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Reactivity of Molecules Containing Element-Element Bonds. 2. Transition Elements

Fausto Calderazzo,*† Alberto Juris,† Rinaldo Poli,†‡ and Fausto Ungari†,§

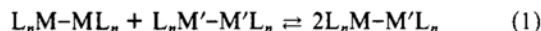
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Exchange reactions between homodinuclear species to give the heterodinuclear complexes $(Mn_2(CO)_{10} + Re_2(CO)_{10} \rightleftharpoons 2MnRe(CO)_{10})$; $Mo_2Cp_2(CO)_6 + W_2Cp_2(CO)_6 \rightleftharpoons 2MoWCp_2(CO)_6$ have been studied under different conditions (both thermally and photochemically). For the systems $Mn_2(CO)_{10}/Re_2(CO)_{10}$ and $Mo_2Cp_2(CO)_6/W_2Cp_2(CO)_6$ (the latter photochemically only), the reactions were found to reach an equilibrium value close to the statistical distribution. For the $Mn_2(CO)_{10}/Re_2(CO)_{10}$ system, a small enthalpy contribution, if any, was inferred from the equilibrium data measured as a function of temperature, both in solution (decahydronaphthalene) and in the melt. On the other hand $Cr_2Cp_2(CO)_6$ reacts thermally with E_2Ph_4 ($E = As, Sb, Bi$) at room temperature to give the exchange product $CrCp(CO)_3-EPh_2$. The molybdenum and tungsten analogues, $M_2Cp_2(CO)_6$, which did not react in the dark, exchange with Bi_2Ph_4 under exposure to normal laboratory daylight.

Introduction

In part 1 of this series,¹ the reactions of systems containing single element-element bonds of main-group elements have been investigated. The lower bond energy on increasing the atomic number along a main group is expected to facilitate insertion inbetween the element-element bond. On the other hand, the generally observed increase of ΔH_{at} of the metals² down a vertical sequence of transition elements suggests a correspondingly stronger cohesive force. In molecular complexes, the strength of the metal-metal bond may be suggested³ to follow a similar trend, although the data are still subject to some uncertainty. The spectroscopic bond dissociation energies for diatomic molecules⁴ also generally increase down groups of transition elements.

Exchange reactions of the type shown in eq 1 have been studied to some extent for nontransition elements.⁵ On the other hand,



not much is known for similar reactions of transition elements. The equilibrium between $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ to give the mixed-metal carbonyl $MnRe(CO)_{10}$ was reported to be endothermic, 8.2 ± 0.3 kcal/mol.⁶

Vahrenkamp and Madach reported that several homodinuclear metal carbonyls readily undergo the formation of the mixed system.⁷

An interesting reaction in systems containing single metal-metal bonds is the exchange reaction 1 when M and M' are transition and nontransition elements, respectively.

In this paper, we have concentrated our attention on the dimeric complexes of chromium(I), molybdenum(I) and tungsten(I) of general formula $M_2(Cp)_2(CO)_6$, ($Cp = \eta^5-C_5H_5$), and we have studied their reactions with E_2Ph_4 ($E = P, As, Sb, Bi$). In an earlier paper, we had investigated the reaction of $Co_2(CO)_8$ with Bi_2Ph_4 .⁸ Also, we report on the exchange between $Mo_2Cp_2(CO)_6$ and $W_2Cp_2(CO)_6$ under photochemical conditions and on the thermal and photochemical behavior of the $Mn_2(CO)_{10}/Re_2(CO)_{10}$ system.

Experimental Section

Solvents were dried before use by conventional methods. The following products were prepared according to the literature: $Cr_2Cp_2(CO)_6$,⁹ $Mo_2Cp_2(CO)_6$,^{9a} $W_2Cp_2(CO)_6$,^{9a} $WCp(CO)_3I$,¹⁰ $Mn_2(CO)_{10}$,¹¹ $Na[Mn(CO)_5]$,¹² $Re_2(CO)_{10}$,¹³ $ReX(CO)_5$,¹⁴ P_2Ph_4 ,¹⁵ As_2Ph_4 ,¹⁶ Sb_2Ph_4 ,¹⁷ $BiPh_4Cl$,¹⁸ Bi_2Ph_4 ,¹ $Fe_2Cp_2(CO)_4$ (Fluka) and $Co_2(CO)_8$ (Strem Chemicals) were commercial products purified by recrystallization or sublimation, respectively. The mixed complex $MnRe(CO)_{10}$ was prepared according to the literature¹⁹ from $Na[Mn(CO)_5]$ (0.31 g; 1.42 mmol) and $ReI(CO)_3$ (0.64 g; 1.41 mmol) in tetrahydrofuran (40 mL). The yellow crystalline product was found to be of high purity by IR and mass spectra. The IR spectrum (decane) had bands at 2053, 2014, and 1979 cm^{-1} .

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The IR spectra were measured with a Perkin-Elmer 283 instrument equipped with a grating. ¹H and ¹³C NMR spectra were measured with Varian XL100 and Bruker WP200 instruments, respectively; the ¹³C NMR spectra were ¹H WALTZ decoupled; the ⁵⁵Mn-NMR spectra were measured with a Varian XL 300 spectrometer.

The X-ray diffractometric measurements on $MnRe(CO)_{10}$ were made with a Philips PW 1100 diffractometer.

Mass spectra were measured with a VG-MM 16F instrument operating at 70 eV with a direct insertion system and a source temperature of 200 °C. Elemental analyses (C, H) were determined by the micro-analytical laboratory of the Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified dinitrogen.

Reaction of $K[MoCp(CO)_3]$ with $WCp(CO)_3I$. The following operations were carried out at room temperature and under rigorous exclusion of light.

This reaction was carried out under slightly modified conditions with respect to those reported in the literature for the preparation of $MoWCp_2(CO)_6$.²⁰ A solution of $K[MoCp(CO)_3]$,²¹ prepared in situ from $Mo_2Cp_2(CO)_6$ (0.36 g, 0.73 mmol) and an excess of sodium-potassium alloy (0.4 g of sodium and 0.9 g of potassium), in tetrahydrofuran (50 mL) was treated with $WCp(CO)_3I$ (0.63 g; 1.37 mmol). The reaction was complete in 15 days, as evidenced by the IR spectrum in the

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carbonyl stretching region; the solvent was evaporated under reduced pressure, and the red residue was added of toluene (50 mL). The resulting suspension was filtered and dried in vacuo (0.19 g) and analyzed by mass spectral data and ^1H and ^{13}C NMR spectra. The mass spectrum showed the molecular ions of $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ and $\text{W}_2\text{Cp}_2(\text{CO})_6$, in addition to the fragment MoWCp_2^+ . The ^1H NMR spectrum had the following resonances (δ , ppm from TMS, C_6D_6 , relative intensity in parentheses): 4.73 (1), 4.71 (1), 4.69 (1), 4.67 (1). The ^{13}C NMR spectrum had the following resonances (δ , ppm from TMS, toluene- d_8): 93.02 (1), 92.92 (1), 91.46 (1), 91.34 (1). Similar results were obtained by treating $\text{Li}[\text{MoCp}(\text{CO})_3]^{22}$ with $[\text{WCp}(\text{CO})_3]\text{BF}_4^{23}$ in thf as solvent.

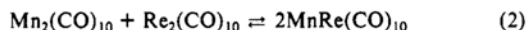
Exchange Reactions. The following exchange reactions were studied thermally and/or photochemically: (a) $\text{Co}_2(\text{CO})_8 + \text{Fe}_2\text{Cp}_2(\text{CO})_4$; (b) $\text{Mo}_2\text{Cp}_2(\text{CO})_6 + \text{W}_2\text{Cp}_2(\text{CO})_6$; (c) $\text{Mn}_2(\text{CO})_{10} + \text{Re}_2(\text{CO})_{10}$.

Thermal Reactions. (a) A toluene solution (10 mL) containing $\text{Fe}_2\text{Cp}_2(\text{CO})_4$ (0.05 g, 0.14 mmol) and $\text{Co}_2(\text{CO})_8$ (0.05 g, 0.15 mmol) was kept at room temperature *in the dark* for several days. The initial IR spectrum showing the bands of the homonuclear dimers ($M = \text{Fe}$, 1998 s, 1953 s, 1782 s cm^{-1} ; $M = \text{Co}$, 2069 s, 2038 s, 2018 s, 1846 m br cm^{-1}) remained unchanged. The ^{13}C NMR spectrum of a benzene (+ benzene- d_6) solution of the two dimers after a week showed resonances at $\delta = 89.12$ (Cp), 240.62 (CO, $\text{Fe}_2\text{Cp}_2(\text{CO})_4$), and 202.0 (CO, $\text{Co}_2(\text{CO})_8$) ppm (from TMS).

(b) A solution about 10^{-2} M in both $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ and $\text{W}_2\text{Cp}_2(\text{CO})_6$ in toluene- d_8 was sealed in a 12-mm NMR tube under a carbon monoxide atmosphere and kept *in the dark* for several days at room temperature. The solution showed the ^{13}C NMR peaks at $\delta = 92.77$ (Mo), 91.51 (W), 223.02 (Mo), and 215.25 (W) ppm (from TMS) attributed, respectively, to the cyclopentadienyl and carbonyl carbons of the starting metal complexes indicated in parenthesis. Heating in the dark for 48 h at about 50 °C did not change the spectral pattern.

(c) $\text{Mn}_2(\text{CO})_{10}$ (0.021 g, 0.055 mmol) and $\text{Re}_2(\text{CO})_{10}$ (0.035 g, 0.054 mmol) were dissolved in decahydronaphthalene (9.46 mL) under CO at atmospheric pressure. The resulting solution was partitioned in several sealed glass vials, which were introduced in a electrically heated tubular oven maintained at 187 ± 2 °C for the time required to reach the equilibrium. During the last hours of the heat treatment, the vial to be used next was transferred into the same spot of the oven occupied by the previous sample. The vials, rapidly cooled at room temperature, were opened at any given time and the content was analyzed by IR spectroscopy. Each vial was used once.

The equilibrium was studied by starting from the heterodinuclear compound $\text{MnRe}(\text{CO})_{10}$, too. In a typical experiment $\text{MnRe}(\text{CO})_{10}$ (0.059 g, 0.114 mmol) was dissolved in decahydronaphthalene (10.33 mL), heated at 187 ± 2 °C, and analyzed as described above. The equilibrium constant for the exchange reaction between $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, see eq 2, to give $\text{MnRe}(\text{CO})_{10}$, and vice versa, was calculated



from the absorbance of both the 2069- cm^{-1} band of the rhenium dimer ($\epsilon = 6800 \text{ M}^{-1} \text{ cm}^{-1}$; $\nu = 2071 \text{ cm}^{-1}$, $\epsilon = 8369 \text{ M}^{-1} \text{ cm}^{-1}$ in isooctane²⁴) and the 2053- cm^{-1} band of the mixed product ($\epsilon = 7600 \text{ M}^{-1} \text{ cm}^{-1}$; $\nu = 2055 \text{ cm}^{-1}$, $\epsilon = 8900 \text{ M}^{-1} \text{ cm}^{-1}$ in isooctane²⁴). For each experiment, several IR determinations were carried out at various time intervals, until equilibrium was considered to be reached, as judged by the substantial invariance of the absorbance with time, and even further.

For the study of the effect of temperature on equilibrium (2), known amounts of $\text{Mn}_2(\text{CO})_{10} + \text{Re}_2(\text{CO})_{10}$ or $\text{MnRe}(\text{CO})_{10}$ were sealed in vials under carbon monoxide at atmospheric pressure at room temperature. The vials were then introduced into the electrically heated oven and maintained above the melting temperature, as indicated in Table I ($\text{Mn}_2(\text{CO})_{10}$, mp = 153–5 °C; $\text{Re}_2(\text{CO})_{10}$, mp = 177 °C;²⁵ $\text{MnRe}(\text{CO})_{10}$, mp = 170–1 °C). The vials, rapidly cooled to room temperature, were opened at the appropriately chosen times and the contents were dissolved in decaline to obtain about 10^{-3} M solutions, which were analyzed by IR spectroscopy as described above. The results of the thermal reactions regarding equilibrium (2) are in Table I.

Photochemical Reactions of the $\text{Mo}_2\text{Cp}_2(\text{CO})_6/\text{W}_2\text{Cp}_2(\text{CO})_6$ System. By exposure to sunlight, a solution containing both $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ and $\text{W}_2\text{Cp}_2(\text{CO})_6$ obtained as specified above (see point b)), after 1 h, gave a new ^{13}C NMR spectrum with two peaks at $\delta = 91.43$ and 93.04 ppm

Table I. Equilibrium $\text{Mn}_2(\text{CO})_{10} + \text{Re}_2(\text{CO})_{10} \rightleftharpoons 2\text{MnRe}(\text{CO})_{10}$ ^a

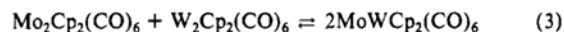
run no.	starting material	t , °C	reacn time, h	K_a ^b
In Solution ^c (Decahydronaphthalene)				
1	$\text{Mn}(\text{Re}(\text{CO})_{10})$	187 ± 2	18	6.6
2			40	6.4
3			95	6.5
4			232	6.0
5			333	5.8
6	$\text{Mn}_2(\text{CO})_{10} + \text{Re}_2(\text{CO})_{10}$		48	8.0
7			119	7.6
8			216	7.5
9			353	8.0
In the Melt				
10	$\text{MnRe}(\text{CO})_{10}$	182 ± 2	5	9.1
11		213 ± 2	16	7.2
12		198 ± 2	22	7.4
13		200 ± 2	49	8.0
14		182 ± 2	143	7.7, 7.7 ^d
15	$\text{Mn}_2(\text{CO})_{10} + \text{Re}_2(\text{CO})_{10}$	186 ± 2	48	4.6
16		183 ± 2	95 ^e	4.5
17		184 ± 2	33	5.7
18		182 ± 2	23	7.1

^a Each sample was sealed in a glass vial under CO at atmospheric pressure and at room temperature; IR spectra were measured on samples in a 0.101-mm CaF_2 cell. ^b Calculated by using the absorbance of both the 2069- cm^{-1} ($\text{Re}_2(\text{CO})_{10}$) and the 2053- cm^{-1} ($\text{MnRe}(\text{CO})_{10}$) bands; see Experimental Section. ^c Initial concentrations: from $\text{MnRe}(\text{CO})_{10}$, about 10^{-2} M; from $\text{Mn}_2(\text{CO})_{10} + \text{Re}_2(\text{CO})_{10}$, about 6×10^{-3} M of each component. ^d Measured by ^{55}Mn NMR spectrometry. A portion of the equilibrium solution, after IR analysis, was sealed in a 12-mm NMR tube, after addition of some C_6D_6 (about one-third of the volume). The spectra were measured at 74.354 MHz at room temperature. Chemical shift, δ , in ppm, with respect to aqueous KMnO_4 : $\text{MnRe}(\text{CO})_{10}$, 2062; $\text{Mn}_2(\text{CO})_{10}$, 2270. Reference 26 reports δ 2325 ppm for $\text{Mn}_2(\text{CO})_{10}$ from the same reference in thf as solvent. A synthetic mixture obtained by dissolving $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, and $\text{MnRe}(\text{CO})_{10}$ in the same solvent mixture in the molar ratio 1:1:2, maintained and measured at room temperature gave an apparent equilibrium constant of 4. ^e Some decomposition was noted.

attributed to the cyclopentadienyl groups of the mixed complex $\text{MoWCp}_2(\text{CO})_6$.

With a similar procedure, a solution about 2×10^{-3} M in both $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ and $\text{W}_2\text{Cp}_2(\text{CO})_6$ in C_6D_6 was sealed in a NMR tube under exclusion of light: the spectrum showed ^1H NMR peaks at $\delta = 4.70$ (Mo) and 4.69 (W) ppm (from TMS), due, respectively, to the cyclopentadienyl hydrogens of the starting homodinuclear complexes. Exposure of the solution to visible light from a 100-W lamp for about $1/2$ h resulted in a new ^1H NMR spectrum showing peaks at $\delta = 4.73$ (1), 4.70 (1), 4.69 (1), and 4.66 (1) ppm (relative intensities in parentheses).

A C_6D_6 5×10^{-3} M solution in both $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ and $\text{W}_2\text{Cp}_2(\text{CO})_6$ was prepared in the dark and introduced under CO into a specially designed quartz cell. Photolysis in the UV region was performed between 313 and 366 nm with a system constituted by a filtered ultraviolet light source (mercury lamp, 125 W). Ferrioxalate actinometry was performed for each experiment.²⁷ Photolysis in the visible region was performed at 510 nm with a system constituted by a filtered tungsten source. Fulgide actinometry was performed for each experiment.²⁸ Analysis of the solution was by ^1H NMR measurements at suitable irradiation times. The quantum yields were found to be 0.15 and 0.14, under ultraviolet and visible irradiation, respectively. These values were measured at about 10% conversion; see eq 3.



Photochemical Reactions of the $\text{Mn}_2(\text{CO})_{10}/\text{Re}_2(\text{CO})_{10}$ System. A 5×10^{-3} M solution in both $\text{Re}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_{10}$ in decahydronaphthalene was prepared in the dark and introduced under carbon monoxide into the quartz cell, as described above. Photolysis was performed at room temperature between 313 and 366 nm with a system using a filtered ultraviolet light source (mercury lamp, 125 W). Ferrioxalate actinometry was performed for each experiment.²⁷ The solution was monitored by IR spectroscopy in the carbonyl stretching region by

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Table II. IR Spectral Data for Carbonyl Derivatives of Chromium(II), Molybdenum(II), and Tungsten(II)^a

compound	ν_{CO} , cm^{-1}		
CrCp(AsPh ₂)(CO) ₃	1988 s	1934 m	1989 s
CrCp(SbPh ₂)(CO) ₃	1990 s	1931 m	1915 s
CrCp(BiPh ₂)(CO) ₃	1983 s	1926 m	1904 s
MoCp(BiPh ₂)(CO) ₃ ^b	1997 s	1932 m	1906 s
WCp(BiPh ₂)(CO) ₃ ^b	1993 s	1924 m	1899 m-s
WCpI(CO) ₃	2038 m-s	1963 s	1950 m-s
MoCp(BiPh ₂)(CO) ₂ PPh ₃		1910 m	1847 s
		1905 m ^c	1832 s ^c
WCp(BiPh ₂)(CO) ₂ PPh ₃		1907 m ^c	1835 s ^c

^a *n*-Heptane solution. ^b ¹³C NMR (C₆D₆) data for MoCp(BiPh₂)(CO)₃: δ (ppm) 90.9 (5, Cp), 231 (1, CO_{trans}), 224.0 (2, CO_{cis}), 139.0 (4, C_{arom-ortho}), 130.4 (4, C_{arom-meta}), 127.8 (2, C_{arom-para}); for WCp(BiPh₂)(CO)₃: δ (ppm) 89.6 (5, Cp), 219.1 (1, CO_{trans}), 213.5 (2, CO_{cis}), 138.7 (4, C_{arom-ortho}), 130.4 (4, C_{arom-meta}), 127.8 (2, C_{arom-para}). ^c Toluene solution.

using the 2069 (Re₂(CO)₁₀) and 2053 (MnRe(CO)₁₀) cm⁻¹ bands as reference.

A similar experiment was carried out by starting with a 10⁻² M solution of MnRe(CO)₁₀ in the same solvent.

For the determination of the initial quantum yield in the forward and reverse reaction (see eq 2), about 15% of the initial complex was converted. Starting from MnRe(CO)₁₀, we obtained a quantum yield of 0.014. The determination of the quantum yield from the homodinuclear complexes was more difficult, since although light was completely absorbed by the sample, it was absorbed differently by the two complexes (for example, the absorbances of 5 × 10⁻⁵ M solutions of Mn₂(CO)₁₀ and Re₂(CO)₁₀ were as follows (wavelength (nm) in parentheses): 0.313 and 0.788 (313), 0.396 and 0.005 (366)). Moreover, only the disappearance of the 2069-cm⁻¹ IR band could be followed because the 2053-cm⁻¹ band of the mixed complex was partially obscured by the absorption due to Mn₂(CO)₁₀, which is predominant due to low conversion. Assuming that one Mn₂(CO)₁₀ molecule reacts *per* Re₂(CO)₁₀ molecule, as required by the stoichiometry of eq 2, a quantum yield (transformed moles/absorbed quanta) of 0.056 was obtained for the forward reaction.

Photolyses over long times, usually from 50 to 100 h, i.e. until no further change in the IR spectrum (carbonyl stretching region) could be observed, were carried out at room temperature under carbon monoxide at atmospheric pressure, starting from both MnRe(CO)₁₀ and Mn₂(CO)₁₀ + Re₂(CO)₁₀. The three carbonyl species were observed with equilibrium constants (see eq 2) of 6.7 (from MnRe(CO)₁₀) and 6.1 (from Mn₂(CO)₁₀ + Re₂(CO)₁₀).

Reaction of Cr₂Cp₂(CO)₆ with E₂Ph₄ (E = As, Sb, Bi). Preparation of CrCp(EPh₂)(CO)₃. The preparation of the bismuth derivative, CrCp(BiPh₂)(CO)₃, is described in detail. The bismuth dimer (0.79 g, 1.09 mmol) was added to a toluene solution of Cr₂Cp₂(CO)₆ (0.35 g, 0.87 mmol) at room temperature to cause an immediate color change from emerald green to orange-brown. The solution was evaporated to dryness under reduced pressure, and the residue was recrystallized from hot *n*-heptane (25 mL) to give the chromium(II) derivative, CrCp(BiPh₂)(CO)₃, in 68% yield as red crystals. Anal. Calcd for C₂₀H₁₅BiCrO₃: C, 42.6; H, 2.7. Found: C, 42.5; H, 2.6. The IR spectral data in the carbonyl stretching region are given in Table II. The IR spectrum (Nujol) has bands at 3105 (vw), 3065 (w), 3040 (w), 3020 (w), 1975 (vs), 1965 (vs), 1907 (vs), 1880 (vs), 1569 (m), 1428 (m-s), 1330 (vw), 1300 (vw), 1262 (w), 1190 (w), 1158 (w), 1065 (w), 1050 (w), 1010 (m), 994 (m), 920 (vw), 855 (m), 846 (m), 840 (m-s), 835 (m), 723 (s), 696 (w), 690 (m-s), 649 (m-s), 636 (w), 625 (m-s), 620 (s), 607 (s), 552 (m-s), 521 (m), 484 (w), 445 (w) and 440 (m) cm⁻¹.

In a similar manner were prepared the orange arsenic and the red antimony derivatives, CrCp(AsPh₂)(CO)₃ and CrCp(SbPh₂)(CO)₃, respectively. The IR data in the carbonyl stretching region are given in Table II. Anal. Calcd. for C₂₀H₁₅AsCrO₃: C, 55.8; H, 3.5. Found: C, 56.0; H, 3.2. Anal. Calcd for C₂₀H₁₅CrO₃Sb: C, 50.3; H, 3.2. Found: C, 49.5; H, 2.9.

A gas-volumetric control of the reaction was carried out with As₂Ph₄ (22.5 °C) or Sb₂Ph₄ (24.3 °C) under an atmosphere of CO: in no case was evolution of CO observed upon contact of the reagents.

Preparation of MCp(BiPh₂)(CO)₃ (M = Mo, W). (a) From [MCp(CO)₃]⁻ and BiPh₂Cl. The reaction of the molybdenum derivative is described in detail, the tungsten analogue being prepared similarly. A solution of K[MoCp(CO)₃]⁻,²¹ prepared *in situ* from Mo₂Cp₂(CO)₆ (0.90 g, 1.84 mmol) and an excess of sodium-potassium alloy (0.4 g of sodium and 0.9 g of potassium) in tetrahydrofuran (50 mL) was treated with BiPh₂Cl (1.35 g, 3.39 mmol) at room temperature. Within 1 h the color

of the solution became red-orange. The solvent was evaporated to dryness under reduced pressure, and the resulting solid was treated with toluene and the suspension filtered. The solution was evaporated to a small volume, *n*-heptane (30 mL) was added, and the mixture was maintained at about 5 °C overnight. The red crystalline diphenylbismuthide derivative was collected by filtration and dried *in vacuo* (0.4 g, 19% yield). Anal. Calcd for C₂₀H₁₅BiMoO₃: C, 39.5; H, 2.5. Found: C, 39.8; H, 2.4. The IR carbonyl stretching vibrations in *n*-heptane solution are given in Table II. ¹³C NMR (C₆D₆) of MoCp(BiPh₂)(CO)₃, δ (ppm): 90.9 (5, Cp), 231 (1, CO_{trans}), 224.0 (2, CO_{cis}), 139.0 (4, C_{arom-ortho}), 130.4 (4, C_{arom-meta}), 127.8 (2, C_{arom-para}).

The tungsten analogue was obtained in 24% yield as red crystals. Anal. Calcd for C₂₀H₁₅BiO₃W: C, 34.5; H, 2.2. Found: C, 34.4; H, 2.0. The carbonyl stretching vibrations are listed in Table II. ¹³C NMR (C₆D₆) of WCp(BiPh₂)(CO)₃, δ (ppm): 89.6 (5, Cp), 219.1 (1, CO_{trans}), 213.5 (2, CO_{cis}), 138.7 (4, C_{arom-ortho}), 130.4 (4, C_{arom-meta}), 127.8 (2, C_{arom-para}).

(b) **Irradiation of M₂Cp₂(CO)₆ (M = Mo, W) in the Presence of Bi₂Ph₄.** Toluene equimolar solutions of Bi₂Ph₄ and M₂Cp₂(CO)₆ did not react at 20.0 °C in the dark even over long reaction times (6 days). On the contrary, exposure of a solution of Mo₂Cp₂(CO)₆ (0.07 g, 0.14 mmol) and Bi₂Ph₄ (0.16 g, 0.22 mmol) to the normal laboratory daylight produced complete reaction in 3 days to give MoCp(BiPh₂)(CO)₃. The IR spectrum of the crude solution is superimposable on that obtained with a toluene solution of an authentic sample prepared as reported above. A similar behavior was found for W₂Cp₂(CO)₆.

Reaction of CrCp(SbPh₂)(CO)₃ with Iodine. The antimony-chromium(II) derivative (0.37 g, 0.78 mmol) was reacted with I₂ (0.20 g, 0.79 mmol) in toluene (10 mL) at 23.1 °C in a reactor connected with a gas-volumetric apparatus. Within 1 min after the reagents were mixed, through the intermediacy of a yellow-brown color, the solution turned violet without gas evolution. The solution was filtered and evaporated to a small volume under reduced pressure, *n*-heptane (10 mL) was added, and the mixture was left at about -30 °C overnight. The violet crystalline solid of CrCpI(CO)₃ (elemental analysis, IR²⁹) was separated by handpicking from the yellow SbPh₂I. Similar iodine reactions were carried out with CrCp(BiPh₂)(CO)₃ or WCp(BiPh₂)(CO)₃, and CrCpI(CO)₃ or WCpI(CO)₃,³⁰ respectively, were obtained.

Substitution Reaction of MCp(BiPh₂)(CO)₃ (M = Mo, W) with Triphenylphosphine. (a) M = Mo. The diphenylbismuthide complex MoCp(BiPh₂)(CO)₃ (0.33 g, 0.54 mmol) was treated at room temperature with triphenylphosphine (0.15 g, 0.57 mmol) under rigorous exclusion of light in toluene (10 mL). After about 15 h of stirring, a yellow precipitate was present, and the IR spectrum of the supernatant solution, measured after about 40 h, did not show any band attributed to the starting material. Heating the reaction mixture led to dissolution of the precipitate: the solution was filtered while still warm, and when it was cooled to room temperature, 0.12 g (26% yield) of MoCp(BiPh₂)(CO)₂PPh₃ was collected by filtration and drying *in vacuo* as yellow-orange crystals. Anal. Calcd for C₃₇H₃₀BiMoO₂P: C, 52.7; H, 3.6. Found: C, 52.6; H, 3.6. The IR spectral data in the carbonyl stretching region are given in Table II. The ¹H NMR spectrum had the following resonances (δ , ppm from TMS, C₆D₆): 7.2-6.5 (25 H, H_{arom}, multiplet), 4.04 (5 H, H_{Cp}, doublet, *J*_{H-P} = 1.0 Hz).

(b) M = W. The diphenylbismuthide complex WCp(BiPh₂)(CO)₃ (0.38 g, 0.55 mmol) was treated at room temperature with triphenylphosphine (0.15 g, 0.57 mmol) in toluene (20 mL) initially under exclusion of light. An IR spectrum measured after 24 h stirring did not show any change of the initial spectrum (bands at 1986, 1915, and 1891 cm⁻¹ in the carbonyl stretching region). The solution was then irradiated with a mercury lamp for 24 h at room temperature. The final solution had the bands of the substitution product, WCp(BiPh₂)(CO)₂PPh₃, indicated in Table II.

With the chromium complex, CrCp(BiPh₂)(CO)₃, no substitution reaction was observed at room temperature, even under irradiation with a mercury lamp. Decomposition took place instead.

The Mn₂(CO)₁₀/Bi₂Ph₄ System. (a) **Thermal Treatment of Mn₂(CO)₁₀ with Bi₂Ph₄.** Mn₂(CO)₁₀ (0.03 g, 0.08 mmol) and Bi₂Ph₄ (0.07 g, 0.09 mmol) were dissolved in 10 mL of toluene. The resulting orange solution was maintained at room temperature: after 48 h, the IR spectrum revealed, in the carbonyl stretching region, the presence in solution of the starting materials only (a dark solid resulting from the thermal decomposition of Bi₂Ph₄ was also present).

(b) **Photochemical Reaction of Mn₂(CO)₁₀ with Bi₂Ph₄.** Mn₂(CO)₁₀ (0.33 g, 0.84 mmol) and Bi₂Ph₄ (0.60 g, 0.82 mmol) were introduced *in the dark* and under CO, in 30 mL of toluene, thus obtaining an orange suspension of the two solids (IR spectrum in the carbonyl region: 2045

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m, 2006 s, and 1981 s cm^{-1}). The system was irradiated at room temperature with filtered visible light ($\lambda_{\text{max}} = 400 \text{ nm}$). After 2 h, the solution became brown and a dark solid was present in suspension. The IR spectrum showed the presence of a new product (IR bands at 2082 m, 2045 m, 2008 s, and 1992 s (sh) cm^{-1}). Further irradiation of the system for some hours did not change the IR spectrum significantly, but produced an increased amount of the dark solid in suspension. After filtration of the solution, excess $\text{Mn}_2(\text{CO})_{10}$ was precipitated by cooling at about -80°C . The solution was evaporated to dryness under reduced pressure and $\text{Mn}_2(\text{CO})_{10}$ was sublimed in vacuo at room temperature. The resulting brown solid was treated with 10 mL of *n*-heptane, thus obtaining a red-brown solution. An orange-brown solid precipitated from the solution cooled at -30°C : it was recovered by decanting the solution out and then dried in vacuo (0.4 g; 40% yield). Anal. Calcd for $\text{C}_{17}\text{H}_{10}\text{BiMnO}_5$, $\text{Mn}(\text{CO})_5\text{BiPh}_2$: C, 36.6; H, 1.8. Found: C, 36.7; H, 1.8. IR spectral data, in the carbonyl stretching region: thf, 2083 m, 2027 w (sh), and 1992 s cm^{-1} ; *n*-heptane, 2083 m, 2019 w, 1996 s cm^{-1} .

Results and Discussion

Exchange Reactions Involving Transition-Metal Complexes. (a)

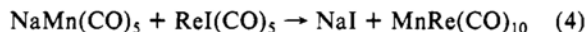
Thermal Reactions. Previous work^{5a} from these laboratories on the exchange between P_2Ph_4 and As_2Ph_4 had shown that the formation of the mixed compound $\text{Ph}_2\text{P}-\text{AsPh}_2$ is a slightly endothermic reaction ($\Delta H^\circ = +1.3 \text{ kcal/mol}$), the driving force to the mixed compound being therefore essentially entropic in nature. The exchange reaction^{5b} between P_2Me_4 and As_2Me_4 has been reported to be equally fast; the equilibrium constant, however, is small (0.26 at 25°C). From these preliminary experiments, the formation of mixed heterometallic single bonds between elements of the same group, group 15, does not appear to be a thermodynamically favorable process.

As far as transition elements are concerned, the mixed-metal complex $\text{MnRe}(\text{CO})_{10}$ was reported⁶ to be formed in an endothermic reaction, as mentioned in the Introduction. In agreement with the results reported by Marcomini and Poë,⁶ we also find that the thermal reaction between $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ occurs above 170°C at a reasonable rate.³¹ The equilibrium constants for reaction 2 are specified in Table I. The most important difference between our results and those reported earlier⁶ is that the equilibrium constant of reaction 2 does not appear to be greatly affected by temperature, in the range between 182 and 213°C ; see Table I. The values of the equilibrium constant are dispersed around an average value of 6.9 ± 1.0 in the temperature range used, whereas one obtains a value of 7.0 ± 1.0 at $187 \pm 2^\circ\text{C}$ from the solution experiments. It is worthwhile mentioning that increasing the temperature of the experiment above 213°C would have in fact led to considerable decomposition; on the other hand, the reaction times were long, in order to be sure that equilibrium had been attained in most cases. By examination of Table I, it will be noted that in run no. 10 in the melt, in which the reaction time was 5 h only, the equilibrium position had presumably not been reached. Moreover, both in the solution and in the molten samples, the experiments were carried out under an atmosphere of carbon monoxide, in order to minimize the decomposition. We can conclude by saying that our equilibrium constants corresponding to the formation of the heterodinuclear species do not show any significant temperature effect and that the enthalpy change should therefore be small. Consequently, the exchange reaction between $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ to give the heterodinuclear species appears to be essentially driven by entropy.

It is interesting to note, in this connection, that a recent reinvestigation³² of the molecular structure³³ of the mixed-metal carbonyl has shown the Mn-Re distance ($2.909(1) \text{ \AA}$) to be

somewhat shorter than the sum of the metal covalent radii obtained from the $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ crystal structures, $1.447(1)^{34}$ and $1.521(1)^{35} \text{ \AA}$, respectively.

In the course of this study, the heterodinuclear compound of rhenium(0) and manganese(0), $\text{MnRe}(\text{CO})_{10}$, has been prepared according to the literature¹⁹ from the usual syn-proportionation of eq 4. The purity of the compound so obtained was verified



by IR and by mass spectrometry. A diffractometric experiment carried out on a single crystal of the heterodinuclear species³⁶ showed the compound to have crystal data, bond distances, and bond angles in agreement with those already established in the revised crystal structure determination.³² Although some statistical disorder may complicate the interpretation of the crystallographic data, and although solid-state effects may be partly responsible for the unusually short metal-metal distance found in the heterodinuclear compound, we would like to note that the new findings about equilibrium 2 can be better reconciled with the solid-state data than the earlier ones.⁶

Also the exchange reaction between $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ and $\text{W}_2\text{Cp}_2(\text{CO})_6$ (see eq 3) was studied in some detail. The thermal reaction does not proceed at least up to 50°C , which is the maximum temperature at which we could operate in view of the labile nature of these products (the experiments were carried out under an atmosphere of carbon monoxide to minimize the formation of the tetracarbonyl dimers $\text{M}_2\text{Cp}_2(\text{CO})_4$).³⁷ In agreement with some earlier finding,^{7,38} exchange reaction 3 proceeds under irradiation, as explained in the next paragraph. We were unable to verify this information from both sides, i.e. starting from the heterodinuclear compound $\text{MoW}(\text{Cp})_2(\text{CO})_6$. As a matter of fact, a syn-proportionation reaction of type 4 (from $\text{KMoCp}(\text{CO})_3 + \text{WCp}(\text{CO})_3\text{I}$ or from $\text{LiMoCp}(\text{CO})_3 + \text{WCp}(\text{CO})_3\text{BF}_4$), even under rigorous exclusion of light, in our hands always proceeded to give the mixture of the three products $\text{Mo}_2\text{Cp}_2(\text{CO})_6/\text{W}_2\text{Cp}_2(\text{CO})_6/\text{MoW}(\text{Cp})_2(\text{CO})_6$. This agrees with, and completes, the earlier findings by Madach and Vahrenkamp.^{7a} The failure to obtain the heterodinuclear molybdenum-tungsten dimer through such a reaction²⁰ is attributed to a fast electron transfer taking place between the anionic (molybdenum) and the cationic (tungsten) species, leading to the corresponding 17-electron radical species, which may have a sufficiently long life to recombine and give the equilibrium mixture of the three compounds (vide infra). The fact that the same results are obtained also in the system devoid of any halide ligand ($\text{LiMoCp}(\text{CO})_3 + \text{WCp}(\text{CO})_3\text{BF}_4$) suggests that the electron transfer does not require a bridging halide to occur.

Also the exchange between $\text{Co}_2(\text{CO})_8$ and $\text{Fe}_2\text{Cp}_2(\text{CO})_4$ does not occur at room temperature *in the dark* in toluene solution. No attempt was made to heat the solution or to irradiate it.

(b) Photochemical Reactions. As mentioned above, the reaction of $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ with $\text{W}_2\text{Cp}_2(\text{CO})_6$ (see eq 3 in the Experimental

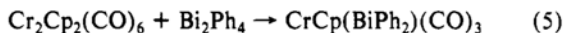
- (31) Decacarbonyldimanganese(0) (0.22 g; 0.56 mmol) and decacarbonyldirhenium(0) (0.36 g; 0.56 mmol) were dissolved in toluene (5 mL) at 100°C and maintained at this temperature for some minutes. When cooled, the yellow microcrystalline precipitate of the solid solution thus obtained showed the mass spectrometric fragments due to $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, without any significant fragment attributable to the heterodinuclear species.
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- (35) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.
- (36) Crystals of the heterodinuclear compound $\text{MnRe}(\text{CO})_{10}$ suitable for the X-ray diffractometric experiment were obtained from *n*-heptane at -30°C . The intensities were measured at room temperature with Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). One octant of reciprocal space was surveyed with $3.0 < \theta < 26.0^\circ$. Of the 2817 reflections measured, 1478 were independent and 977 had $I \geq 3\sigma(I)$ and were used subsequently throughout the analysis. An empirical absorption correction (Ψ scan) and an anisotropic refinement were made. The final refinement converged to $R = 0.0355$. Crystal data: $a = 17.625(5) \text{ \AA}$, $b = 7.124(2) \text{ \AA}$, $c = 14.737(4) \text{ \AA}$, $\beta = 128.09^\circ$, $Z = 4$, monoclinic, space group $C2/c$. By application of the $\bar{1}0\bar{1}/010/001$ matrix, the following cell was obtained, which agrees with the data reported in the literature:³² $a = 14.400 \text{ \AA}$, $b = 7.124 \text{ \AA}$, $c = 14.737 \text{ \AA}$; $\beta = 105.57^\circ$, space group $I2/a$. Some selected bond distances (\AA) and angles (deg) are as follows: Mn-Re, 2.908; M-C, 1.93-1.98; C-O, 1.12-1.15 \AA ; Mn-Re-C, 177.1, 85.6-90.0; C-M-C, 172.5, 175.9, 87.8-94.7; M-C-O, 177-178.
- (37) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85.
- (38) Vahrenkamp, H. Private communication.

Section) does not take place in the dark up to 50 °C. On the other hand, irradiation of an equimolar mixture of the two homodinuclear compounds with sunlight or visible light from a tungsten lamp produced the heterodinuclear species in equilibrium with the starting reagents in the approximate molar ratio 2:1:1. The quantum yield of the forward reaction (0.14 or 0.15, substantially independent of the wavelength) is considerably lower than previously reported for the same system in carbon tetrachloride,³⁹ presumably, in the latter case, the intermediates can be more readily intercepted to give the products, i.e. the chloro complexes of molybdenum and tungsten.⁴⁰ Prolonged irradiation of the molybdenum and tungsten dimers led to the same photostationary state, independent of the wavelength used, the experiments being carried out both in the 313–366-nm region and around 510 nm, corresponding to the $\sigma \rightarrow \sigma^*$ and to the $\pi-d \rightarrow \sigma^*$ transition, respectively, of the metal–metal bond.³⁹

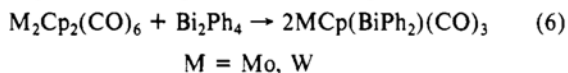
In the $\text{Mn}_2(\text{CO})_{10}$ – $\text{Re}_2(\text{CO})_{10}$ system, the irradiation at room temperature led to the heterodinuclear species in equilibrium with the starting reagents, the product distribution being similar to that found in the thermal experiments. The constant of equilibrium 2 over long irradiation times was found to be 6.6 (from $\text{MnRe}(\text{CO})_{10}$) or 6.1 (from the equimolar mixture of the homodinuclear compounds), i.e., identical, within experimental error, with the average value (6.9 ± 1.0) of the thermal experiments. This further confirms that the enthalpy change of reaction 2 is small.

Exchange Reactions between Dimeric Systems Involving Transition and Nontransition Elements. The reaction of $\text{Cr}_2\text{Cp}_2(\text{CO})_6$ with Bi_2Ph_4 to give the product containing the Cr–Bi bond (see eq 5) represents an example of an exchange reaction between systems containing transitional and nontransitional element–element bonds.



Reaction 5 provides a rather uncommon example of a metal complex containing a terminal BiR_2 group⁴¹ and has a precedent in our earlier finding that $\text{Co}_2(\text{CO})_8$ reacts very promptly with Bi_2Ph_4 to give $\text{Co}(\text{BiPh}_2)(\text{CO})_4$.⁸ On the other hand, it is also known that $\text{Cr}_2\text{Cp}_2(\text{CO})_6$ reacts with Pb_2Ph_6 to give $\text{CrCp}(\text{PbPh}_3)(\text{CO})_3$.⁴² Reaction 5 may be regarded as occurring through a radical mechanism, generating the monomeric $\text{CrCp}(\text{CO})_3$ species. Evidence for the presence of the latter species in solution has been gathered by ¹H NMR spectra.^{43,44}

While the dimeric chromium(I) cyclopentadienyl derivative reacts promptly with Bi_2Ph_4 , no reaction was observed with the corresponding molybdenum and tungsten species, unless visible light was present; see eq 6. These new products have been



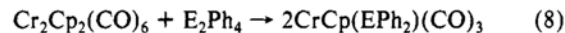
prepared also by the reaction of the metal carbonyl anions with BiPh_2Cl ; see eq 7. The failure of the molybdenum and tungsten

$[\text{MCp}(\text{CO})_3]^- + \text{BiPh}_2\text{Cl} \rightarrow \text{Cl}^- + \text{MCp}(\text{BiPh}_2)(\text{CO})_3 \quad (7)$

complexes to react with Bi_2Ph_4 in the absence of light contrasts with the behavior observed with chromium and agrees with the expected increase of the metal–metal bond energy on descending the vertical sequence of metals. Note that, at variance with the facile reaction between $\text{Co}_2(\text{CO})_8$ and Bi_2Ph_4 ,⁸ no reaction was

observed⁴⁵ between Bi_2Ph_4 and $\text{Mn}_2(\text{CO})_{10}$, in agreement with the increase of the metal–metal bond energy on going from $\text{Co}_2(\text{CO})_8$ ⁴⁶ to $\text{Mn}_2(\text{CO})_{10}$.⁴⁷

The rather weak chromium–chromium bond of $\text{Cr}_2\text{Cp}_2(\text{CO})_6$ is readily cleaved, in the dark, in the presence of As_2Ph_4 or Sb_2Ph_4 , thus yielding the corresponding chromium(II) species; see eq 8.



It is interesting to note that, consistent with the expected increase of the element–element bond energy in ascending the vertical sequence of group 15 elements, no product of oxidative addition across the Cr–Cr bond was observed with P_2Ph_4 .

The conclusion from these experiments is that the exchange reactions were found to be most easily performed in the Cr/Bi combination of the dimeric homometallic species, i.e. for the systems presumably characterized by the weakest M–M and E–E bonds.

The tricarbonyl complexes $\text{MCp}(\text{EPh}_2)(\text{CO})_3$ (M = Cr, E = Sb, Bi; M = W, E = Bi) react smoothly at room temperature with I_2 to give the corresponding iodo complexes; see eq 9. In the case



of $\text{CrCp}(\text{SbPh}_2)(\text{CO})_3$, the reaction occurred rapidly through the intermediacy of another unstable product. On the basis of the findings by Malisch and co-workers⁴⁸ on the reaction of $\text{MCp}(\text{EMe}_2)(\text{CO})_3$ (M = Cr, Mo, W; E = As, Sb) with X_2 (X = Cl, Br), the intermediacy of $\text{CrCp}(\text{SbI}_2\text{Ph}_2)(\text{CO})_3$, corresponding to the addition of I_2 to coordinated antimony, may be suggested.

The products of general formula $\text{MCp}(\text{BiPh}_2)(\text{CO})_3$ react with PPh_3 to give the corresponding dicarbonyl derivatives: however, while the molybdenum species reacts at room temperature in the dark, the tungsten complex reacts under irradiation, and no reaction was observed with the chromium derivative even under irradiation.

This reactivity is consistent with what is generally observed in carbonyl substitution reactions, namely that the 4d element is usually more reactive than the 3d or 5d.⁴⁹

The IR data of Table II suggest that the EPh_2 -substituted products of chromium(II), molybdenum(II), and tungsten(II), $\text{MCp}(\text{EPh}_2)(\text{CO})_3$, have similar structures, in view of the similar spectra measured in the carbonyl stretching region. The two possible structures might be a trigonal bipyramid (C_{3v}) or a square pyramid (C_4). In the former possibility, two strong CO stretchings would be expected, while the second structure should give rise to three medium to strong CO stretching vibrations, similar to what is observed. Several solid-state structures of compounds of this type have been found to show C_3 symmetry.⁵⁰ The square-pyramid structure is therefore preferred. In agreement with this proposal, the ¹³C NMR spectra show the presence of two carbonyl resonances in the ratio 2:1, corresponding to the cis and trans carbonyl groups in a square-pyramidal structure.⁵¹

Conclusions

This paper has pointed out a number of relevant facts. The $\text{Co}_2(\text{CO})_8/\text{Fe}_2\text{Cp}_2(\text{CO})_4$ and $\text{Mo}_2\text{Cp}_2(\text{CO})_6/\text{W}_2\text{Cp}_2(\text{CO})_6$ reac-

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tions do not occur at room, or slightly higher, temperature under exclusion of light. The $\text{Mo}_2\text{Cp}_2(\text{CO})_6/\text{W}_2\text{Cp}_2(\text{CO})_6$ reaction was shown to occur photochemically, and its quantum yield was measured. In the case of the $\text{Mn}_2(\text{CO})_{10}/\text{Re}_2(\text{CO})_{10}$ system, which is characterized by a higher thermal stability, it has been shown that the equilibration to the heterodinuclear system $\text{MnRe}(\text{CO})_{10}$ occurs both thermally and photochemically. Our data are complementary to those reported by Madach and Vahrenkamp.⁷ From the limited amount of quantitative data available, a thermodynamic pattern appears to arise: intragroupal exchanges ($\text{Mn}_2(\text{CO})_{10}/\text{Re}_2(\text{CO})_{10}$, $\text{Mo}_2\text{Cp}_2(\text{CO})_6/\text{W}_2\text{Cp}_2(\text{CO})_6$, $\text{As}_2\text{Ph}_4/\text{P}_2\text{Ph}_4$) appear to be favored mainly entropically, whereas intergroupal exchanges ($\text{Mn}_2(\text{CO})_{10}/\text{Bi}_2\text{Ph}_4$, $\text{Cr}_2\text{Cp}_2(\text{CO})_6/\text{E}_2\text{Ph}_4$, $\text{M}_2\text{Cp}_2(\text{CO})_6/\text{Bi}_2\text{Ph}_4$) are both entropy and enthalpy driven.

Many more quantitative data should be collected before generalizations can be offered in this domain of the metal-metal single-bond-containing systems.

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