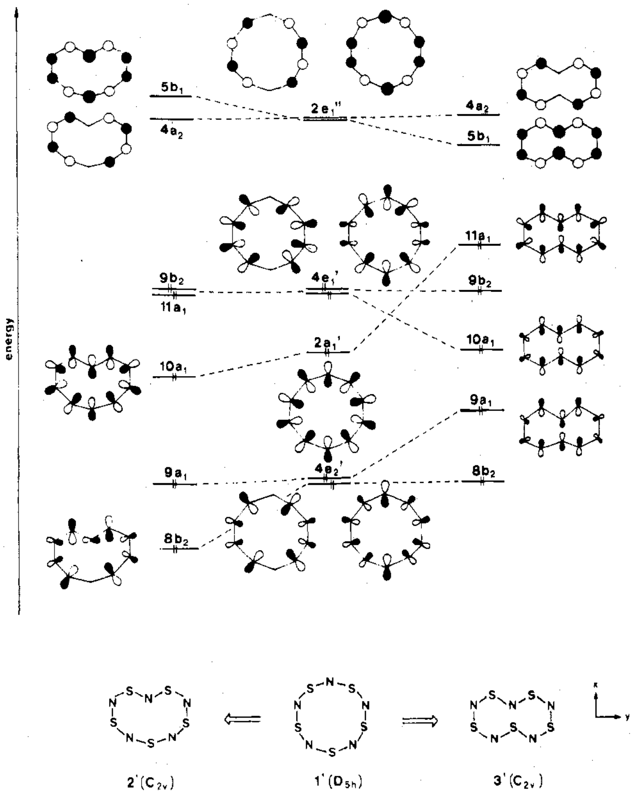

Figure 4. Comparison of the highest occupied σ MO's and lowest unoccupied π MO's of **1'** with those of **2'** and **3'**. The numbering refers to the valence orbitals only.

parameters (method I) suggested by Zahradník et al.[10]

We find only a small difference between the calculated transitions for the various model structures. This is anticipated since all six structures posess the same topology. In our all-valence-electron calculation a lone-pair combination is predicted to be the highest occupied molecular orbital for all six structures. This suggests the possibility that a π* ← n transition is contributing to one of the first two bands.

Concluding Remarks

Our MO calculations carried out on the six different structural possibilities **1'** to **4''** for $S_5N_5^+$ suggest that the configuration **4'** is a minimum on the $S_5N_5^+$ manifold. This structure provides a minimum of lone-pair interactions together with planarity of the system. The other structures investigated are at most local minima. This result suggests that a careful reexamination of the experimental x-ray data should clarify the question of the existence of two stable conformations of $S_5N_5^+$.

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Reaction Mechanisms of Metal–Metal Bonded Carbonyls. 18.[1] Kinetic Measurement of the Strengths of Some Metal–Metal Bonds

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The kinetics of some reactions in decalin of several substituted dimanganese carbonyl complexes have been studied. Activation enthalpies have been assigned to homolytic fission of the Mn–Mn bonds and provide a kinetic measure of the strengths of these bonds. Electronic absorption spectra of these and some related dimetal carbonyls are reported, and bands corresponding to the excitation of an electron from the metal–metal σ-bonding orbitals to the corresponding antibonding orbitals have been assigned. The effects of substituents on these transitions are interpreted in terms of a strengthening of the metal–metal interactions associated with increasing σ-donor character, increasing π acidity, and decreasing size of the substituents. A linear correlation is found between the activation enthalpies for homolytic fission and the values $h\nu(\sigma \rightarrow \sigma^*)$ for the decacarbonyls and several dimanganese carbonyls with one axial substituent or with two smaller ones. However, activation enthalpies for dimanganese complexes containing larger substituents lie below the linear plot by amounts directly related to the cone angles of the substituents. This is interpreted in terms of a substantial residual steric weakening effect on the kinetic bond strengths over and above the steric effect on the Mn–Mn σ interaction.

Introduction

The strengths of transition metal–transition metal bonds have been a matter of interest ever since the determination of the length of the Mn–Mn bond in $Mn_2(CO)_{10}$ suggested that the Mn–Mn bond was weak.[2] Subsequent thermochemical studies[3] have been undertaken in an attempt to provide quantitative measurement of the strengths of such bonds, but bond energies obtained in this way depend on a

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number of assumptions and are only very approximate. Mass spectroscopic studies[4] have also provided values of the strengths of the Mn–Mn, Tc–Tc, Mn–Re, and Re–Re bonds in the decacarbonyls, but the assumptions involved, the exact definition of the strengths so measured,[5] and their small number make them of limited usefulness. Force constants[6] for metal–metal stretching vibrations suffer from similar limitations. On the other hand, kinetic studies of reactions of $Mn_2(CO)_{10}$,[7] $MnRe(CO)_{10}$,[7] $Tc_2(CO)_{10}$,[8] and $Re_2(CO)_{10}$,[9] and of some of their substituted derivatives,[1,10] have provided good evidence that reversible homolytic fission is the major primary step in some of their reactions. Activation enthalpies for homolytic fission provide a kinetic measure of the strengths of the metal–metal bonds, and we report here kinetic data for reactions of a number of axially substituted dimanganese carbonyls. Evidence that these reactions also proceed by initial homolytic fission is discussed, and the effects of the substituents on the kinetic strengths of the metal–metal bonds in these and other related complexes are analyzed. UV–vis spectra of a number of substituted derivatives of such dimetal carbonyls are reported and the effects of substitution on the spectra are compared with those on the kinetics.

Experimental Section

Baker analyzed decalin was dried over molecular sieves and used without further treatment. Decacarbonyldimanganese (Strem Chemicals) was used either as received or after recrystallization from methanol. Tricyclohexylphosphine (Strem Chemicals), triphenyl phosphite (BDH, Ltd.), tri-*n*-butylphosphine and trimethyl phosphite (Baker Chemicals), and triphenylarsine (Eastman Organic Chemicals) were all used as received for the preparation of the substituted complexes.

The bis-substituted complexes $[Mn(CO)_4L]_2$ (L = PPh_3, PEt_3, PBu_3, $P(C_6H_{11})_3$, and $AsPPh_3$) were prepared by photochemical reaction of $Mn_2(CO)_{10}$ with a fivefold excess of ligand according to the method of Osborne and Stiddard.[11] Reactions were carried out in cyclohexane under argon in Schlenk tubes sealed with rubber serum caps and irradiated with light from a Hanovia medium-pressure mercury lamp. When L = PPh_3 and $AsPh_3$, the product crystallized continuously on the walls of the tube and the crystals were removed several times during the reaction. The crude products, obtained after removal of solvent under reduced pressure where appropriate, were recrystallized from dichloromethane–methanol mixtures. Irradiation times were 15–40 h and yields were 50–80%.

$[Mn(CO)_4P(OMe)_3]_2$ was prepared by refluxing $Mn_2(CO)_{10}$ (420 mg, 1.1 mmol) with $P(OMe)_3$ (63 mg, 5.1 mmol) in xylene (10 cm^3) for 18 h. Removal of solvent under reduced pressure yielded an orange oil which was chromatographed on a foil-wrapped Florisil column (Fisher, 100–200 mesh) made up in hexane. Unreacted $Mn_2(CO)_{10}$ was eluted with toluene in hexane (15% v/v). A broad yellow band of product was eluted with dichloromethane in hexane (≤45% v/v). Removal of solvent, followed by recrystallization from a CH_2Cl_2–MeOH mixture, yielded yellow crystals of product in 25% yield.

$Mn_2(CO)_9(PBu_3)$ was prepared by photochemical reaction (22 h) of $Mn_2(CO)_{10}$ with 1 equiv of PBu_3. Removal of solvent yielded an orange oil which was chromatographed on a foil-wrapped silica gel column (Grace Chemical Co., 100–200 mesh). Elution with hexane yielded unreacted $Mn_2(CO)_{10}$ followed by the monosubstituted product which was isolated in 45% yield as a yellow oil after removal of the solvent. $Mn_2(CO)_9P(OPh)_3$ was prepared by refluxing $Mn_2(CO)_{10}$ (300 mg, 0.77 mmol) with 1 equiv of $P(OPh)_3$ in xylene (10 cm^3) for 17 h. The oil remaining after removal of solvent was chromatographed on silica gel (100–200 mesh). Unreacted $Mn_2(CO)_{10}$ was eluted with hexane, and subsequent elution with toluene in hexane (15% v/v) followed by removal of solvent led to an orange waxy solid in 39% yield. $Mn_2(CO)_9P(C_6H_{11})_3$ was prepared in situ by reacting 4×10^{-4} mol dm^{-3} solutions of $[Mn(CO)_4P(C_6H_{11})_3]_2$ in cyclohexane at 55 °C for 15 h under an atmosphere of carbon monoxide. The absence of any IR bands due to $Mn_2(CO)_{10}$ or $[Mn(CO)_4P(C_6H_{11})_3]_2$ showed the product to be spectroscopically pure $Mn_2(CO)_9P(C_6H_{11})_3$ (IR bands at 2090 (s), 2002 (sh), 1994 (vs), 1974 (m), and 1930 (m) cm^{-1}). Similar reaction of a more concentrated solution, followed by evaporation of most of the solvent, led to a small yield of a spectroscopically identical product after the solution was allowed to stand for several weeks at −30 °C. IR spectra of all the complexes isolated were in excellent agreement with those in the literature.[12–18]

Table I. Electronic Absorption Spectra in Cyclohexane

Complex	λ, nm (rel intens)	
$Mn_2(CO)_{10}$	343 (10)	394 (2)
$Mn_2(CO)_9P(OPh)_3$	351 (10)	415 (2)
$Mn_2(CO)_9PPh_3$	361 (10)	422 (1)
$Mn_2(CO)_9PBu_3$	351 (10)	418 (1.3)
$Mn_2(CO)_9P(C_6H_{11})_3$	357 (10)	420 (0.6)
$[Mn(CO)_4P(OPh)_3]_2$	355 (10)	408 (2)
$[Mn(CO)_4P(OMe)_3]_2$	349 (10)	400 (2)
$[Mn(CO)_4PPh_3]_2$	376 (10)	440 (1)
$[Mn(CO)_4PEt_3]_2$	356 (10)	423 (1.5)
$[Mn(CO)_4PBu_3]_2$	356 (10)	422 (1)
$[Mn(CO)_4P(C_6H_{11})_3]_2$	366 (10)	419 (1.5)
$[Mn(CO)_4AsPh_3]_2$	375 (10)	459 (1)
$MnRe(CO)_{10}$	324 (10)	366 (4)
$MnRe(CO)_8(PPh_3)_2$	347 (10)	398 (2)
$Re_2(CO)_{10}$	276 (8)	311 (10)
$[Re(CO)_4PPh_3]_2$	300 (10)	340 (4)
$Tc_2(CO)_{10}$	316 (10)	Ca. 350 (2)
$[Tc(CO)_4PPh_3]_2$	<310	

Argon (99.998%), carbon monoxide (CP grade, 99.5%), and oxygen were "Linde" Specialty gases from Union Carbide of Canada, Ltd. An O_2–N_2 mixture (5.4% ± 0.1% O_2) was obtained from Matheson of Canada, Ltd.

Spectra of solutions were measured in the C–O stretching region with Perkin-Elmer 257 or 180 spectrophotometers calibrated with polystyrene film. Electronic spectra were recorded with a Cary 16K recording spectrophotometer, the cells being contained in a cell block thermostated at 22 °C. The spectroscopic data are shown in Table I.

Kinetic runs were performed by standard techniques.[7,19] For reactions with oxygen, weighed samples of complex were dissolved in decalin in a Schlenk tube and the tube was closed with a rubber septum cap. Oxygen was bubbled through the solution and out of the reaction vessel via stainless steel tubes inserted through the cap for 15 min at room temperature. The exit tube was then removed, and the reaction vessel was wrapped in foil, immersed in an oil bath, and shaken for 2–3 min until thermal equilibrium was attained. A slight positive pressure of oxygen was maintained above the solution during the reaction. Similar procedures were followed for some of the reactions with air. Temperatures were measured with partial immersion thermometers graduated in 0.1 °C divisions (Brinkman Instruments, Canada, Ltd., or Brooklyn Thermometer Co.) and were constant to better than ±0.1 °C. Samples were expressed periodically through stainless-steel tubing either directly into the IR cells for immediate measurement (reaction temperatures ≤100 °C) or into glass vials cooled in ice (reaction temperatures ≥120 °C) for subsequent recording. Some reactions under air were followed directly in silica cells placed in a thermostated cell holder in a Cary 16K or Perkin-Elmer 402 spectrophotometer. Temperatures of these reaction mixtures were measured by use of a thermistor calibrated against partial immersion thermometers or against a platinum resistance thermometer (Minco Products, Inc.) with a digital multimeter (Data Precision Corp., Model 3500). Pseudo-first-order rate plots were made in the usual way. Absorbances at completion of reaction were negligible, and the reactions were followed for ca. 3 half-lives. Reaction with O_2 generally led to complete decomposition, no carbonyl-containing products being formed, and excellent rate plots were obtained in all cases.

The bis(tricyclohexylphosphine) complex was difficult to dissolve and solutions were prepared by heating suspensions in thoroughly degassed decalin under Ar to 80 °C for several minutes with vigorous shaking before cooling and filling the space above the solution with the appropriate gas. No spectroscopic evidence for any reaction during this process was observed. Reaction of $[Mn(CO)_4AsPh_3]_2$ showed some different features. The complex was slow to dissolve in decalin in the cold, and solutions were, therefore, prepared by heating thoroughly degassed suspensions for ca. 1 min at 60 °C. In the absence of added $AsPh_3$ this led to solutions showing IR bands attributable only to $Mn_2(CO)_9AsPh_3$ (2092 (m), 2014 (s), 1966 (vs), 1975 (m), 1939 (s) cm^{-1}). In the presence of added $AsPh_3$, formation of monosubstituted complex in this way was reduced, and negligible amounts were formed for $[AsPh_3] \gtrsim 0.05$ mol dm^{-3}. Subsequent

Table II. First-Order Rate Constants for Decomposition of $Mn_2(CO)_{10-n}L_n$ in Decalin under Oxygen[a]

L	n	10^6k_{obsd}, s^{-1}, at various temperatures
$P(OPh)_3$	1	100.1 °C, 22.6, 23.0, 24.0, 22.0; 109.9 °C, 75.5,[b,d] 74.8;[b,d] 110.0 °C, 87.4, 87.2, 85.0, 85.6; 120.6 °C, 312, 313, 306; 130.2 °C, 965, 942, 932, 961
PPh_3	1	70.0 °C, 11.1, 10.9, 11.0; 80.0 °C, 52.8, 51.7, 51.6,[b] 51.2; 90.0 °C, 214, 215, 214; 100.0 °C, 842, 825, 838, 863
PBu_3	1	80.0 °C, 9.71, 9.60, 9.43,[b] 9.62,[b] 9.42;[b] 90.0 °C, 40.6, 41.0, 41.3, 42.1; 100.2 °C, 171, 170, 169, 171, 166; 109.9 °C, 662, 621,[b] 562,[b] 649, 613;[b] 110.0 °C, 504,[c,d] 586[c,d]
$P(C_6H_{11})_3$	1	54.9 °C, 8.06;[b] 65.0 °C, 47.4,[b] 51.0;[b] 74.7 °C, 160,[b] 164, 159,[b] 162; 84.9 °C, 659,[b,e] 669; 85.0 °C, 661,[b] 681; 89.9 °C, 1230, 1280[b]
$P(OMe)_3$	2	70.0 °C, 6.76, 6.70, 7.03; 80.0 °C, 29.9, 30.9, 29.8, 29.9; 90.0 °C, 136, 131, 134, 132; 100.0 °C, 527, 528, 524, 537; 110.0 °C, 1930,[b] 2040,[b] 2050,[b] 1990, 2000, 1960
PEt_3	2	30.0 °C, 6.88,[f] 7.46,[f] 7.32,[f] 6.63;[f] 40.2 °C, 58.8,[f] 52.5;[f] 50.0 °C, 241,[f] 237,[f] 216, 213,[f] 212, 206; 50.2 °C, 241,[f] 237,[f] 216, 213,[f] 212, 206; 50.2 °C, 230,[b] 249;[b] 59.8 °C, 949; 60.1 °C, 1040,[b] 1060,[b] 1050[b]
PBu_3	2	30.5 °C, 9.98,[b] 9.79;[b] 40.5 °C, 55.7, 57.2;[b] 50.5 °C, 300, 309,[b] 295;[b] 60.4 °C, 1210,[b] 1190,[b] 1220[b]
$P(C_6H_{11})_3$	2	10.2 °C, 58.0,[g] 54.0;[g] 20.0 °C, 254,[g] 264;[g] 29.9 °C, 993, 1040, 989,[g] 998;[g] 40.0 °C, 3440,[g] 3510,[g] 3290[g]
$AsPh_3$[h]	2	24.9 °C, 32.3,[i] 32.0;[i] 35.2 °C, 204,[i] 192,[i] 171;[i] 45.0 °C, 1040,[i] 1000,[i] 1100,[i] 969,[i] 998

[a] $[Complex]_0$ = ca. 3 × 10^{-4} mol dm^{-3} and reactions were studied by IR methods unless otherwise specified. [b] Reactions under air. [c] Reactions under 5% O_2 in O_2–N_2 mixtures. [d] Not used in estimation of activation parameters. [e] Reaction using isolated $Mn_2(CO)_9P(C_6H_{11})_3$; all other solutions of this complex were prepared in situ (see text). [f] Reactions under air followed at 376 nm, $[complex]_0$ = 1.2 × 10^{-4} mol dm^{-3}. [g] Reactions under air followed at 366 nm, $[complex]_0$ = 2 × 10^{-4} mol dm^{-3}. [h] $[AsPh_3]$ = 0.89 mol dm^{-3}. [i] Reaction under air followed at 375 nm, $[complex]_0$ = 2 × 10^{-4} mol dm^{-3}.

Table III. First-Order Rate Constants for Reactions of $[Mn(CO)_4L]_2$ in Decalin with *syn*-$C_2H_2Cl_4$

L = PPh_3, 39.9 °C

$10^3[C_2H_2Cl_4]$, mol dm^{-3}	5.0	10.0	25.0	50.0	100	100	950
10^4k_{obsd}, s^{-1}	0.60[a]	2.0	5.35	7.38	7.80	7.83	6.95

L = PBu_3, 60.0 °C

$10^3[C_2H_2Cl_4]$, mol dm^{-3}	1.40	9.30	10.5	400
10^4k_{obsd}, s^{-1}	11.1	11.0	12.2	12.8[b]

L = $P(C_6H_{11})_3$, 29.9 °C

$10^3[C_2H_2Cl_4]$, mol dm^{-3}	400	400	380	400	410
10^4k_{obsd}, s^{-1}	10.7	10.2	9.90	10.2[c]	10.3[c]

[a] From initial gradient; gradient increases with time. [b] $[PBu_3]$ = 6 × 10^{-2} mol dm^{-3}. [c] $[P(C_6H_{11})_3]$ = 4.3 × 10^{-2} mol dm^{-3}.

reaction under air led to complete loss of the bis(arsine) complex and formation of more $Mn_2(CO)_9AsPh_3$ in amounts that also decreased with increasing $[AsPh_3]$. The final yield of mono(arsine) complex was ca. 20% when $[AsPh_3]$ = 0.05 mol dm^{-3} but it was negligible when $[AsPh_3] \geq 0.5$ mol dm^{-3}. No spectroscopic evidence was obtained for formation of any arsenido-bridged complex $[Mn(CO)_4AsPh_2]_2$, known to be formed at higher temperatures.[20] Kinetic data were obtained with $[AsPh_3]$ = 0.89 mol dm^{-3} where no $Mn_2(CO)_9AsPh_3$ was formed and all first-order rate plots were linear for 3 half-lives.

The complexes $[Mn(CO)_4L]_2$ [L = PPh_3, PBu_3, and $P(C_6H_{11})_3$] were also reacted with 1,1,2,2-tetrachloroethane in decalin under an inert atmosphere. When L = PPh_3, bands grew at 2095 (s), 2028 (s), 2009 (vs), and 1960 (s) cm^{-1} and identified the product as *cis*-$Mn(CO)_4Cl(PPh_3)$.[21] When L = PBu_3 and $P(C_6H_{11})_3$, bands grew at 2087 (930), 2020 (1750), 2001 (4000), and 1945 (3000) cm^{-1} and at 2085 (1750), 2015 (2060), 1998 (5500), and 1943 (4070) cm^{-1}, respectively, and these products can also be characterized as the analogous cis complexes. The absorption coefficients of the IR bands, shown above in parentheses, were obtained after isolation of the product complexes. The values enabled the yields of the products of the reactions with $C_2H_2Cl_4$ in solution to be shown to be very nearly quantitative. Reactions in the presence of free L were also followed kinetically when the initial mono(phosphine) products were found to react further to form bis(phosphine) complexes. Good first-order rate plots were obtained.

Rate constants for all these reactions are shown in Tables II and III, and corresponding activation parameters, together with those for reactions of some closely related complexes, are shown in Table IV. Activation parameters were obtained by an unweighted, least-squares analysis of the dependence of log (k_{obsd}/T) on $1/T$. Each measurement of k_{obsd} was assumed to have the same percentage uncertainty so that all values of log (k_{obsd}/T) have the same absolute uncertainty, estimates of which are given by the analysis. Only limiting values of k_{obsd}, independent of $[O_2]$, were used. The approximate standard deviations obtained from the least-squares analysis were multiplied by the t factor appropriate to the number of degrees of freedom to give 95% confidence limits. These were divided by 1.96 to give estimates of standard deviations independent of the number of degrees of freedom, and it is these standard deviations that are quoted in Table IV.

Discussion

Positive kinetic evidence for reversible homolytic fission in reactions of $Mn_2(CO)_{10}$,[7] $MnRe(CO)_{10}$,[7] $Tc_2(CO)_{10}$,[8] and $Re_2(CO)_{10}$[9] with O_2 in decalin has been obtained, and the activation parameters are listed in Table IV. No evidence for a CO-dissociative path was obtained.[7] The reaction of the axially substituted complex $[Mn(CO)_4P(OPh)_3]_2$ with O_2 also shows kinetic behavior characteristic of initial, reversible homolytic fission,[1] and the possibility of a phosphite-dissociative path was conclusively disproved. The activation parameters for the substitution reaction with CO are indistinguishable from those for reaction with O_2.[1]

The substitution reactions of $[Mn(CO)_4PPh_3]_2$ with $P(OPh)_3$ and CO in cyclohexane also show kinetic behavior characteristic of initial, reversible homolytic fission and are quite inconsistent with a PPh_3- or CO-dissociative path.[10] Reaction with *syn*-$C_2H_2Cl_4$ leads to *cis*-$Mn(CO)_4Cl(PPh_3)$ at a limiting rate equal to that for decomposition under O_2 suggesting that these reactions also occur via homolytic fission and subsequent reaction of the $Mn(CO)_4PPh_3$ radicals produced. Activation parameters for substitution with CO and decomposition with O_2 are virtually indistinguishable.[23]

The complexes $[Mn(CO)_4L]_2$ [L = PBu_3 and $P(C_6H_{11})_3$] also react with $C_2H_2Cl_4$ and form *cis*-$Mn(CO)_4ClL$ in essentially quantitative yields at limiting rates equal to their rate of reaction with O_2 and are quite unaffected by the presence of free phosphine. Benner and Balch have used spin-trapping techniques to demonstrate qualitatively that the complexes $[Mn(CO)_4L]_2$ [L = $P(OEt)_3$, PEt_3, $AsPh_3$, etc.] undergo thermal homolytic fission in dichloromethane.[25] It, therefore, seems reasonable to conclude that the complexes with L = $P(OMe)_3$, PEt_3, and $AsPh_3$ undergo rate-limiting homolytic fission in their thermal reactions with O_2 in decalin. The activation enthalpies for reactions with oxygen, shown in Table IV, provide, therefore, a quantitative, kinetic measure of the strengths of the metal–metal bonds in these complexes.

The strengths of the Mn–Mn bonds in $[Mn(CO)_4L]_2$ vary with L in the order L = CO ~ $P(OMe)_3$ ~ $P(OPh)_3$ > PEt_3 ≳ PBu_3 ~ $AsPh_3$ > PPh_3 > $P(C_6H_{11})_3$, the quantitative effect of these different substituents being quite large. The sequence is not related to the σ-donor character of the phosphorus ligands as quantified by the relative half-neutralization potentials[26] (Table V). It is, however, related closely to the size of the substituents, a plot of the values of $\Delta H^{\ddagger}$ for homolytic fission, $\Delta H^{\ddagger}_{hf}$, against the cone angles[27,28] of the substituents being shown in Figure 1. The cone angle for $AsPh_3$ has not been measured but it has been assumed[28] to be similar to that for PPh_3. We would prefer to argue that it has a smaller cone angle than PPh_3 because the larger As atom removes the phenyl groups further away from other

Table IV. Activation Parameters[a] for Reactions in Decalin

No.	Complex	Reactant	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\sigma(k_{\text{obsd}})$, %	Ref
1	$Mn_2(CO)_{10}$	O_2	153.8 ± 1.6	73.6 ± 3.8		22
2	$Mn_2(CO)_9P(OPh)_3$	O_2	151.2 ± 0.9	69.5 ± 2.2	3.1	This work
3		$P(OPh)_3$[b]	155.5 ± 5.4	83.6 ± 15.1		13
4	$Mn_2(CO)_9(PBu_3)$	O_2	154.0 ± 0.9	93.5 ± 2.2	3.7	This work
5		PBu_3[b]	140.9 ± 3.3	61.5 ± 9.2		13
6	$Mn_2(CO)_9PPh_3$	O_2	150.7 ± 0.4	98.1 ± 1.3	1.8	This work
7		CO	123.9 ± 0.9	13.8 ± 2.5	3.5	23
8		PPh_3	133.1 ± 2.1	50.2 ± 5.4	5.0	23
9	$Mn_2(CO)_9P(C_6H_{11})_3$	O_2	141.0 ± 1.5	86.4 ± 4.0	6.3	This work
10	$[Mn(CO)_4P(OMe)_3]_2$	O_2	152.5 ± 0.4	99.2 ± 1.3	2.6	This work
11	$[Mn(CO)_4P(OPh)_3]_2$	O_2	151.0 ± 2.1	81.4 ± 5.4	8.6	1
12		CO	149.3 ± 2.5	75.5 ± 6.5	9.5	1
13	$[Mn(CO)_4(PBu_3)]_2$	O_2	133.2 ± 1.6	97.7 ± 5.1	6.9	This work
14	$[Mn(CO)_4(PEt_3)]_2$	O_2	136.0 ± 1.6	105.2 ± 5.0	6.7	This work
15	$[Mn(CO)_4(PPh_3)]_2$	O_2[c]	120.0 ± 0.6	77.8 ± 1.7	2.8	23
16		CO[c]	117.2 ± 0.8	64.4 ± 2.5	3.5	23
17	$[Mn(CO)_4P(C_6H_{11})_3]_2$	O_2	99.1 ± 1.3	24.2 ± 4.4	6.4	This work
18	$[Mn(CO)_4(AsPh_3)]_2$	O_2	133.4 ± 2.4	116.3 ± 7.5	7.6	This work
19	$MnRe(CO)_{10}$	PPh_3	162.8 ± 0.8	77.3 ± 2.1	4.2	8
20	$MnRe(CO)_8(PPh_3)_2$	CO	155.2 ± 1.3	94.6 ± 3.8	3.0	8
21	$Tc_2(CO)_{10}$	PPh_3	160.1 ± 0.8	82.6 ± 2.1	4.0	8
22	$[Tc(CO)_4(PPh_3)]_2$	CO	138.0 ± 2.2	42.3 ± 5.4	3.8	8
23	$Re_2(CO)_{10}$	PPh_3	165.5 ± 0.8	66.9 ± 1.7	4.6	24
24	$[Re(CO)_4(PPh_3)]_2$	CO	162.2 ± 2.1	89.9 ± 6.3	6.5	17

[a] From rate constants independent of [reactant]. [b] In xylene; parameters recalculated from data in ref 13. [c] In cyclohexane.

Table V. Energies of the $\sigma \rightarrow \sigma^*$ Transitions and Some Related Parameters

Complex	$h\nu(\sigma \rightarrow \sigma^*)$, kJ mol^{-1}	$\Delta(\Delta H^{\ddagger})$,[a] kJ mol^{-1}	Substituent cone angle,[26] deg	Δ(hnp),[b] mV
$Mn_2(CO)_{10}$	349	−1.2 ± 1.6		
$Mn_2(CO)_9P(OPh)_3$	341	−1.7 ± 0.9	128	875
$Mn_2(CO)_9(PBu_3)$	341	+1.1 ± 0.9	130	131
$Mn_2(CO)_9(PPh_3)$	331	+0.6 ± 0.4	145	573
$Mn_2(CO)_9P(C_6H_{11})_3$	335	−10.2 ± 1.5	179	33
$[Mn(CO)_4P(OMe)_3]_2$	342	−0.6 ± 0.4	107	520
$[Mn(CO)_4P(OPh)_3]_2$	338	−1.0 ± 2.1	128	875
$[Mn(CO)_4(PBu_3)]_2$	337	−18.5 ± 1.6	130	131
$[Mn(CO)_4(PEt_3)]_2$	337	−15.7 ± 1.6	132	111
$[Mn(CO)_4(PPh_3)]_2$	318	−26.5 ± 0.6	145	573
$[Mn(CO)_4P(C_6H_{11})_3]_2$	327	−49.9 ± 1.3	179	33
$[Mn(CO)_4(AsPh_3)]_2$	319	−13.4 ± 2.4	<145	
$MnRe(CO)_{10}$	370	+2.0 ± 0.8		
$MnRe(CO)_8(PPh_3)_2$	346	+1.1 ± 1.3	145	573
$Tc_2(CO)_{10}$	379	−3.2 ± 2.1		
$[Tc(CO)_4(PPh_3)]_2$	>387	−(>28)	145	573
$Re_2(CO)_{10}$	386	+0.4 ± 0.8		
$[Re(CO)_4(PPh_3)]_2$	398	−6.3 ± 2.1	145	573

[a] $\Delta H^{\ddagger}$ assigned to homolytic fission *minus* $\Delta H^{\ddagger}$ expected from linear plot in Figure 2. [b] Relative half-neutralization potentials for titration of free substituent ligand against perchloric acid in nitromethane.[26] Basicity of ligand increases with decreasing Δ(hnp).

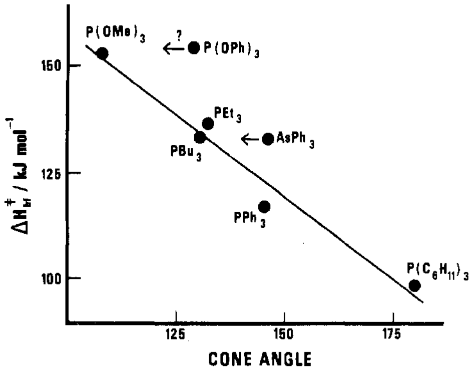

Figure 1. Dependence of the enthalpy of activation assigned to homolytic fission of $[Mn(CO)_4L]_2$ on the cone angle of L.

neighboring ligands. The cone angle for $P(OPh)_3$ is quite large and suggests that a kinetic effect should show up in $[Mn(CO)_4P(OPh)_3]_2$ to almost the same extent as in $[Mn(CO)_4PEt_3]_2$. It appears,[27] however, that the size of $P(OPh)_3$ is not as precisely defined as for the other ligands so we do not regard this anomaly as serious. This kinetic demonstration of the primacy of steric effects in determining the ease of homolytic fission runs directly counter to the conclusion of Balch et al.,[25] based on qualitative observations, that homolysis results from electronic effects.

The mechanisms of reaction of the complexes $Mn_2(CO)_9L$ are less clear. If homolytic fission were the only initial step for substitution or decomposition, then the limiting-rate constants for reaction with O_2, L, and CO should be identical. This is not the case. For L = PPh_3 and PBu_3, $\Delta H^{\ddagger}$ for reaction with O_2 is higher than that for reaction with L although, when L = $P(OPh)_3$, the values for the two reactions are almost identical. $\Delta H^{\ddagger}$ for reaction of $Mn_2(CO)_9(PPh_3)$ with CO is even lower than that for reaction with PPh_3 and it has been argued[23] that it is the former value that should be used as a measure of the kinetic strength of this Mn–Mn bond. This problem cannot be resolved until the reactions of the monosubstituted complexes have received further study. In any case, values of $\Delta H^{\ddagger}$ for reaction of the other monosubstituted complexes with CO are not yet available for comparison. If the values for reaction with O_2 are considered appropriate, however, then the kinetic bond strengths in $Mn_2(CO)_9L$ vary as L = CO ~ PBu_3 ~ $P(OPh)_3$ ~ PPh_3 > $P(C_6H_{11})_3$. The steric effect shows up only for the largest ligand, which is not unreasonable. If values of $\Delta H^{\ddagger}$ for reaction with L are considered, then the steric effect also shows up for L = PPh_3 and PBu_3 and to an extent expected from their sizes.

Electronic Spectra. Gray and co-workers[29,30] have assigned the more intense band in the near-UV region of the electronic spectra of $M_2(CO)_{10}$ (M_2 = Mn_2, MnRe, Tc_2, and Re_2), $Mn_2(CO)_9(PPh_3)$, and $[Mn(CO)_4(PPh_3)]_2$ to the excitation of an electron from the bonding σ orbitals to the corresponding antibonding orbitals involved in the metal–metal bonds. The energies of the transitions are, therefore, a measure of the strengths of the attractive interactions between the two metals. They do not reflect directly any other attractive or repulsive interactions between the halves of each molecule which remain unaltered during the excitation. Although the significance of the energies is greater when they are obtained from low-temperature spectra, it seems likely that the relative energies from room-temperature spectra are of significance in the series of closely related complexes considered here. The shapes of the spectra are all very similar and we have assigned the more intense band in the near-UV in each case to the $\sigma \rightarrow \sigma^*$ transition by analogy to the assignments of Gray et al.[29,30] The energies (Table V) are, where comparable, very close to those obtained in other solvents[25,31] and can be correlated with the electronic and steric properties of the substituents as follows.[32]

For the complexes $[Mn(CO)_4L]_2$ (L = phosphine), the strength of the Mn–Mn interaction increases with increasing σ-donor character of L but decreases with increasing size. Thus $h\nu(\sigma \rightarrow \sigma^*)$ increases from L = PPh_3 to L = PEt_3 and PBu_3, but it then decreases sharply for the still more basic but much larger L = $P(C_6H_{11})_3$. In spite of its large size, however, when L = $P(C_6H_{11})_3$ the Mn–Mn interaction is greater than when L = PPh_3, thus illustrating the importance of basicity in enhancing the interaction. When L = phosphite or CO, the interactions are considerably stronger than when L = phosphine and this can be associated with their greater π-acid character and, to some extent, with their smaller size. The former prevents the accumulation of d_π electron density on the Mn atoms and so diminishes d_π–d_π repulsive energies[30] while the latter reduces interligand repulsion effects. The exact mode of operation of these π-acid and steric effects is not clear, however, because neither of them appears to influence the Mn–Mn σ interaction through effects on the Mn–Mn bond length. If anything, phosphine substituents tend to shorten the Mn–Mn bond.[33] The similar energies when L = PPh_3 and $AsPh_3$ suggest that the effect of the weaker σ-donor (and, possibly, π-acid) character of $AsPh_3$ is balanced by its smaller effective size. The trends for the $Mn_2(CO)_9L$ complexes for which data are available are identical with those for $[Mn(CO)_4L]_2$, although the effects are smaller as might be expected.

The effect of PPh_3 substituents on the Mn–Re, Tc–Tc, and Re–Re interactions can be seen in similar terms. The PPh_3 ligands in $[Re(CO)_4(PPh_3)]_2$ actually increase the Re–Re interaction slightly[31] so that the strengthening effect of their basicity is not overcome by their weaker π acidity and/or larger size. Both of the latter effects would be expected to diminish with increasing metal–metal distance. Only a lower limit for the Tc–Tc interaction in $[Tc(CO)_4(PPh_3)]_2$ is known because the spectrum was measured with a sample produced in situ in the presence of an excess of PPh_3 which obscured the absorption maximum due to the complex.[8] The substituents must, however, increase the interaction by at least 8 kJ mol^{-1}, and this is comparable with the substituent effect on the Re–Re bond which is of closely similar length.[2,34] The effect of the PPh_3 in $MnRe(CO)_8(PPh_3)_2$ is intermediate between that in $[Mn(CO)_4(PPh_3)]_2$ and $[Re(CO)_4(PPh_3)]_2$, as might be expected from the intermediate nature of the Mn–Re bond length,[35] although it is rather closer to the former. This analysis bears out the belief of Lemoine et al.[31] that the electron-donating character of PPh_3 is not sufficient to account for its spectroscopic effects in such complexes.

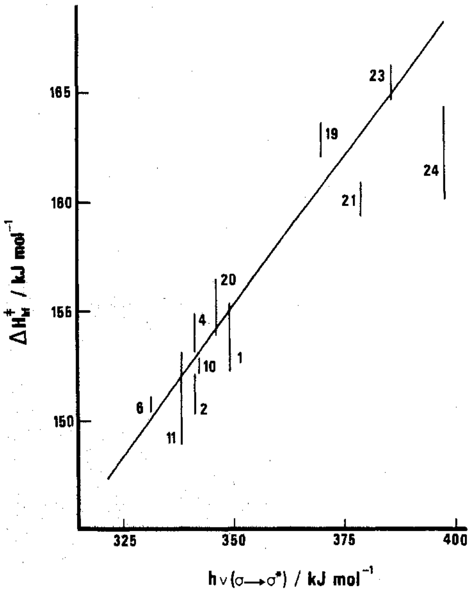

Figure 2. Dependence of enthalpies of activation for homolytic fission on the energies of the corresponding $\sigma \rightarrow \sigma^*$ transitions. Reaction numbering is taken from Table IV.

Correlations between Kinetic and Spectroscopic Parameters. Another set of spectroscopic data related to the strengths of the metal–metal bonds in such complexes is provided by the stretching force constants for the metal–metal vibrations.[6] There is an excellent linear correlation between the force constants and the activation enthalpies for homolytic fission for the four decacarbonyls,[36] but force constants are not available for the substituted complexes for which, by contrast, values of $h\nu(\sigma \rightarrow \sigma^*)$ are so readily obtainable. When values of $\Delta H^{\ddagger}_{hf}$ for the decacarbonyls are plotted against values of $h\nu(\sigma \rightarrow \sigma^*)$, a straight line can be drawn through the points with only minor deviations.[36,37] The data for $[Mn(CO)_4P(OPh)_3]_2$ and $[Mn(CO)_4P(OMe)_3]_2$ (for which homolytic fission has been demonstrated) also lie on this line, as do those for several other complexes (Figure 2). The relatively low gradient of ca. 0.3 is not inconsistent with there being extensive metal–metal bond breaking in the transition state because the value of $h\nu(\sigma \rightarrow \sigma^*)$ is a measure only of one part of the total interaction, attractive and repulsive, between the halves of the molecule. It cannot, for instance, reflect *directly* any increased enthalpy in the molecule due to repulsions between the two sets of equatorial ligands. As the halves of the molecule separate, there will be a decrease in the repulsions between the two sets of equatorial ligands and also a decrease in any repulsions between the five ligands on any one metal. This will tend to reduce the values of $\Delta H^{\ddagger}_{hf}$ compared with the energies of the electronic transitions during which no change of atomic positions occurs. These effects will make the gradient less than it would have been if only M–M bond breaking contributed to the value of $\Delta H^{\ddagger}_{hf}$.

If the linear relationship between $\Delta H^{\ddagger}$ and $h\nu(\sigma \rightarrow \sigma^*)$ in Figure 2 is accepted as, at least, an empirical measure of the dependence of $\Delta H^{\ddagger}_{hf}$ on the metal–metal interaction, then the deviations from the line (Figure 3) of data for other Mn_2

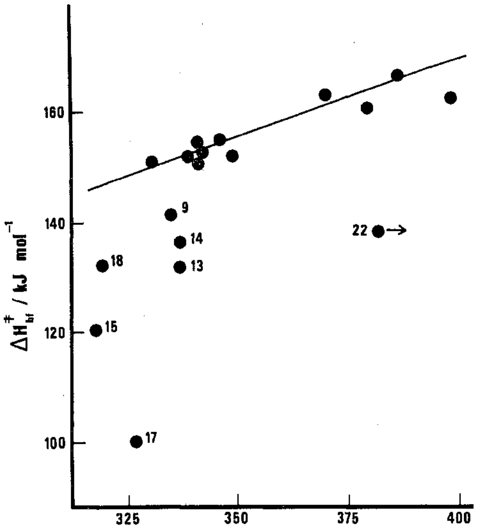

Figure 3. Steric weakening of the kinetic bond strengths due to the presence of large substituents as shown by deviations from the linear relationship between $\Delta H^{\ddagger}_{hf}$ and $h\nu(\sigma \rightarrow \sigma^*)$ that is obeyed by the decacarbonyls and their derivatives containing two relatively small substituents or only one substituent. Reaction numbering is taken from Table IV.

complexes can be considered as follows. The values of $\Delta H^{\ddagger}$ all lie below the line by amounts, shown in Table V as $\Delta(\Delta H^{\ddagger})$, which are directly related to the size of the substituents. Thus, although the Mn–Mn interaction can be decreased to some extent by steric effects, a residual steric effect on the kinetics is also shown with larger substituents. It is relieved only when the Mn–Mn bond stretches to form the transition state when interligand repulsions are decreased as each Mn atom approaches a five-coordinate state. While differences in the metals involved, or the presence of relatively small substituents, do have closely related effects on the metal–metal σ interactions and the kinetic bond strengths, the residual steric effects of larger substituents in weakening the kinetic strengths of the Mn–Mn bonds is much greater. Thus, the total range of $\Delta H^{\ddagger}_{hf}$ values for complexes lying on the line is only ca. 15 kJ mol^{-1}, whereas the residual steric effect of two $P(C_6H_{11})_3$ substituents lowers the kinetic strength of the Mn–Mn bond by 50 kJ mol^{-1} (i.e., ca. 30%). The overall weakening of the Mn–Mn σ interaction by the two $P(C_6H_{11})_3$ ligands is shown by a decrease of only 20 kJ mol^{-1} (ca. 5%) in $h\nu(\sigma \rightarrow \sigma^*)$.

The effect of two PPh_3 substituents on the Mn–Mn, Mn–Re, Tc–Tc, and Re–Re bonds can be considered in a similar way. Evidence has been adduced for initial homolytic fission in reactions of CO with $[Mn(CO)_4(PPh_3)]_2$[10,23] and $[Re(CO)_4(PPh_3)]_2$,[17] and this mechanism can be assigned by analogy to the same reactions of $MnRe(CO)_8(PPh_3)_2$ and $[Tc(CO)_4(PPh_3)]_2$.[8] The presence of two PPh_3 ligands in the Mn_2 complex decreases the Mn–Mn σ interaction by 30 kJ mol^{-1} but there is a residual steric effect that leads to a value of –30 kJ mol^{-1} for $\Delta(\Delta H^{\ddagger})$. Two PPh_3 ligands attached to a Mn–Re bond decrease the σ interaction to a slightly lesser extent (24 kJ mol^{-1}) but no residual steric effect is exhibited on the kinetics. In the case of the Re_2 complexes, $h\nu(\sigma \rightarrow \sigma^*)$ appears to be increased by two PPh_3 substituents, the value of $\Delta(\Delta H^{\ddagger})$ is small, and the residual steric effect is again almost negligible. The Tc_2 complexes also show an increase in the σ interaction on substitution. However, the residual steric effect is large [$-\Delta(\Delta H^{\ddagger}) > 28$ kJ mol^{-1}] and the reason for this is not clear.

The only monosubstituted complex for which there is a clear residual steric effect on the kinetics is $Mn_2(CO)_9P(C_6H_{11})_3$ for which $\Delta(\Delta H^{\ddagger})$ is –10 kJ mol^{-1}, or ca. 20% of that for $[Mn(CO)_4P(C_6H_{11})_3]_2$. This is reasonable since the $Mn(CO)_5$ group in the monosubstituted complex should more easily adjust to steric repulsions caused by the $Mn(CO)_5P(C_6H_{11})_3$ than would another $Mn(CO)_4P(C_6H_{11})_3$ group.

Summary

(i) Mechanistic studies enable values of $\Delta H^{\ddagger}$ to be assigned to homolytic fission for quite a large number of metal–metal bonds in group 7B dimetal carbonyls.

(ii) This kinetic measure of the metal–metal bond strengths shows that substituents in $Mn_2(CO)_{10}$ weaken the Mn–Mn bond to an extent dependent on their sizes.

(iii) The bands assignable to an electronic $\sigma \rightarrow \sigma^*$ transition (involving electrons in the metal–metal bond) suggest that axial ligands strengthen the metal–metal interaction to an extent dependent on their σ basicities, but the interactions can also be strengthened by ligands with high π-acid character and weakened by those with large cone angles.

(iv) With larger substituents, the steric effect is not fully reflected in a weakening of the metal–metal σ interaction. It shows itself also in an increase in the total enthalpy of the molecule (due to ligand–ligand repulsion) which is released during homolytic fission. These residual steric effects on the kinetics can be very much larger than those on the metal–metal σ interactions.

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Registry No. $Mn_2(CO)_9P(OPh)_3$, 24476-72-0; $Mn_2(CO)_9PPh_3$, 10170-71-5; $Mn_2(CO)_9PBu_3$, 24476-71-9; $Mn_2(CO)_9P(C_6H_{11})_3$, 59930-02-8; $Mn_2(CO)_8[P(OMe_3]_2$, 15529-61-0; $Mn_2(CO)_8(PEt_3)_2$, 15529-60-9; $Mn_2(CO)_8(PBu_3)_2$, 15609-33-3; $Mn_2(CO)_8[P(C_6H_{11})_3]_2$, 15662-81-4; $Mn_2(CO)_8(AsPh_3)_2$, 15662-84-7; $[Mn(CO)_4PPh_3]_2$, 10170-70-4; 1,1,2,2-tetrachloroethane, 79-34-5; $Mn_2(CO)_{10}$, 10170-69-1; $[Mn(CO)_4P(OPh)_3]_2$, 15529-62-1; $MnRe(CO)_{10}$, 14693-30-2; $MnRe(CO)_8(PPh_3)_2$, 51371-63-2; $Re_2(CO)_{10}$, 14285-68-8; $[Re(CO)_4PPh_3]_2$, 14172-94-2; $Tc_2(CO)_{10}$, 14837-15-1; $[Tc(CO)_4PPh_3]_2$, 61663-90-9.

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(37) A plot made by using values of $h\nu(\sigma \rightarrow \sigma^*)$ from low-temperature spectra is somewhat better, with data for $M_2(CO)_{10}$ (M_2 = Mn_2, MnRe, and Re_2) lying exactly on a straight line and those for $Tc_2(CO)_{10}$ being slightly below it. However, since values of $h\nu(\sigma \rightarrow \sigma^*)$ for almost all the substituted complexes are available only from room-temperature spectra, we shall continue to use them.

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Preparation and Photochemistry of Metal–Metal Bonded Heterodinuclear Precursors to Tetracarbonylcobalt(0), Tricarbonyl(η^5-cyclopentadienyl)molybdenum(I), Tricarbonyl(η^5-cyclopentadienyl)tungsten(I), and Dicarbonyl(η^5-cyclopentadienyl)iron(I)

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Photochemistry and electronic spectra of $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$ and $(\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5)$ (M = Mo, W) are reported. These heterodinuclear (M–M′) species have been prepared by photolysis of mixtures of the appropriate homodinuclear metal carbonyls M–M and M′–M′. These M–M′ species exhibit low-energy absorptions which are attributable to $d\pi \rightarrow \sigma^*$ (absorption maximum 510–545 nm, ϵ in the range 460–1340 L mol^{-1} cm^{-1}) and $\sigma_b \rightarrow \sigma^*$ (absorption maximum 340–398 nm, ϵ in the range 10 000–14 000 L mol^{-1} cm^{-1}) transitions. The spectral data allow a prediction of the position of the $\sigma_b \rightarrow \sigma^*$ absorption as ~415 nm in the nonbridged form of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$. Photoexcitation of the M–M′ complexes results in chemistry implicating homolytic cleavage of the metal–metal bond. In degassed benzene solutions, flash photolysis of M–M′ results in the formation of a 1:1 ratio of products M–M and M′–M′. Based on the disappearance of M–M′, the yield of M–M and M′–M′ is >90%. Irradiation of M–M′ in degassed CCl_4 solution at 366 nm gives essentially stoichiometric amounts of $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, but the fate of $Co(CO)_4$ was found to be mainly coupling to form $Co_2(CO)_8$. The M–M′ disappearance quantum yield in CCl_4 at 366 nm is in the range 0.3–0.5. Irradiation of M–M′ in benzene solutions of 0.1 M 1-IC_5H_{11} or CCl_4 results in a mixture of M–M, M′–M′, and metal carbonyl halides. Such data establish the ordering of metal radical reactivity toward halogen atom abstraction as $(\eta^5\text{-}C_5H_5)W(CO)_3$ > $(\eta^5\text{-}C_5H_5)Mo(CO)_3$ > $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ > $Co(CO)_4$.

Photochemical studies of dinuclear metal carbonyls containing a direct metal–metal bond have shown that population of the lowest excited states results in efficient homolytic cleavage of the metal–metal bond, reaction 1.[2–11]

$$M\text{–}M \xrightarrow{h\nu} M\cdot + \cdot M \tag{1}$$

The resulting $17e^-$ species (1) can be trapped with spin-traps,[3,4] (2) react with halocarbons to give net abstraction products,[2,5,6] (3) couple at essentially diffusion-controlled rates,[7,8] (4) are substitution labile,[2,9] and (5) apparently disproportionate under certain conditions resulting in the formation of metal carbonyl anions.[10,11] In a preliminary account[12] we reported on the photochemistry of some heterodinuclear metal–metal bonded compounds in connection with ordering the reactivity of the $17e^-$ fragments. In this paper we report the synthesis, characterization, and photochemistry of $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$ and $(\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5)$ (M = Mo, W). According to the d^n configuration at the central metal, these molecules can be categorized as "d^5–d^9" and "d^5–d^7" dimers. Thus, these molecules are precursors to $17e^-$ fragments of d^5, d^7, or d^9 configurations.

Results and Discussion

Preparation of the Complexes. The M–M′ bonded complexes have been prepared by the near-UV irradiation of the appropriate M–M and M′–M′ complexes in hydrocarbon solvents, reactions 2 and 3. The details are given in the Experimental Section but it is noteworthy that the photochemical procedure gives respectable yields of the products based on the $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ disappearance. The photosensitivity of the products precludes truly high product yields, but the procedure does allow the synthesis of useful quantities of the M–M′ species.

$$Co_2(CO)_8 + (\eta^5\text{-}C_5H_5)_2M_2(CO)_6 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4 \tag{2}$$

M = Mo, W

$$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4 + (\eta^5\text{-}C_5H_5)_2M_2(CO)_6 \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)(CO)_3MFe(CO)_2(\eta^5\text{-}C_5H_5) \tag{3}$$

M = Mo, W

Spectral Properties of the Complexes. The electronic spectra of the four complexes in EPA solution at 298 and 77 K are given in Figure 1, and band maxima and absorptivities are listed in Table I. By analogy to other dinuclear metal–metal bonded complexes,[2,5,13] we assign the near-UV absorption to a $\sigma_b \rightarrow \sigma^*$ transition, and the visible band is attributable to a $\pi d \rightarrow \sigma^*$ transition. We note that the $\sigma_b \rightarrow \sigma^*$ absorption is at higher energy for the W compared to the analogous Mo complex. Further, it has been noted that the $\sigma_b \rightarrow \sigma^*$ position of M–M′ complexes is often situated between that for the M–M and M′–M′ complexes. A major conclusion drawn from such considerations is that the M–M′ bonding in the heterodinuclear metal carbonyls has relatively little ionic character. Thus, the $\sigma_b \rightarrow \sigma^*$ absorptions for $Co_2(CO)_8$ (nonbridged) and

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