Coordination Chemistry Reviews, 120 (1992) 209–221
Elsevier Science Publishers B.V., Amsterdam

Properties and reactivity of homodinuclear and heterodinuclear systems containing single element–element bonds*

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(Received 30 October 1991)

CONTENTS

A. INTRODUCTION

Many elements form molecular compounds containing single element–element bonds. This property can be found with elements, either non-metallic or metallic (a d transition metal or a main group metal), in homodinuclear or in homopolynuclear systems (see, for example, catenation in carbon and sulphur chemistry [1]). Among homodinuclear systems, which will be especially treated in this article, we can further distinguish between diatomic molecules and molecules which contain, in addition to the single element–element bond constituting the central core, some additional ligands: for example, the dinuclear organometallic compounds of bismuth(II), of general formula Bi_2R_4 [2], shown [3] to contain a bismuth–bismuth bond in Bi_2Ph_4, have been obtained only recently.

The formation, strength and reactivity of the single element–element bond represents an interesting subject per se and also for the implications in catalysis. Several compounds containing heteronuclear transition metal systems have been proposed [4] to play an important role in catalysis. Thus, the stability of such

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* Dedicated to Professor Luigi Sacconi in recognition of his outstanding contributions to coordination chemistry.

0010-8545/92/$15.00

heteronuclear systems is an important problem for which no detailed information is available in the literature.

Equations (1a) and (1b) exemplify the equilibrium between homodinuclear and heterodinuclear compounds in a given metallic or main group non-metallic system, respectively. Throughout this article, M will stand for a transition or a non-transition metal, E will usually indicate a main group non-metallic element and L will be a neutral or an anionic monovalent *terminal* ligand.* Equilibria (1a) and (1b) depend on the strength of the M—M or E—E bond being broken and that of the M—M′ or E—E′ bond being formed.

$$L_nM{-}ML_n + L'_nM{-}M'L_n \rightarrow 2L_nM{-}M'L_n \quad (1a)$$

$$L_nE{-}EL_n + L_nE'{-}E'L_n \rightarrow 2L_nE{-}E'L_n \quad (1b)$$

If one considers the element–element bond energy as a function of the valence shell, it is found that such an energy, for non-metallic elements, decreases as the principal quantum number increases**.

The element of the second period ($n = 2$) belonging to the groups from 15 (N) to 17 (F) has an exceptionally low bond energy, usually attributed to the effect of the non-bonding lone pair [6].

As far as the transition elements are concerned, the situation is known to a lower degree of accuracy, due both to experimental difficulties*** and to the restricted number of compounds containing a single-bonded M—M core free from supporting bridging ligands. On the other hand, a trend to an increase of the M—M bond energy from the 3d to the 5d system is suggested by the experimental data available until now. For example, in the series of the $M_2(CO)_8(PPh_3)_2$ metal–metal bonded dimers, the metal–metal bond dissociation enthalpy has been evaluated [16] to be 120 (M = Mn), 138 (M = Tc) and 162 (M = Re) kJ mol^{-1}, according to kinetic methods in solution. The dissociation enthalpies of the decacarbonyls of Group 6 [17] and of some diatomic molecules M_2 [17] also support the proposition that the metal–metal

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* Dinuclear systems containing bridging ligands will not be considered.

** Accepted values of bond energies (kJ mol^{-1}) are as follows [5]. Group 14: C, 347; Si, 176; Ge, 157; Sn, 142. Group 15: N, 160; P, 214; As, 134; Sb, 126; Bi, 104. Group 17: F, 153; Cl, 242; Br, 193; I, 151. It is interesting to note that bismuth is the only chemically relevant element belonging to the sixth period ($n = 6$) for which Lewis-base properties might, in principle, be expected.

*** As a typical example, the Mn—Mn dissociation energy in $Mn_2(CO)_{10}$ covers a range from 67 [7] to 171 kJ mol^{-1} [8], depending on the experimental method. The most recent evaluation [9] of the equilibrium between $Mn_2(CO)_{10}$ and the $Mn(CO)_5$ radical ($K = 5.3 \times 10^{-19}$) suggests a rather high value for the Mn—Mn bond enthalpy. It is interesting to note that the reaction of $Mn_2(CO)_{10}$ with H_2, a special type of reaction (1a) with $n = 0$ for one of the reagents and M = E, to give $MnH(CO)_5$ [10(a)] [$Mn_2(CO)_{10} + H_2 \rightleftharpoons 2MnH(CO)_5$] is apparently endothermic [10(b)]. Octacarbonyldicobalt, $Co_2(CO)_8$, behaves similarly, $CoH(CO)_4$ being formed [11] in a slightly endothermic reaction [12]. Thus, if the cobalt–cobalt bond enthalpy is lower [13] than that of the corresponding metal–metal bond in $Mn_2(CO)_{10}$, then the Co—H bond enthalpy must be lower than that of the Mn—H bond in $MnH(CO)_5$, which agrees with a recent compilation of data [14]. Consistent with this is the fact that $MnH(CO)_5$ is a weaker Brønsted acid than $CoH(CO)_4$ [15].

bond enthalpy contribution increases in the 3d < 4d < 5d sequence within the same group of elements, at least within typical transition metals. For example, V_2 and Nb_2 have dissociation energies of 241 ± 13 and 503 ± 10 kJ mol^{-1}, respectively: a similar increase is observed on going from Cr_2 ($D_0 = 151 \pm 29$ kJ mol^{-1}) to Mo_2 ($D_0 = 404 \pm 20$ kJ mol^{-1})*.

Molecular compounds and condensed systems of the same metal may have some fundamentally common features. It is conceivable that the condensed state of a metal [i.e. $(M)_nM{-}M(M)_n$] can be distinguished from a diatomic molecule in the gas phase (M—M) or from a homodinuclear molecular complex ($L_nM{-}ML_n$) on the basis of the type of bond and of the coordination number (metals: replicative bonds, CN 8 or 12; coordination compounds: $CN = n + 1$; diatomic molecules: CN = 1). Presumably, similar intragroupal trends therefore should be observed, as far as the M—M enthalpy contribution is concerned, on going from molecular complexes to condensed sytems. Some information about this problem can therefore originate from the sublimation enthalpies of the metals, i.e. for the process $M_{(s)} \rightarrow M_{(g)}$. When typical non-transition elements are considered, the enthalpy of sublimation decreases on descending a given group, whereas the opposite trend is observed for transition metals [5]: this is the case for the sequences of Groups 6 (Cr–Mo–W) and 8 (Fe–Ru–Os), for example, whereas the borderline elements of Group 10 (Ni–Pd–Pt) show an irregularity at palladium (see last footnote) and, finally, the trend is reversed at Group 12 (Zn–Cd–Hg).

B. THE SINGLE ELEMENT–ELEMENT BOND IN NON-TRANSITION ELEMENTS

In these laboratories, the interest in the energetics of the element–element bond in non-transition elements has a rather fortuitous origin. Earlier work [18] in collaboration with Prof. Ivan Bernal of the University of Houston and Prof. Jerry L. Atwood of the University of Alabama had shown that complexes of the general type $M_2X_2(CO)_6E_2R_{2n}$ (M = Mn, Re; X = Cl, Br, I; $n = 1$, E = S, Se, Te; $n = 2$, E = P, As, Sb) could be prepared, all having the hetero multiple bridge (HMB) type of structure, i.e. with both X and E_2R_{2n} as bridging ligands. In an attempt to study some competitive ligand equilibria in solution in poorly coordinating solvents, the reaction of $M_2X_2(CO)_6P_2Ph_4$ with As_2Ph_4 was studied (see eqn. (2))**. We failed to establish the position of the equilibrium, but it was realized instead that an unprecedented scrambling reaction between the phosphorus and the arsenic dimeric species (see eqn. (3)) had occurred in solution. Equilibrium was readily reached at room

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* Interestingly, in the Ni–Pd sequence, i.e. with a d shell almost completely filled, the dissociation energies (in parentheses, kJ mol^{-1}) do not conform to the typical trend [17]: Ni_2 (258), Pd_2 (105 ± 21). A similar trend is observed for the enthalpy associated with the vaporization of the corresponding metals, i.e. for the process $M_{(s)} \rightarrow M_{(g)}$ (vide infra).

** Similar studies on manganese(I) [19] and vanadium(I) [20] systems had shown that the complex with the heavier chalcogen was slightly favoured, i.e. S < Se < Te.

temperature, the reaction being monitored by ^{31}P NMR spectrometry. The equilibrium was found [21] to vary little with the solvent (at 30 ± 0.1°C, $K = 0.37$ in benzene and 0.31 in Et_2O) and the study as a function of temperature gave the following parameters: $\Delta H° = 5.4 \pm 1.2$ kJ mol^{-1}; $\Delta S° = 15 \pm 4$ J mol^{-1} K^{-1}. Thus, the formation of the heterodinuclear compounds from the homodinuclear compounds proceeds by about 30% and the equilibrium constant is smaller than the statistical value of 4.

$$M_2X_2(CO)_6P_2Ph_4 + As_2Ph_4 \rightarrow M_2X_2(CO)_6As_2Ph_4 + P_2Ph_4 \quad (2)$$

$$P_2Ph_4 + As_2Ph_4 \rightleftharpoons 2AsPPh_4 \quad (3)$$

The results suggest that the equilibrium concentration of the heterodinuclear compound is smaller than expected for the statistical distribution because of an unfavourable enthalpy change. This was a remarkable and rather unexpected result. On the other hand, attempts to prepare the heterodinuclear compound $AsPPh_4$ [22] by reacting $AsPh_2^-$ with PPh_2Cl failed and the equilibrium mixture of the homodinuclear and heterodinuclear compounds was obtained instead, thus confirming the results of our study of equilibrium (3).

There was an interest in preparing the bismuth analogue of the dinuclear compounds $M_2X_2(CO)_6E_2R_4$ in order to explore the Lewis-base properties of E_2R_4 (E = Bi) compounds towards transition elements. On the other hand, this project had to take into account the fact that the methyl and ethyl derivatives of bismuth(II), Bi_2R_4, had been reported [2] to be thermally unstable. In view of the well-established higher stability of phenyl derivatives, it was decided to attempt the preparation of Bi_2Ph_4. Several synthetic routes to this compound were successful, as shown in eqns. (4) and (5). Initially [23], the reduction of $BiPh_2X$ (X = Cl, I) with sodium in liquid ammonia was used; later [24], biscyclopentadienylcobalt(II), $CoCp_2$, was found to be a more convenient reducing agent for $BiPh_2I$*. Further improvement came from the observation that the preliminary preparation of $BiPh_2I$ can be avoided, and the reduction can be carried out on a toluene solution of BiI_3 and $BiPh_3$ in the 1:2 molar ratio**.

$$BiPh_2X + Na \xrightarrow{\text{liq. } NH_3} \tfrac{1}{2}Bi_2Ph_4 + NaCl \quad (4)$$

$$BiPh_2I + CoCp_2 \xrightarrow[(X=Cl,I)]{\text{toluene}} \tfrac{1}{2}Bi_2Ph_4 + CoCp_2I \quad (5)$$

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* The use of $CoCp_2$ as a reducing agent of bismuth(III) halo compounds is most advantageous when the unstable tetra-alkyldibismuthines have to be prepared. With $BiMe_2Br$, reduction by $CoCp_2$ occurs at about −40°C in tetrahydrofuran [25] to give Bi_2Me_4 (identified spectroscopically); the half-life of the compound at room temperature in CD_2Cl_2 solution is about 20 min [26].

** Using ^{13}C NMR spectra, it was established that similar equilibrium mixtures of $BiPh_3$, $BiPh_2I$, $BiPhI_2$ and, presumably, BiI_3 are obtained in solution by any of the following routes: $BiPh_3 + BiI_3$ (2:1), $Bi_2Ph_4 + I_2$, and $BiPh_3 + I_2$. Thus, in whatever system $BiPh_2I$ is generated, it is in equilibrium with all the possible redistribution products, although its concentration is predominant.

The X-ray structure [3,23] shows that Bi_2Ph_4 has a staggered trans conformation, as already found [27] for Sb_2Ph_4. The coordination around bismuth is approximately pyramidal. The bismuth–bismuth distance of 2.990(2) Å is slightly longer than the 2.936(2) and 2.941(2) Å found [28] in the Bi_4^{2-} anion, and slightly shorter than the nearest-neighbour distance (3.071(1) Å) in elemental bismuth [29]. The angles around bismuth, especially the two C–Bi–Bi′ (91.6(5)° and 90.9(5)°) bond angles not involving possible steric repulsion between the aromatic rings, are close to 90°, thus suggesting that the lone pair at bismuth has essentially *s* character, and no important *s*–*p* hybridization is required to explain the bonding features in Bi_2Ph_4. This may be proposed as a further example of the "inert pair effect" for post-transition elements [6].

In agreement with the notion that the strength of the element–element single bond decreases along a group of post-transition elements from the third period downwards, tetraphenyldibismuthine quite readily undergoes cleavage of the bismuth–bismuth bond with a number of reagents. Oxidative insertion across the Bi–Bi bond was observed [23] with I_2, *p*-benzoquinone, elemental sulphur and diazomethane (see eqns. (6)–(9)). These reactions are fast at room temperature and occur in a chemoselective way with the stoichiometric amount of reagents. They are believed to arise from an attack at the Bi–Bi bond, presumably through electron donation to an antibonding orbital centred on the Bi–Bi vector or to a higher empty bismuth orbital*. It is interesting to note that diazomethane has been found to insert between the chalcogen–chalcogen bond [30], while dichlorocarbene inserts in the tin–tin bond of $R_3Sn{-}SnR_3$ [31]. On the other hand, transition metal complexes react with diazomethane when they contain metal–metal double bonds [32]. A rare case of diazomethane insertion between a single metal–metal bond in the transition series was described for the diphosphine-bridged system of platinum(I), $Pt_2Cl_2(L{-}L)_2$ [33].

$$Bi_2Ph_4 + I_2 \rightarrow 2BiPh_2I \qquad (6)$$

$$Bi_2Ph_4 + p\text{-}C_6H_4O_2 \rightarrow Ph_2BiOC_6H_4OBiPh_2 \qquad (7)$$

$$Bi_2Ph_4 + \tfrac{1}{8}S_8 \rightarrow (Ph_2Bi)_2S \qquad (8)$$

$$Bi_2Ph_4 + CH_2N_2 \rightarrow (BiPh_2)_2CH_2 \qquad (9)$$

As mentioned earlier, the homodinuclear species are favoured with respect to the heterodinuclear species in the P_2Ph_4/As_2Ph_4 system (see eqn. (3)). Moreover, no reaction was found to occur in the P_2Ph_4/Sb_2Ph_4 system [21] at room temperature either in chloroform or in tetrahydrofuran. Also, compounds E_2R_4 and E'_2R_4 give redistribution equilibria (see eqn. (10)) [34], which suggests that the heterodinuclear compounds in these *intragroupal* combinations are not highly favoured, presumably due to an insufficient enthalpy contribution.

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* An alternative possibility is a radical mechanism triggered by the $BiPh_2$ monomer. However, no evidence of any monomer–dimer equilibrium was gathered.

On the other hand, Bi_2Ph_4 reacts with diphenyldichalcogenides to give the corresponding heterodinuclear compounds (see eqn. (11)). The reactions were found [24] to go to completion and the heterodinuclear compounds were isolated and characterized by ^{13}C NMR spectra. The Bi–Se compound was studied by X-ray diffraction methods: the coordination geometry around bismuth can best be described as pyramidal with angles at bismuth of 97.4(3)° and 87.4(3)°, i.e. considerably less than the tetrahedral value, thus confirming what was established earlier for Bi_2Ph_4. In agreement with these results, the literature [35] reports the isolation of heterodinuclear compounds of the type ER_2–E′R with Group 15 (E) and Group 16 (E′) elements: these compounds have also been obtained by redistribution reactions of the type of equation

$$E_2Me_4 + E'_2Me_4 \rightleftharpoons 2EE'Me_4$$
$$(E = P, E' = As; E = Bi, E' = Sb; E = Sb, E' = As; E = Bi, E' = As) \quad (10)$$

$$Bi_2Ph_4 + E_2Ph_2 \rightarrow 2Ph_2Bi\text{–}EPh$$
$$(E = S, Se, Te) \quad (11)$$

C. THE SINGLE METAL–METAL BOND IN TRANSITION METAL COMPOUNDS

As mentioned earlier, a limited number of systems containing single metal–metal bonds *without supporting bridging ligands* exists in the literature, the most relevant examples being the cyclopentadienyl derivatives of Group 6, $M_2Cp_2(CO)_6$ (M = Cr, Mo, W) and the decacarbonyls of Group 7, $M_2(CO)_{10}$, (M = Mn, Tc, Re). In a study aimed at looking at intragroupal trends, a limiting factor is the availability of all three systems from the 3d to the 5d analogue. In their pioneering work in this field, Madach and Vahrenkamp [36] carried out a series of experiments showing that dinuclear compounds of transition elements undergo redistribution reactions leading to heterodinuclear complexes. The $Mo_2Cp_2(CO)_6/W_2Cp_2(CO)_6$ and $Fe_2Cp_2(CO)_4/Co_2(CO)_8$ sytems were taken into consideration and the reaction products were studied by spectroscopic methods to show that equilibrium mixtures were obtained in certain cases (e.g. in the $Mo_2Cp_2(CO)_6/W_2Cp_2(CO)_6$ system) and that only the heterodinuclear species were found in other cases. Moreover, Marcomini and Poë [37] discovered that the $Mn_2(CO)_{10}/Re_2(CO)_{10}$ system at about 170°C and above gives an equilibrium mixture containing the heterodinuclear compound $MnRe(CO)_{10}$.

Both the Mo/W and the Mn/Re systems have been reinvestigated using a carbon monoxide atmosphere in order to minimize any decomposition [38] (see eqns. (12) and 13)). The Mo/W system was found to undergo no exchange under thermal conditions in the dark [39] at room temperature for several days or at 50°C for 48 h. On the other hand, exposure to sunlight of an equimolar mixture of $Mo_2Cp_2(CO)_6$ and $W_2Cp_2(CO)_6$ in toluene gave the heterodinuclear compound, as shown by ^{13}C NMR spectra. In quantitative experiments carried out at room temperature, photolysis in the visible region (510 nm) with a filtered tungsten source gave an equilibrium mixture of the two homodinuclear complexes and of the heterodinuclear compound in the 1:1:2 molar ratio. Thus, within experimental error, the statistical distribution of products was obtained. Equilibrium (12) could not be studied starting from $MoWCp_2(CO)_6$ [40] because, in our hands, the heterodinuclear compound could not be obtained from either $KMoCp(CO)_3/WCp(CO)_3I$ (see reaction (14)) or $LiMoCp(CO)_3/[WCp(CO)_3]BF_4$. In each case, the same equilibrium mixture of the three compounds was obtained, even under rigorous exclusion of light. Evidently, the electron transfer between $MoCp(CO)_3^-$ and $WCp(CO)_3^+$ leads to $MCp(CO)_3$ radicals which have a sufficiently long life to rearrange and give the thermodynamic mixture of products. Thus, this and the photochemical experiment follow similar pathways.

$$Mo_2Cp_2(CO)_6 + W_2Cp_2(CO)_6 \overset{h\nu}{\rightleftharpoons} 2MoWCp_2(CO)_6 \tag{12}$$

$$Mn_2(CO)_{10} + Re_2(CO)_{10} \rightleftharpoons 2MnRe(CO)_{10} \tag{13}$$

$$KMoCp(CO)_3 + WCp(CO)_3I \xrightarrow{THF} \left\{\begin{array}{l} Mo_2Cp_2(CO)_6 \\ W_2Cp_2(CO)_6 \\ MoWCp_2(CO)_6 \end{array}\right. \tag{14}$$

In agreement with the experiments by Marcomini and Poë [37], it was found that the thermal reaction between $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ occurs above 170°C at a reasonable rate*. The most important difference between these results and those reported earlier [37] is that equilibrium (13) is not greatly affected by temperature. The values of the equilibrium constant are distributed around the average value of 7.0 ± 1.0, thus suggesting that the formation of the heterodinuclear species from the homodinuclear species is accompanied by a small enthalpy change and is essentially entropy driven. In this case, the equilibrium could be studied from both sides, i.e. also from $MnRe(CO)_{10}$. This heteronuclear compound can be prepared in a pure state [38,41] from $NaMn(CO)_5$ and $ReI(CO)_5$ at room temperature. In this case, the electron transfer from manganese(I) to rhenium(I) apparently occurs in a concerted way and the radical fragments $Mn(CO)_5$ and $Re(CO)_5$ are not set free in solution. The heterodinuclear compound is the kinetic product of the reaction, as the temperature of the experiment is too low to allow any rearrangement to the homodinuclear

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* The reaction was studied [38] both in decahydronaphthalene solution and in the melt (m.p. of $Mn_2(CO)_{10}$, 153–155°C; m.p. of $Re_2(CO)_{10}$, 177°C) between 182 and 213°C, starting from both $Mn_2(CO)_{10} + Re_2(CO)_{10}$ and $MnRe(CO)_{10}$.

complexes*. The purity of $MnRe(CO)_{10}$ was checked by IR spectroscopy and by mass spectra. A single crystal was subjected to a new X-ray diffraction experiment, which confirmed the data that have appeared in the literature [41(c)]. Interestingly, the Mn–Re distance is 0.059 Å shorter than the sum of the covalent radii of manganese [41(e)] (1.447(1) Å) and rhenium [41(f)] (1.521(1) Å), as deduced from the corresponding crystal structure determinations in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.

The heterodinuclear species can be obtained from the homodinuclear compounds under irradiation at room temperature. Thus, equilibrium (13) can be established photochemically by irradiation in the 313–366 nm region, which corresponds to the $\sigma \rightarrow \sigma^*$ electronic transition of the metal–metal bond [42]. The constant of the equilibrium, over long irradiation times, was found to be 6.6 (from $MnRe(CO)_{10}$) or 6.1 (from the equimolar mixture of the homodinuclear compounds), substantially identical to the average value (7.0 ± 1.0) found in the thermal experiment. As the photochemical experiment was carried out at room temperature, the small enthalpy change associated with equilibrium (13) was further confirmed.

D. COMBINATIONS BETWEEN NON-TRANSITION AND TRANSITION ELEMENTS

Under this heading will be discussed those compounds obtained by reacting homodinuclear systems of transition elements with similar systems of non-transition elements, according to the general stoichiometry (15). The ligand L may be neutral or charged and, in the case of the non-transition element, *m* may be zero. Reactions of the type

$$L_nM{-}ML_n + L_mE{-}EL_m \rightarrow 2L_nM{-}EL_m \qquad (15)$$

have been known for many years, the best studied examples perhaps being those of homodinuclear metal carbonyls with halogens [43] ($m = 0$) to give halocarbonyl metal complexes, as specified in eqn. (15a) for the reaction leading to $MnI(CO)_5$. As the electronegativity of the element E is higher than that of the transition metal M, reactions (15) may be regarded as oxidations. Furthermore, if a homodinuclear metal carbonyl does not lose CO upon reaction with the element–element bond-containing species, we are dealing with a simple oxidative addition pattern [44].

$$Mn_2(CO)_{10} + I_2 \rightarrow 2MnI(CO)_5 \qquad (15a)$$

Again in agreement with the proposition that metal–metal single bonds are weaker for 3d systems and that element–element single bonds are weaker for post-transition elements as the principal quantum number increases, prompt reactions occur in the $Co_2(CO)_8/E_2Ph_4$ [44] and in the $Cr_2Cp_2(CO)_6/E_2Ph_4$ [38] combina-

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* A toluene solution containing equimolar quantities of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ was heated at 100°C and maintained at that temperature for some minutes without any appreciable formation of the mixed compound $MnRe(CO)_{10}$ [38].

tions (see eqns. (16), (18) and (20)). Well crystallized, presumably monomeric (a X-ray crystal determination for $Co(CO)_3BiPh_2(PPh_3)$ exists [44] to confirm this point) compounds were obtained by treatment of the products of reactions (16), (18) and (20) with PPh_3. The $BiPh_2$ derivative of cobalt(I) contains a terminally bonded $BiPh_2$ ligand around the trigonal bipyramidal cobalt atom containing equatorial carbonyl groups. The angles at the axially coordinated bismuth atom are 100.9, 98.5 and 95.7°, far from the tetrahedral value, although somewhat larger than in Bi_2Ph_4 [3,24].

$$Co_2(CO)_8 + Bi_2Ph_4 \rightarrow Co(CO)_4BiPh_2 \tag{16}$$

$$Co(CO)_4BiPh_2 + PPh_3 \rightarrow Co(CO)_3BiPh_2(PPh_3) \tag{17}$$

$$Co_2(CO)_8 + E_2Ph_4 \rightarrow Co_2(CO)_6(\mu\text{-}EPh_2)_2 + 2CO \tag{18}$$

$$Co_2(CO)_6(\mu\text{-}EPh_2)_2 + 2PPh_3 \rightarrow 2Co(CO)_3EPh_2(PPh_3) \tag{19}$$

(E = As, Sb)

$$Cr_2Cp_2(CO)_6 + E_2Ph_4 \rightarrow 2CrCp(CO)_3EPh_2 \tag{20}$$

(E = As, Sb, Bi)

A relevant difference of reactivity exists between Bi_2Ph_4 on one side and E_2Ph_4 (E = As, Sb) on the other. Reaction (16), an oxidative addition, is not followed by CO substitution to give the hypothetical $BiPh_2$-bridged $[Co(CO)_3(\mu\text{-}BiPh_2)]_2$. On the other hand, no evidence of the simple oxidative addition product $Co(CO)_4EPh_2$ was observed with the arsenic and antimony derivatives. This is consistent with the low availability of the second lone pair on bismuth, thus minimizing its tendency to form the $BiPh_2$-bridged product.

The data of Table 1 lend themselves to some consideration. The ν_{CO} values normally decrease in the sequence As > Sb > Bi for the compounds containing the terminally bonded EPh_2 groups, with (M = Co) or without an additional PPh_3 group. The data show a definite effect of the heteroatom of the terminally bonded EPh_2 group, namely there is a decrease in the ν_{CO} values from the lighter to the heavier pnicogen, similar to that found earlier [19,20] for bridging or terminal ER_2 groups or bridging ER groups with chalcogen as the donor atom. Earlier work [18] on manganese(I) and rhenium(I) complexes and on manganese(I) and vanadium(I) complexes [19,20] had suggested an increasing σ-contribution within the M—E bond in the sequence S < Se < Te. Recently, the dialkylchalcogenide substitution in $MCp(CO)_3(C_4H_8E)$ was found [45] to become faster in the sequence Te < Se < S, thus suggesting that heavier chalcogenide forms more stable complexes.

Both $Co_2(CO)_8$ and $Cr_2Cp_2(CO)_6$ are believed to contain a rather weak metal–metal bond. The cobalt–cobalt bond enthalpy in $Co_2(CO)_8$ has been estimated to be about 56 kJ mol^{-1} [13] and $Cr_2Cp_2(CO)_6$ has been noted [46] to have an exceedingly long chromium–chromium distance of 3.281(1) Å and has been proposed [47] to exist in solution in equilibrium with the corresponding monomer $CrCp(CO)_3$.

TABLE 1

Carbonyl stretching vibrations (cm^{-1}) of cobalt(I) and M(II), (M = Cr, Mo, W) derivatives containing terminal EPh_2 groups

Compound	E			Ref.
	As	Sb	Bi	
$Co(CO)_3EPh_2(PPh_3)$	2030 vw 1967 s	2026 vw 1959 s	2013 vw 1957 s 1948 s	44
$Cr(CO)_3Cp(EPh_2)$	1998 s 1934 m 1929 s	1990 s 1931 m 1915 s	1983 s 1926 m 1904 s	38
$Mo(CO)_3Cp(EPh_2)$	–	–	1997 s 1932 m 1906 s	38
$WCp(CO)_3(EPh_2)$	–	–	1993 s 1924 m 1899 m–s	38

[a] Heptane solution.

Thus, the smooth reactions (16) and (20) are in accord with expectation. The molybdenum and tungsten analogues, $M_2Cp_2(CO)_6$, which are believed to have a stronger metal–metal bond, do not react with Bi_2Ph_4 in the dark [38]: exposure to normal laboratory daylight gave the oxidative addition products (see eqn. (21)). The resulting tricarbonyl derivatives are suggested to possess a square-pyramidal structure of C_s symmetry, in agreement with the carbonyl stretching vibrations (see Table 1). In accordance with this proposal, the ^{13}C NMR spectrum shows two carbonyl resonances at 231.0 and 224.0 ppm (M = Mo) and at 219.1 and 213.5 ppm (M = W) in the ratio 1 : 2 for the cis and the two trans carbonyl groups, respectively.

$$M_2Cp_2(CO)_6 + Bi_2Ph_4 \xrightarrow{h\nu} 2MCp(CO)_3BiPh_2 \tag{21}$$

E. CONCLUDING REMARKS

The limited number of experimental results summarized in this article suggests a pattern of reactivity for homodinuclear compounds which may be summarized as follows. Intragroupal redistribution reactions of type (1a) or (1b) are essentially driven by entropy (i.e. $Mn_2(CO)_{10}/Re_2(CO)_{10}$; $Mo_2Cp_2(CO)_6/W_2Cp_2(CO)_6$; P_2Ph_4/As_2Ph_4), whereas intergroupal redistributions are possibly driven by both entropy and enthalpy. Of course, changing the nature of the ligand bonded to the central element may modify its electronic properties so much as to generate a sufficiently high enthalpy change in an intragroupal redistribution (see the case of the stable compounds $R_2E{-}E'R'_2$ ($E = P$, $E' = As$) for drastically different R groups [35,48]).

ACKNOWLEDGEMENTS

The author wishes to thank the Consiglio Nazionale delle Ricerche (C.N.R., Rome) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (M.U.R.S.T.) for financial support, and all his coworkers, whose names appear in the list of references, for their enthusiasm within this research project. Thanks are due to Professor A. Poë, University of Toronto, Professor H. Vahrenkamp, Universität Freiburg, and Professor G. Wilkinson, Imperial College of Science and Technology, for helpful discussions.

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