + SnCl_3^-} \tag{7}$$

$$\mathrm{Co(CO)_3B^+ + B \xrightarrow{\text{fast}} Co(CO)_3B_2^+} \tag{8}$$

termination steps

$$\mathrm{2\ Co(CO)_4 \xrightarrow{k_5} Co_2(CO)_8} \tag{9}$$

$$\mathrm{2\ Co(CO)_3B \xrightarrow{k_6} Co_2(CO)_6B_2} \tag{10}$$

$$\mathrm{Co(CO)_4 + Co(CO)_3B \xrightarrow{k_7} Co_2(CO)_7B} \tag{11}$$

$$\mathrm{SnCl_3B + Co(CO)_3B \xrightarrow{k_8} SnCl_3Co(CO)_3B + B} \tag{12}$$

$$\mathrm{SnCl_3B + Co(CO)_4 \xrightarrow{k_9} SnCl_3Co(CO)_4 + B} \tag{13}$$

$$\mathrm{2\ SnCl_3B \xrightarrow{k_{10}} Sn_2Cl_6 + 2\ B} \tag{14}$$

Scheme 3. Mechanism for the disproportionation of $Co(CO)_4SnCl_3$ with phosphines (B = phosphine).

(iii) Cobalt complexes

The first thorough kinetic study on a disproportionation reaction was carried out on the reaction of $Co(CO)_4SnCl_3$ with phosphines (eqn. 23) [45,46].

$$\mathrm{Co(CO)_4SnCl_3 + 2\ PR_3 \rightarrow Co(CO)_2(PR_3)_2^+ + SnCl_3^- + 2\ CO} \tag{23}$$

The reaction was found to be inhibited by oxygen and galvinoxyl and strongly catalyzed by light. These results suggested a radical chain mechanism (Scheme 3), a proposal supported by the kinetic evidence. The rate expression derived from the mechanism is

$$\frac{-\mathrm{d}[\mathrm{Cl_3SnCo(CO)_4}]}{\mathrm{d}t} = \left(\frac{k_1 K}{k_6}\right)^{1/2} [\mathrm{Cl_3SnCo(CO)_4}]^{3/2} \times \left[k_{31} K [\mathrm{B}]^{3/2} + k_{32} [\mathrm{B}]^{1/2}\right] \tag{24}$$

Scheme 3 shows a 3/2-order dependence on dimer concentration (eqn. 24). This result was confirmed experimentally. The ligand dependence is somewhat more complex but the reported kinetic data are also consistent with eqn. (24) [45,46].

The radical chain pathway was easily extended to the disproportionation of $\mathrm{Co_2(CO)_8}$ with phosphines (eqn. 13), as shown in Scheme 4 [29,47]. It is important to note that the phosphine disproportionation reaction is highly light sensitive [46]. This sensitivity is to be expected as light is known to cleave the Co–Co bond generating $\mathrm{Co(CO)_4}$ radicals (eqn. 25).

$$\mathrm{Co_2(CO)_8} \xrightarrow{h\nu} 2\ \mathrm{Co(CO)_4} \tag{25}$$

Photochemical entry into the chain process should occur via the homolytic cleavage reaction instead of eqns. (1) and (2) of Scheme 4. The photochemically produced radicals are available for substitution (see Scheme 4) and hence propagation of the chain.

$$\mathrm{Co_2(CO)_8} + \mathrm{L} \rightleftharpoons \mathrm{Co_2(CO)_8L} \tag{1}$$
$$\mathrm{Co_2(CO)_8L} \rightarrow \mathrm{Co(CO)_3L} + \mathrm{Co(CO)_4} + \mathrm{CO} \tag{2}$$
$$\mathrm{Co(CO)_3L} + \mathrm{Co_2(CO)_8} \rightarrow \mathrm{Co(CO)_3L^+} + \mathrm{Co_2(CO)_8^-} \tag{3}$$
$$\mathrm{Co_2(CO)_8^-} \rightarrow \mathrm{Co(CO)_4^-} + \mathrm{Co(CO)_4} \tag{4}$$
$$\mathrm{Co(CO)_3L^+} + \mathrm{L} \rightarrow \mathrm{Co(CO)_3L_2^+} \tag{5}$$
$$\mathrm{Co(CO)_4} \rightarrow \mathrm{Co(CO)_3} + \mathrm{CO} \tag{6}$$
$$\mathrm{Co(CO)_3} + \mathrm{L} \rightarrow \mathrm{Co(CO)_3L} \tag{7}$$
$$\mathrm{Co(CO)_3L} + \mathrm{Co(CO)_4} \rightarrow \mathrm{Co_2(CO)_7L} \tag{8}$$
$$\mathrm{Co(CO)_3L} + \mathrm{Co(CO)_3L} \rightarrow \mathrm{Co(CO)_6L_2} \tag{9}$$
$$\mathrm{Co(CO)_4} + \mathrm{Co(CO)_4} \rightarrow \mathrm{Co_2(CO)_8} \tag{10}$$

Scheme 4. Mechanism for the disproportionation of $\mathrm{Co_2(CO)_8}$ with phosphines.

The experimental evidence for the application of the radical chain mechanism to $Co_2(CO)_8$ is somewhat less compelling than in the $Co(CO)_4SnCl_3$ case but it is generally consistent [47]. With PPh_3 and $P(n\text{-butyl})_3$ the kinetic plots were found to vary from the idealized order given in eqn. (24). Some O_2 inhibition was observed, although the rate in the presence of O_2 was reported as being erratic. The effect of galvinoxyl was not reported. As Brown points out, these reactions are very susceptible to trace impurities which might account for the erratic kinetic data.

The radical chain mechanism (Scheme 4) has several key steps that should be noted. In all disproportionation reactions, substitution products are observed along with ionic products. The coupling of substituted radicals (eqns. 8 and 9, Scheme 4) explains the formation of these products. The formation of ionic products, however, occurs when a substituted 17-electron fragment reduces a parent dimer (eqn. 3) and the reduced dimer then decomposes to form the observed anion and another radical (eqn. 4). The oxidized monosubstituted fragment acquires another ligand to give the observed cation (eqn. 5). The radical which results from the decomposition of the reduced dimer serves to propagate the chain (eqns. 3, 4, and 5, Scheme 4).

The steric and electronic characteristics of the ligand exert a strong influence on the disproportionation reactions of $Co_2(CO)_8$. Brown claimed that ligands react with $Co_2(CO)_8$ by two pathways. One pathway involved carbonyl loss followed by substitution (Scheme 5) and the other is as in the radical chain process (Scheme 4). It was proposed that the electron donating ability and steric properties of the ligands determined the relative efficiencies of the two pathways [29,47,48]. Sterically bulky ligands cannot attack the dimer (eqns. 1 and 2, Scheme 4) and rupture the metal–metal bond. Hence, large ligands (e.g. $P(t\text{-butyl})_3$) and weak donors (e.g. $AsPh_3$ and $P(CH_2CH_2CN)_3$) result in substitution products (via Scheme 5) with no disproportionation. Strong bases that are not too sterically hindered react rapidly through the radical mechanism to produce ionic products.

The radical chain mechanism itself is affected by the steric and electronic character of the ligands. The electron transfer step (eqn. 3, Scheme 4) should become less efficient as the donating ability of the substituting ligand decreases. Brown and coworkers reported a decrease in the reaction rate for disproportionation with decreasing basicity [29,47]. Increased steric bulk of

$$Co_2(CO)_8 \rightarrow Co_2(CO)_7 + CO \qquad (1)$$

$$Co_2(CO)_7 + L \rightarrow Co_2(CO)_7L \qquad (2)$$

Scheme 5

$$Co_2(CO)_8 + L \rightleftharpoons Co_2(CO)_8L$$

$$Co_2(CO)_8L + L \rightleftharpoons Co_2(CO)_8L_2$$

$$Co_2(CO)_8L_2 + L \rightleftharpoons Co_2(CO)_7L_3 + CO$$

$$Co_2(CO)_7L_3 \rightarrow Co(CO)_2L_3^+ + Co(CO)_4^- + CO$$

Scheme 6. L = amine.

the ligand, which prevents close approach of the "oxidant" and hinders electron transfer, also results in a slower reaction rate [29,47].

While kinetic evidence for thermal substitution and disproportionation strongly suggests the existence of two pathways, it is not clear how a photochemically-induced disproportionation would behave. The ability of any ligand to substitute a 17-electron fragment is much greater than its ability to attack the dimer and, hence, the radical chain process would be expected to proceed photochemically with ligands that do not disproportionate thermally.

Related work on the thermal disproportionation of $Co_2(CO)_8$ by amines also invoked an initial step in which $Co_2(CO)_8$ reacts with an entering amine. Subsequent steps, however, are not similar to the Brown disproportionation mechanism (Scheme 6) in that the pathway is not a radical chain [49]. It is difficult to believe that phosphines react by one mechanism (i.e. a radical chain) but that amines react by a non-chain mechanism. Clearly the thermal reactions of $Co_2(CO)_8$ with amines should be reexamined in the light of Brown's work.

(iv) $Cp_2Mo_2(CO)_6$ complexes

Stiegman et al. published a mechanistic study of the photochemical disproportionation of $Cp_2Mo_2(CO)_6$ in the presence of phosphines and phosphites [36].

$$Cp_2Mo_2(CO)_6 + 2\,PR_3 \xrightarrow{h\nu} CpMo(CO)_2(PR_3)_2^+ + CpMo(CO)_3^- + CO \qquad (26)$$

PR_3 = phosphines or phosphites

Quantum yields in excess of unity with a great deal of scatter in the data were observed, a result which suggests that a radical chain mechanism is operating. The mechanism proposed for this reaction is similar to that proposed by Brown for $Co_2(CO)_8$ but with a notable exception: an important new intermediate was proposed to explain the essential electron transfer step that yields ionic products (Scheme 7).

$$\mathrm{Cp_2Mo_2(CO)_6 \overset{h\nu}{\rightarrow} 2\ CpMo(CO)_3} \quad (1)$$

$$\mathrm{CpMo(CO)_3 + L \rightleftharpoons CpMo(CO)_2L + CO} \quad (2)$$

$$\mathrm{CpMo(CO)_2L + L \rightleftharpoons CpMo(CO)_2L_2} \quad (3)$$

$$\mathrm{CpMo(CO)_2L_2 + Cp_2Mo_2(CO)_6 \rightarrow CpMo(CO)_2L_2^+ + Cp_2Mo_2(CO)_6^-} \quad (4)$$

$$\mathrm{Cp_2Mo_2(CO)_6^- \rightarrow CpMo(CO)_3^- + CpMo(CO)_3} \quad (5)$$

$$\mathrm{CpMo(CO)_3 + CpMo(CO)_3 \rightarrow Cp_2Mo_2(CO)_6} \quad (6)$$

$$\mathrm{CpMo(CO)_3 + CpMo(CO)_2L \rightarrow Cp_2Mo_2(CO)_5L} \quad (7)$$

$$\mathrm{CpMo(CO)_2L + CpMo(CO)_2L \rightarrow Cp_2Mo_2(CO)_4L_2} \quad (8)$$

Scheme 7. Photochemical disproportionation of $\mathrm{Cp_2Mo_2(CO)_6}$ in the presence of phosphines and phosphites.

In this mechanism the initial step is again production of radicals via photochemical homolysis of the metal–metal bond. After substitution (eqn. 2, Scheme 7) the 17-electron metal species have several reactivity options. They can recombine to form substituted dimers (eqns. 7 and 8, Scheme 7) or they can undergo an electron transfer reaction. It is the electron transfer step of Scheme 7 (eqn. 4) that varies greatly from that in the Brown mechanism. Brown proposed that the substituted 17-electron fragment reduced the parent dimer (eqn. 3, Scheme 4) with the resulting 16-electron cation acquiring a ligand to form the observed product (eqn. 5, Scheme 4). Tyler and coworkers [36], however, observed that the reduction potentials for these dimers are high, ranging from −1.4 V for $\mathrm{Cp_2Mo_2(CO)_6}$ to −1.7 V for $\mathrm{Mn_2(CO)_{10}}$ in organic solvents. They argued that it was doubtful whether an already electron-deficient 17-electron radical fragment would be able to reduce these dimers, especially as this would result in an even more electron-deficient 16-electron fragment. Thus, they proposed that the 17-electron fragment first acquired another ligand thereby becoming an electron-rich 19-electron fragment (eqn. 3, Scheme 7). A 19-electron species would be a strong reducing agent capable of transferring an electron to the dimers (eqn. 4, Scheme 7). Kinetic evidence provided support for the proposed 19-electron intermediate. For example, high ligand concentrations and bidentate ligands increase the efficiency of the disproportionation as required by the mechanism.

As previously discussed, the disproportionation of the $\mathrm{Cp_2Mo_2(CO)_6}$ was found to be energy dependent [44]: irradiation ($\lambda < 290$ nm) of $\mathrm{Cp_2Mo_2(CO)_6}$ and triphenylphosphine in benzene solution gave $\mathrm{CpMo(CO)_3^-}$ and

$CpMo(CO)_2(PPh_3)_2^+$ but lower energy excitation gave only $Cp_2Mo_2(CO)_5PPh_3$. Note that the existence of the high energy disproportionation serves to preclude the possibility of the substituted 17-electron fragment acting as a reducing agent. The argument goes as follows. If the 17-electron fragment were acting as a reducing agent then the cation $CpMo(CO)_2(PPh_3)^+$ would be produced. The cation would readily add PPh_3 into the vacant coordination site to form the known complex $CpMo(CO)_2(PPh_3)_2^+$. That PPh_3 does not yield disproportionation products at low energy even though radicals of the form $CpMp(CO)_2(PPh_3)$ are present precludes the possibility of electron transfer from the substituted 17-electron species.

Tyler and coworkers [36] also reported on the ligand dependence observed in the disproportionation reactions of $Cp_2Mo_2(CO)_6$. They observed, as did Forbus and Brown for $Co_2(CO)_8$ [48], that the electron donating ability of the entering ligands has a profound effect on the course of the reaction. In order to determine if there was a correlation between electron donating ability and the ability to lead to disproportionation, they ranked a large number of ligands according to electron donating ability. Their general ordering (Table 1) shows the existence of an absolute electronic cutoff, below which no disproportionation occurs. This cutoff is explained in terms of the

TABLE 1

Ligand electron donating ability as indicated by *trans* CO stretching frequencies for $Mo(CO)_5L$: low ν values indicate good electron donors, poor donors have higher ν values

Ligand	$\nu(C{\equiv}O)$ (cm^{-1})	Does disproportionation of $Cp_2Mo_2(CO)_6$ occur? (broadband irradiation)
NEt_3	1915	Yes
C_6H_5N	1917	Yes
NH_2Ph	1917	Yes
CH_3CN	1924	Yes
$P(i\text{-propyl})_3$	1933	No
$P(cyclohexyl)_3$	1937	No
$P(n\text{-butyl})_3$	1940	Yes
$AsPh_3$	1948	Yes
PPh_3	1950	Yes
$PPh_2(i\text{-propyl})_3$	1951	No
$P(O\text{-}i\text{-propyl})_3$	1960	Yes
$P(OCH_3)_3$	1964	Yes
$P(O\text{-}n\text{-butyl})_3$	1964	Yes
		electronic cutoff
$P(O\text{-}C_6H_4\text{-}OCH_3)_3$	1966	No
$P(O\text{-}C_6H_4\text{-}CH_3)_3$	1969	No
$P(OPh)_3$	1970	No

19-electron intermediate: when L is a poorly donating ligand then the 19-electron intermediate does not have sufficient reduction potential to reduce the dimer molecule; stronger donating ligands form a 19-electron intermediate with more reducing ability so the dimer reduction (eqn. 4, Scheme 7) will occur.

A general steric ordering using Tolman's cone angle parameter [50] explains the inability of P(i-propyl)$_3$, P(cyclohexyl)$_3$, and PPh$_2$(i-propyl) in Table 1 to lead to disproportionation. A list correlating cone angles and reactivity patterns is given in Table 2.

The inability of large ligands to cause disproportionation was attributed to the inability of the 19-electron intermediate to form because of steric crowding. Note that P(i-propyl)$_3$, P(cyclohexyl)$_3$, and PPh$_2$(i-propyl) are the biggest ligands in Table 2.

One intermediate which appears in both the Brown and Tyler mechanisms is the reduced dimer (eqn. 3, Scheme 4 and eqn. 4, Scheme 7). This intermediate decomposes to form a radical and an anion. There are several precedents in the literature [51] for the decomposition of dimer anions to these species and Tyler et al. were able to give experimental support for this type of intermediate by generating it with sodium and observing the subsequent formation of disproportionation products.

Another interesting observation concerning the $Co_2Mo_2(CO)_6$ disproportionation reactions is the intensity dependence of the product distribu-

TABLE 2

The relationship of the cone angle to the substitution products that form upon irradiation ($\lambda = 505$ nm) of $(MeCp)_2Mo_2(CO)_6$ in cyclohexane and to the occurrence of disproportionation

Ligand	Cone angle (°C)	Does $(MeCp)_2Mo_2(CO)_5L$ form?	Does $(MeCp)_2Mo_2(CO)_4L_2$ form?	Does disproportionation occur? (broad band irradiation)
P(OCH$_3$)	107	Yes	Yes	Yes
P(OC$_2$H$_5$)$_3$	109	Yes	Yes	Yes
P(O–i-propyl)$_3$	130	Yes	Yes	Yes
P(n-butyl)$_3$	132	Yes	Yes	Yes
PPh$_2$(CH$_3$)	136	Yes	Yes	Yes
PPh$_2$(n-butyl)	140	Yes	Slight	Yes
P(i-butyl)$_3$	143	Yes	No	Yes
PPh$_3$	145	Yes	No	No
PPh$_2$(i-propyl)	150	Yes	No	No
P(i-propyl)	160	Yes	No	No
P(cyclohexyl)$_3$	170	Yes	No	No

TABLE 3

The ratio of the quantum yield of substitution to that of disproportionation as a function of exciting light intensity for the reaction of $(MeCp)_2Mo_2(CO)_6$ with $P(OCH_3)_3$ [a]

Intensity (einsteins min^{-1})	ϕ_{sub}/ϕ_{dispro}
1.2×10^{-6}	0.49
1.2×10^{-7}	0.21
1.2×10^{-8}	0.10

[a] $[(MeCp)_2Mo_2(CO)_6] = 0.012$ M; $[P(OCH_3)_3] = 0.25$ M; $\lambda = 405$ nm; in cyclohexane solution.

tion [52]. At low exciting light intensities, disproportionation dominates over the substitution reaction while at higher intensities more substitution products are seen (Table 3). This phenomenon is accounted for by the mechanism as follows. At low intensities, the steady state concentration of the radicals is lower than at high intensities. Therefore, at low intensities, radicals will encounter a ligand with greater relative efficiency than they will at high intensities, where radical–radical coupling reactions (and hence termination) is relatively more favorable. The 19-electron intermediate is thus formed (relatively) more efficiently at low intensities and relatively more disproportionation occurs.

In the disproportionation reactions with coordinating solvents, it is noteworthy that the cationic products are singly substituted with no carbonyl ligands displaced. A mechanism can be written for this reaction that is analogous to the phosphine case (Scheme 8). A notable characteristic of this mechanism is that, as no substitution occurs, the ligand forms the 19-electron intermediate directly (eqn. 2, Scheme 8). The lack of substitution

$$Cp_2Mo_2(CO)_6 \underset{k_{-1}}{\overset{h\nu;\phi}{\rightleftharpoons}} 2\ CpMo(CO)_3 \tag{1}$$

$$CpMo(CO)_3 + S \underset{k_{-2}}{\overset{k_2,\text{slow}}{\rightleftharpoons}} CpMo(CO)_3S \quad (S = \text{solvent}) \tag{2}$$

$$CpMo(CO)_3S + Cp_2Mo_2(CO)_6 \xrightarrow{k_3} CpMo(CO)_3S^+ + Cp_2Mo_2(CO)_6^- \tag{3}$$

$$Cp_2Mo_2(CO)_6^- \xrightarrow{k_4} CpMo(CO)_3^- + CpMo(CO)_3 \tag{4}$$

$$CpMo(CO)_3S^+ + X^- \xrightarrow[\text{fast}]{} CpMo(CO)_3X + S \quad (X = \text{halide}) \tag{5}$$

$$CpMo(CO)_3S + CpMo(CO)_3 \overset{k_5}{\rightleftharpoons} CpMo(CO)_3S^+ + CpMo(CO)_3^- \tag{6}$$

Scheme 8

products makes the mechanism simpler and the mathematics for deriving a quantum yield expression from the steady state approximation becomes more tractable. The derived rate equation for Scheme 8 has the form shown in eqn. (27)

$$\Phi = \phi\left(1 - \frac{k_{-1}}{k_{-1} + K[\mathrm{B}]}\right) + \left(\frac{K'[\mathrm{B}]}{(k_{-1} + K[\mathrm{B}])^{1/2}}\right)(\phi/I)^{1/2} \tag{27}$$

where $K = k_5 k_2 / k_{-2}$, $K' = k_2 k_3 [\mathrm{M}_2]/k_{-2}$, and $\mathrm{M} = \mathrm{Cp_2Mo_2(CO)_6}$. The quantum yield should show an $I^{-1/2}$ dependence, and indeed plots of the quantum yield vs. $I^{-1/2}$ are linear [30].

The ability of nucleophiles such as acetonitrile and DMSO to disproportionate the $\mathrm{Cp_2Mo_2(CO)_6}$ without first substituting the radical fragments can be attributed to their electron donating ability. The nitrogen and oxygen ligands are much stronger electron donors than are phosphines, and hence only one ligand is required for the 19-electron fragment to be of sufficient oxidation potential to reduce the parent dimer. Substitution products do not form because the 19-electron intermediate, when it is formed with strong electron donor ligands, will transfer an electron rather than lose a carbonyl. With a strong electron donor, the associative attack on the metal increases M–CO π^*-backbonding thereby strengthening the metal–carbon bond.

(v) $\mathrm{Mn_2(CO)_{10}}$

The mechanism of the disproportionation of $\mathrm{Mn_2(CO)_{10}}$ with pyridine (eqn. 7) was proposed by McCullen and Brown [19] to be identical to that proposed for the reaction of $\mathrm{Co_2(CO)_8}$ with phosphines. (The only difference is that the initial production of radicals is photolytic in the $\mathrm{Mn_2(CO)_{10}}$ system.)

McCullen and Brown observed inhibition of the disproportionation by galvinoxyl, a result indicative of a radical mechanism. They also noted a strong ligand dependence in terms of the electron donating ability of the ligand. The rate of the reaction decreased going from alkyl substituted pyridine (good electron donor) to halide substituted pyridine (weak donor). Similarly, the relative amount of ionic products vs. substitution products decreased. This result is consistent with a decrease in the efficiency of the electron transfer step.

Stiegman and Tyler [53] pointed out that the very high quantum yields (greater than unity) that are typical for a radical chain reaction were conspicuously absent in reaction (7). They also suggested that a 19-electron intermediate analogous to that found in the disproportionation of the $\mathrm{Cp_2Mo_2(CO)_6}$ complex was forming in the disproportionation of

$$Mn_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} 2\,Mn(CO)_5 \tag{1}$$

$$\rightarrow Mn(CO)_5 + N \rightarrow Mn(CO)_4N + CO \tag{2}$$

$$Mn(CO)_4N + N \rightarrow Mn(CO)_3N_2 + CO \tag{3}$$

$$Mn(CO)_3N_2 + N \rightarrow Mn(CO)_3N_3 \tag{4}$$

$$Mn(CO)_3N_3 + Mn_2(CO)_{10} \rightarrow Mn(CO)_3N_3^+ + Mn_2(CO)_{10}^- \tag{5}$$

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

$$Mn(CO)_5 + Mn(CO)_4N \rightarrow Mn_2(CO)_9N \tag{7}$$

$$Mn(CO)_4N + Mn(CO)_4N \rightarrow Mn_2(CO)_8N_2 \tag{8}$$

$$Mn(CO)_3N_3 + Mn(CO)_5 \rightarrow Mn(CO)_3N_3^+ + Mn(CO)_5^- \tag{9}$$

Scheme 9. Photochemical disproportionation of $Mn_2(CO)_{10}$ in the presence of amines.

$Mn_2(CO)_{10}$. The inefficiency of the $Mn_2(CO)_{10}$ disproportionation reactions was attributed to the necessity of $Mn_2(CO)_{10}$ to substitute twice and then to add a third ligand to form the 19-electron intermediate. Therefore, a mechanism was proposed that is analogous to that of McCullen and Brown except for the inclusion of a 19-electron intermediate (Scheme 9). It was suggested that if the formation of a 19-electron intermediate was critical then a tridentate ligand should be the most efficient means of forming this intermediate. This prediction was experimentally verified. The quantum yields for diethylenetriamine were very high and well above unity [53]. The use of a tridentate ligand, which allows the substitution of the radical to be thought of as concerted, serves to simplify greatly the kinetics analysis of the mechanism. The derived expression for the quantum yield contains the same $I^{-1/2}$ dependence discussed previously. This dependence was experimentally verified [54].

E. CONCLUSION

The preponderance of data indicates that a radical chain mechanism is operative in the majority of the disproportionation reactions of metal–metal bonded carbonyl dimers. The mechanism, which involves homolysis of the metal–metal bond as the primary photoprocess, explains both the observed product distribution and the complex ligand effects observed in these reactions. There is strong kinetic evidence that this mechanism involves an interesting and previously unknown electron-rich 19-valence electron intermediate. This intermediate is a strong reducing agent [55] and accounts for the electron transfer character of the reactions. It is important to note, however, that alternative mechanisms not involving 19-valence electron species may be important. While further verification of the 19-electron intermediate by spectroscopic means is required, it is not unreasonable to suggest that this type of intermediate may prove to be important in many organometallic electron transfer reactions. Finally, although the possibility of direct heterolytic cleavage of the metal–metal bond is an attractive primary photoprocess in the disproportionation reactions, there is no evidence that this process occurs in any reaction system [56].

ACKNOWLEDGMENTS

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of the work carried out at Columbia University. Professor Ted Brown is thanked for several helpful discussions and Susan Fletcher is thanked for sending us a preprint of ref. 56.

Note added in proof

Recent mechanistic work by Goldman and Tyler has provided powerful evidence for the formation of a 19-electron species in the photochemical disproportionation of $Cp_2Mo_2(CO)_6$ by phosphines [57]. In addition, Mirbach et al. studied the disproportionation of $Co_2(CO)_8$ by P(n-butyl)$_3$ and proposed the intermediacy of a 19-electron Co(CO)$_3$(P(n-butyl)$_3$)$_2$ species [58]. In a related study, Fachinetti et al. showed that the disproportionation of $Co_2(CO)_8$ in THF takes place only when water is present [59].

REFERENCES

1 G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979.

2 (a) R.J. Haines, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc., A (1967) 94–98.
(b) M.S. Wrighton and D.J. Bredesen, J. Organomet. Chem., 50 (1973) C35–C38.

3 A.G. Osborne and M.H.B. Stiddard, J. Chem. Soc., (1964) 634–636.

4 In addition to the homolytic cleavage pathway usually invoked for the substitution mechanisms, recent work suggests that photolytic CO dissociation from the dimers may be an important ligand substitution pathway. See: R.B. Hitam, R.H. Hooker, K.A. Mahmoud, R. Naryanaswamy and A.J. Rest, J. Organomet. Chem., 222 (1981) C9–C13. R.H. Hooker, K.A. Mahmoud and A.J. Rest, J. Organomet. Chem., 254 (1983) C25–C28. A.F. Hepp and M.S. Wrighton, J. Am. Chem. Soc., 105 (1983) 5934–5935. A.F. Hepp, J.P. Blaha, C. Lewis and M.S. Wrighton, Organometallics, 3 (1984) 174–177.

5 R.J. Haines, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc. A, (1968) 43–46.

6 D.M. Allen, A. Cox, T.J. Kemp, Q. Sultana and R.B. Pitts, J. Chem. Soc., Dalton Trans., (1976) 1189–1193.

7 (a) R.A. Levenson, H.B. Gray and G.P. Ceasar, J. Am. Chem. Soc., 92 (1970) 3653–3658.
(b) R.A. Levenson and H.B. Gray, J. Am. Chem. Soc., 97 (1975) 6042–6047.

8 J.V. Caspar and T.J. Meyer, J. Am. Chem. Soc., 102 (1980) 7794–7795.

9 J.L. Hughey, C.R. Bock and T.J. Meyer, J. Am. Chem. Soc., 97 (1975) 4440–4441.

10 H. Huber, E.P. Kündig, G.A. Ozin and A.J. Poë, J. Am. Chem. Soc., 97 (1975) 308–314.

11 A.S. Huffadine, B.M. Reake, J.S. Robinson, P.A. Dawson, J. Organomet. Chem., 121 (1976) 391–403.

12 A. Fox and A.J. Poë, J. Am. Chem. Soc., 102 (1980) 2497–2499.

13 P.J. Fawcett, R.A. Jackson and A.J. Poë, J. Chem. Soc. Chem. Commun., (1975) 733–734. Q. Shi, T.C. Richmond, W.C. Trogler and F. Basolo, J. Am. Chem. Soc., 104 (1982) 4032–4034.

14 D.R. Kidd and T.L. Brown, J. Am. Chem. Soc., 100 (1978) 4095–4103.

15 A.E. Stiegman and D.R. Tyler, Acc. Chem. Res., 17 (1984) 61–66.

16 W. Hieber and W. Schropp, Z. Naturforsch., Teil B, 15 (1960) 271–277.

17 W. Hieber, W. Beck and G. Zeitler, Angew. Chem., 73 (1961) 364–368. Dombek and Angelici later showed that the product believed to be $Mn(CO)_3(NH_2(n\text{-butyl}))_3^+$ was actually *cis*-$Mn(CO)_4(NH_2butyl)(CONHbutyl)$. See B.D. Domlek and R.J. Angelici, J. Organomet. Chem., 134 (1977) 203–217.

18 (a) H. Behrens, E. Ruyter and H. Wakamatsi, Z. Anorg. Allgem. Chem., 349 (1967) 241–250.
(b) M. Herberbold, F. Wehrmann, D. Neugebauer and G. Huttner, J. Organomet. Chem., 152 (1978) 329–336.

19 S.B. McCullen and T.L. Brown, Inorg. Chem., 20 (1981) 3528–3533.

20 S.A. Hallock and A. Wojcicki, J. Organomet. Chem., 54 (1973) C27–C29.

21 A. Hudson, M.F. Lappert and B.K. Nicholson, J. Organomet. Chem., 92 (1975) C11–C14.

22 A. Hudson, M.F. Lappert, J.J. Macquitty, B.K. Nicholson, H. Zainal, G.R. Luckhurst, C. Zannoni, S.W. Bratt and M.C.R. Symons, J. Organomet. Chem., 110 (1976) C5–C8.

23 M.L. Zeigler, H. Haas and R.K. Sheline, Chem. Ber., 98 (1965) 2454–2459.

24 (a) A. Sacco, Gazz. Ital., 93 (1963) 698–707.
(b) C. Busetto, A.M. Matucci, E.M. Cernia and R. Bertani, J. Organomet. Chem., 246 (1983) 183–188.

25 A.E. Stiegman and D.R. Tyler, unpublished results.

26 (a) W. Hieber and H. Schulten, Z. Anorg. Allgem. Chem., 232 (1937) 29–38.
(b) W. Hieber, J. Sedlmeiern and W. Abeck, Chem. Ber., 86 (1953) 45–56.

27 (a) I. Wender, H.W. Sternberg and M. Orchin, J. Am. Chem. Soc., 74 (1952) 1216–1219.
(b) H.W. Sternberg, I. Wender, R.A. Friedel and M. Orchin, J. Am. Chem. Soc., 75 (1953) 3148–3152.

28 (a) A. Sacco and M. Freni, Ann. Chim. (Rome), 48 (1958) 218–224.
(b) A. Sacco and M. Freni, J. Inorg. Nucl. Chem., 8 (1958) 566–568.
(c) E.R. Tucci and B.H. Gwynn, J. Am. Chem. Soc., 86 (1964) 4838–4841.

29 M. Absi-Halabi, J.D. Atwood, N.P. Forbus and T.L. Brown, J. Am. Chem. Soc., 102 (1980) 6248–6254.

30 A.E. Stiegman and D.R. Tyler, J. Am. Chem. Soc., in press.

31 H.B. Abrahamson, M.C. Palazzotto, C.L. Reichel and M.S. Wrighton, J. Am. Chem. Soc., 101 (1979) 4123–4127.

32 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1980.

33 From their experiments with a series of phosphines, Haines, Nyholm, and Stiddard made the important observation that electronegative phosphines led only to substitution of the dimer but less electronegative phosphines gave disproportionation products [5]. A complete explanation is found in the Mechanistic Aspects section, p. 231.

34 (a) R.J. Haines and C.R. Nolte, J. Organomet. Chem., 24 (1970) 725–736.
(b) R.J. Haines, A.L. DuPreez and I.L. Marair, J. Organomet. Chem., 28 (1971) 97–104.

35 R.B. King, K.H. Pannell, C.A. Eggers and L.W. Houk, Inorg. Chem., 7 (1968) 2353–2356.

36 A.E. Stiegman, M. Stieglitz and D.R. Tyler, J. Am. Chem. Soc., 105 (1983) 6023–6037.

37 (a) A.R. Burkett, T.J. Meyer and D.G. Whitten, J. Organomet. Chem., 67 (1974) 67–73.
  (b) T.J. Meyer and J.L. Hughey, Inorg. Chem., 14 (1975) 947–949.

38 In THF, the halides do seem to act as ligands and will disproportionate the dimers. See ref. 30.

39 C.T.R. Burkett-St. Laurent, J.S. Field, R.J. Haines and M. McMahon, J. Organomet. Chem., 181 (1979) 117–130.

40 (a) D.M. Allen, A. Cox, T. Kemp and L.H. Ali, J. Chem. Soc., Dalton Trans., (1973) 1899–1901.
  (b) R.J. Haines and A.L. Dupreez, Inorg. Chem., 8 (1969) 1459–1464.
  (c) A.J. White, J. Organomet. Chem., 168 (1978) 197–202.
  (d) R.B. King, K.H. Pannell, C.A. Eggers and L.W. Houk, Inorg. Chem., 7 (1968) 2353–2356.

41 Under extreme forcing conditions, the following reactions of $Cp_2Fe_2(CO)_4$ also occur.

$$\mathrm{Cp_2Fe_2(CO)_4 + dppe \xrightarrow[2\ days]{170^\circ C} Fe(CO)_3dppe + Cp_2Fe + CO}$$

$$\mathrm{Cp_2Fe_2(CO)_4 + 2\ tripy \xrightarrow{160^\circ C} 2\ Fe(CO)_2(tripy) + (2\ Cp)}$$

See H. Behrens and W. Aquila, Z. Naturforsch., Teil B, 22 (1967) 454.

42 P.C. Ellgen, Inorg. Chem., 10 (1971) 232–239.

43 R.B. King, Inorg. Chem., 2 (1963) 939–944.

44 A.E. Stiegman, D.R. Tyler, J. Am. Chem. Soc., 104 (1982) 2944–2945.

45 The first kinetic study was performed by Heck (R.F. Heck, J. Am. Chem., 85 (1963) 657–661).

46 M. Absi-Halabi and T.L. Brown, J. Am. Chem. Soc., 99 (1977) 2982–2988.

47 N.P. Forbus, R. Oteiza, S.G. Smith and T.L. Brown, J. Organomet. Chem., 193 (1980) C71–C74.

48 N.P. Forbus and T.L. Brown, Inorg. Chem., 20 (1981) 4343–4347.

49 P.L. Stanghelli, R. Rosetti, E. Mentasti and E. Pelizzetti, Inorg. Chim. Acta, 22 (1977) 19–22.

50 B.A. Tolman, Chem. Rev., 77 (1977) 313–348.

51 (a) O.P. Anderson, S.A. Fieldhouse, C.E. Forbes and M.C.R. Symons, J. Organomet. Chem., 110 (1976) 247–255.
  (b) W.L. Waltz, O. Hackelberg, L.M. Dorfman and A. Wojcicki, J. Am. Chem. Soc., 100 (1978) 7259–7264.
  (c) R.E. Dessy, P.M. Weissman and R.L. Pohl, J. Am. Chem. Soc., 88 (1966) 5117–5121.

52 A.E. Stiegman and D.R. Tyler, J. Photochem., 24 (1984) 311–314.

53 A.E. Stiegman and D.R. Tyler, Inorg. Chem., 23 (1984) 527–529.

54 A.E. Stiegman and D.R. Tyler, J. Organomet. Chem., in press.

55 A.E. Stiegman, A.S. Goldman, D.B. Leslie and D.R. Tyler, J. Chem. Soc., Chem. Commun., (1984) 632–633.

56 Turner, Poliakoff, and Fletcher recently observed what they believe to be a direct photochemical heterolytic cleavage of the mixed metal $CpFe(CO)_2Co(CO)_4$ complex at low temperature in a CO doped Ar matrix. (J. Organomet. Chem., submitted for publication.)

57 A.S. Goldman and D.R. Tyler, J. Am. Chem. Soc., 106 (1984) 4066–4067.

58 M.F. Mirbach, M.J. Mirbach and R.W. Wegman, Organometallics, 3 (1984) 900–903.

59 G. Fachinetti, F. Del Cima, G. Braca and T. Funaioli, J. Organomet. Chem., 275 (1984) C25–C29.