

Phosphinidene Complexes and Their Higher Homologues

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Over the last two decades, the synthesis and characterization of compounds containing what might be termed unconventional multiple bonds was within the mainstream of the development of molecular inorganic chemistry. Multiple bonding between transition metals is one of the topics which gradually evolved from its early observation in the sixties to the present common acceptance of this phenomenon.¹

Multiple bonding between the heavier main group elements, discredited by the traditional double-bond rule, is another topic in this area for which some real achievements have been reported in the past few years.² In between these two lines, the chemistry of transition metal-main group multiple bonding made continuous progress, gaining a strong impetus especially from the prominent findings in carbene and carbyne³ as well as nitrene and nitride⁴ coordination chemistry. Transition-metal bonding to the heavier homologues of carbenes has been demonstrated in delicate work⁵ and is a field of continued interest.

The chemistry of compounds showing multiple bonding between transition metals and the higher homologues of nitrenes has also made quite some progress since its beginning some 10 years ago.⁶⁻¹⁰ It is this type of chemistry, which has never been reviewed, that forms the basis of this Account.

The Heavier Homologues of Nitrenes as Ligands

The possible intermediate existence of phosphinidenes in organophosphorus reactions has been critically reviewed.¹¹ It appears that R-P̄: species (R = monovalent substituent) behave like nitrene homologues in some cases,¹¹ but not too much is known about the existence of the heavier group-V(15)⁷⁷ species R-X̄: (X = As, Sb, Bi). The capability of R-X̄: fragments to act as multiply bridging elements in clusters became known in the early seventies¹² and a large amount of work concerning RP-bridged clusters has since accumulated.¹³ While the main emphasis in this type of work is on the propensity of R-X̄: units to hold together the entities of a cluster, the interest in μ₂ bridging RX groups takes another point of view: Compounds with this structural entity may involve metal-X multiple bonding, and it is the study of these unconventional multiple bonds which is of current interest in this respect. This Account will include those well-characterized compounds, [L_nM]₂XR (L_nM = 16-electron transition-metal frag-

ment; X = P, As, Sb, Bi; R = monovalent residue, e.g., alkyl, aryl), for which this type of multiple bonding is obvious from detailed studies. The somewhat related chemistry of phosphonium ion complexes has recently been reviewed^{14,15} and is not included here nor is the chemistry of terminal phosphinidene complexes L_nMPR, which are only known as intermediates.^{7b,16,17} Species [L_nM']₂XR, where L_nM' is a 17-electron fragment and hence monovalent, are as a subclass of com-

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Gottfried Huttner, Bavarian, was born in 1937 and received his Ph.D. from the Technical University of Munich working with Prof. Dr. E. O. Fischer. He formerly held the chair of synthetic inorganic chemistry at the University of Konstanz, FRG; quite recently he moved to the University of Heidelberg, Institute of Inorganic Chemistry. His research interests are in structural, synthetic, and mechanistic aspects of organometallic chemistry.

Kaspar Evertz, born in 1959, studied chemistry at the Rheinisch-Westfälische Technische Hochschule Aachen and received his diploma in 1984 with Prof. Dr. W. Kläui. He has been a member of Prof. Dr. Huttner's research group since 1984.

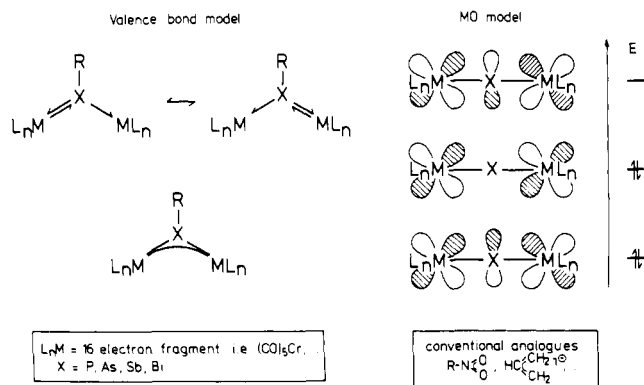


Figure 1. Bonding in $[L_nM]_2XR$ compounds.

mon R_3X : molecules also not considered here.¹⁸

Bonding

μ_2 Bridging $R-\ddot{X}$: ($X =$ Main Group V (15) Element). The very fact that species $R-\ddot{X}$: are sextet entities and hence bond to be unstable in the free state determines their ligand capabilities. While the two n -electron pairs render them effective σ donors, the empty valence orbital makes them effective π acceptors at the same time. For binuclear phosphinidene, arsinidene and stibinidene compounds $[L_nM]_2XR$, where the $R-\ddot{X}$: species are symmetrically embedded between two 16-electron fragments, L_nM , bonding may thus be described as originating from the interaction between X -lone pairs and metal σ -acceptor functions on one hand and back donation from filled metal π -type orbitals into an empty X p orbital of an sp^2 hybridized X center on the other hand^{7,8} (Figure 1).

The MO picture of backbonding results in a three-center 4π model; the four electrons entering this three-level system formally come from the two metal-atom d-type lone pairs. This description of the 4π system is completely equivalent to the description of π bonding in such common compounds as RNO_2 or the allylic anion, to mention just two examples. This model which has been put forward as a qualitative approach,^{7,8} has been substantiated by ab initio calculations.¹⁹ It would lead one to expect some peculiar properties for this type of compound:

Geometry. The main-group centers X should be in a trigonally planar environment. Even if there were no back bonding from the metal atoms, this trigonally planar coordination would be expected from VSEPR rules, since there is no stereochemically active lone pair at the main group center. If, as is to be expected, stabilization of the sextet species RX occurs by back bonding from metal atom lone pairs into the empty X -valence orbital of an sp^2 hybridized main group center, a shortening of the $M-X$ bonds due to the π interaction should ensue.

Spectroscopy. The $M \leftrightarrow X \leftrightarrow M$ π system should profoundly influence the spectroscopic properties of the compounds. The expected relatively weak $M \leftrightarrow X \leftrightarrow M$ π bonding should give rise to a relatively small HOMO-LUMO gap. Electronic transitions within this π system should hence lead to bands in the visible region.

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Reactivity. The low-lying LUMO of the $M \leftrightarrow X \leftrightarrow M$ π system should make the compounds behave as Lewis acids. The three-center 4π system on the other hand might give them allylic type ligand properties.

All of the above generalizations have been substantiated by the actual properties of phosphinidene,^{7,17,20-35,58c} arsinidene,^{8,22,26,28,32,34,36-49} stibinidene,^{9,26,32,34,49-53} and even bismuthidene¹⁰ complexes.⁶

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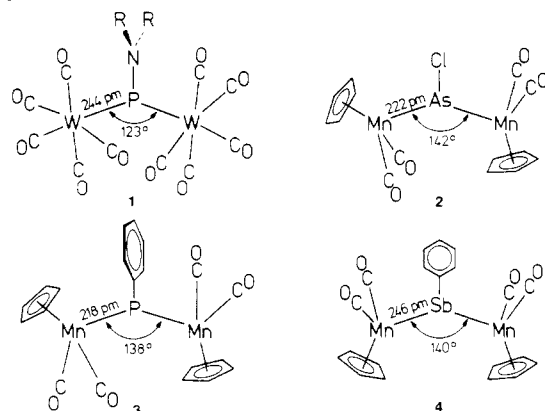
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Structures

A number of $[L_nM]_2XR$ compounds ($X = P,^{7b,20,22-25,29,31-33,35,58c} As,^{8b,22,32,37,39,42-47} Sb,^{9,32,51} Bi^{10}$) have been fully structurally characterized by X-ray methods, and the implications drawn from the characterization of the first compounds of each type^{7b,8b,9,10} have been firmly established. In all cases, cf. 1-4,^{7b,9,33,39} the main group center is in a trigonally planar environment with comparatively short $X \rightarrow M$ bond distances. It is in-



teresting to note that in those cases where the L_nM fragment has energetically different donor orbitals, the "better" donor orbital appears to interact with the X p orbital. Thus, for the $Cp(CO)_2Mn$ fragment the "better" donor orbital is oriented vertical to the mirror plane of the fragment,⁵⁴ and the interaction of this orbital with the central p orbital at the bridging main group center should lead to a preferred orientation with the $Cp(CO)_2Mn$ fragment's mirror plane coinciding with the coordination plane of X.^{7b,9,10,29,32,37,39,42,43,45-47,51}

All of the possible rotameric forms in which the coordination plane of X coincides with the mirror plane of $Cp(CO)_2Mn$ are known from X-ray work. The barrier of rotation around the Mn-X bond is generally so small in solution, however, that on the NMR time scale the signals of the individual rotamers are averaged while on the IR time scale the coexistence of different rotamer forms is clearly apparent. In the structurally related case of trigonally planar μ_3 bridging phosphorus (see below) the occurrence is also evident on the NMR time scale.²⁰

Spectroscopic Data

Visible Spectra. The most eye-catching property of binuclear RX compounds is their brilliant, bright color. Without exception^{7,8b,22,23,28,31-34,38,39,41,42,47,51} the visible spectra of the compounds show a very strong long-wavelength absorption giving rise to intense purple, red, green, or blue colors of the solutions and a metallic lustre of the crystalline solids. As an example the

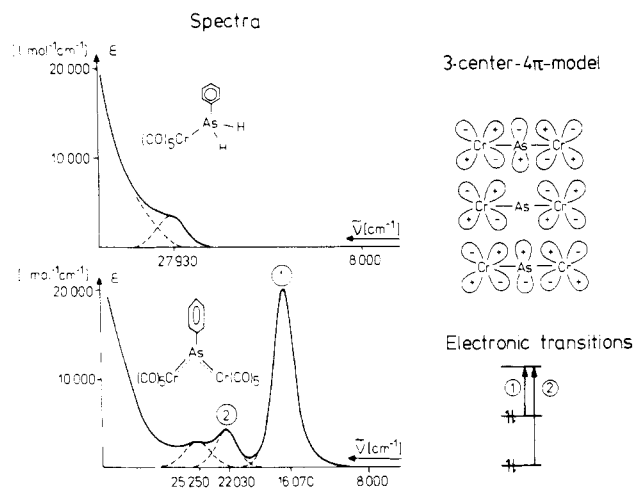
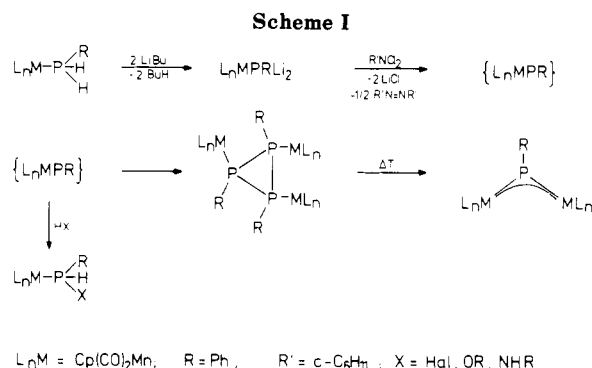


Figure 2. Electronic spectra of arsane and arsinidene complexes.



spectrum of $[(CO)_5Cr]_2AsPh^{8b,39}$ is given in Figure 2.

The spectrum of $(CO)_5CrAsPhH_2$ at the top of Figure 2 illustrates the normal spectroscopic behavior of $(CO)_5CrL$ compounds where L is a spectroscopically "innocent" ligand. Hence, one characteristic of the visible spectra of $(CO)_5CrL$ complexes is that there is no absorption at all in the longer wavelength visible region. In contrast, $[L_nM]_2XR$ compounds (Figure 2, bottom) have their prominent absorption in this very region. The visible absorption bands are due to the chromophoric $M \rightarrow X \rightarrow M$ three-center 4π system, which with its weak π interaction shifts the bands of this allylic anion type chromophore into the visible region.^{8b}

NMR Spectra. The weak π system $M \rightarrow X \rightarrow M$ has an exceptionally strong influence on the ^{31}P NMR shifts observed for the phosphinidene complexes. The observed ^{31}P NMR values are well out of the range of any other type of phosphorus compound,⁵⁵ and the following explanation has been put forward:²³ The small HOMO-LUMO gap allows for a significant admixture of excited states into the ground-state electronic configuration; this will enhance the paramagnetic contribution to the ^{31}P NMR shift.⁵⁶

Synthesis of $[L_nM]_2XR$ Compounds

Most of the synthetic approaches to $[L_nM]_2XR$ compounds are based upon the elimination of reactive substituents A, B from pyramidal $RXAB$ species or their coordination compounds. This elimination may, even in those cases where it appears to be direct (e.g., $A = B = Hal$ or $A = B = H$), in effect be the result of a sequence of reactions. Thus, the synthesis of $[Cp(CO)_2Mn]_2PPh$, the first phosphinidene complex to be reported,^{7b} relies upon a sequence of metalation and

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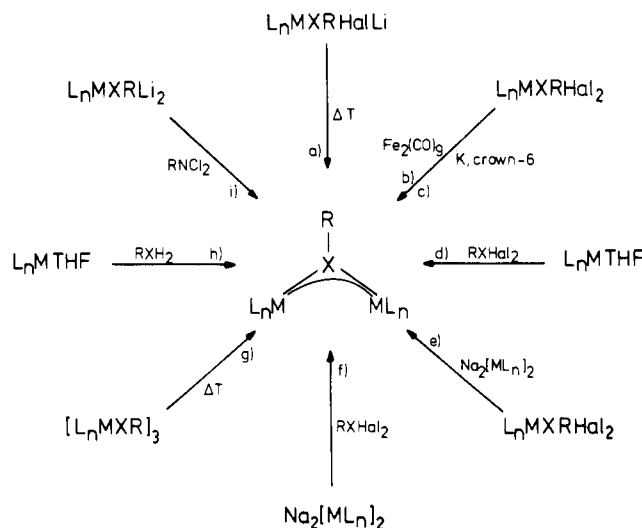
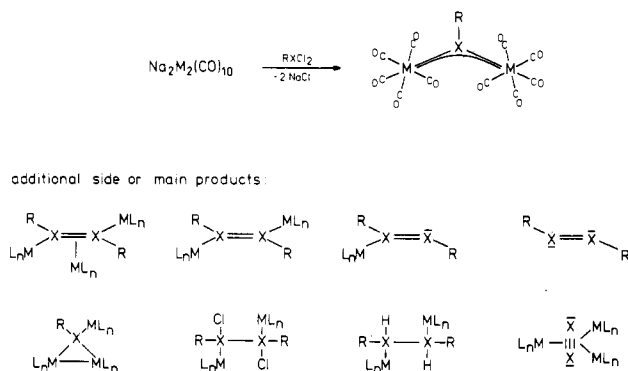


Figure 3. Synthetic routes to "indenyl" compounds. ^aReference 28. ^bReference 37. ^cReference 9. ^dReferences 10, 37. ^eReference 23. ^fReferences 22, 42, 53, 58. ^gReference 7b. ^hReferences 46, 64b. ⁱReference 8a.

Scheme II



demetalation processes (see Scheme I). The occurrence of the mononuclear intermediate $\{L_nM\}PR$ has been substantiated by trapping experiments.^{16,17} In the presence of HX the appropriate phosphine complexes are formed as the insertion products.^{7b} In most other synthetic approaches the reactions are, presumably only apparently, less complicated (Figure 3).

The treatment of $Na_2M_2(CO)_{10}$ ($M = Cr, Mo, W$) with $RXCl_2$ is a more or less general synthetic route.

Although stoichiometrically apparently straightforward, side products indicate complex reaction sequences also in this case. Depending on R and on the coordinating capability of the solvent used, all those side products may eventually be isolated and characterized^{17,22,23,27,30,31,33,34,36,42,44,47,49,51-53,57-61} (Scheme II).

Analogous reactions of sodium salts derived from $Fe(CO)_4$, $Co(CO)_4$, or $CpCo(CO)$ are only effective if R in $RXCl_2$ is a bulky substituent such as $(Me_3Si)_2N$ or $(2,4,6-t-Bu)_3C_6H_2$.^{25,35,62} For smaller groups R clusters are inevitably formed.^{58,60,63} For the reductive dehal-

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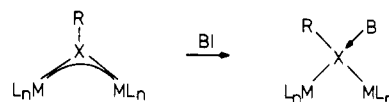
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Scheme III



BI = R_3NI , R_3PI , $R'_2C\bar{S}$, $R'_2C\bar{O}$, $R'_2\bar{O}$

X = P, As, Sb

$L_nM = (CO)_5Cr$, $Cp(CO)_2Mn$, etc.

ogenation of $L_nM\text{PRHal}_2$ by $t\text{-BuLi}$ it has been shown that lithium-halogen exchange leading to $L_nM\text{PRHalLi}$ is the initial step at low temperature.²⁸ α elimination of $LiHal$ occurs at elevated temperature; the final products isolated in this case are binuclear phosphinidene compounds $[L_nM]_2\text{PR}$ or diphosphene derivatives $[L_nM]_2\text{RP}=\text{PR}$ depending on the reaction conditions as well as on R.^{28,29} It appears that the mononuclear intermediates $\{L_nM\}XR$ are very good ligands, which are able to substitute the phosphane ligands in the starting material, because binuclear $[L_nM]_2XR$ compounds are obtained even from reaction mixtures where the only source for L_nM fragments is the starting phosphine complex.

Transformation of primary arsanens into arsinidene compounds is an especially easy reaction and occurs without the need of primarily transforming the X-H bonds into the more reactive X-Li bonds (see above). Thus, $L_nM\text{AsRH}_2$ transforms to the diarsane derivative $L_nM\text{RAsH-AsHRML}_n$ even at room temperature.^{64a} Upon heating this species yields the arsinidene compound $[L_nM]_2\text{AsR}$,^{64b} while catalytic dehydrogenation with Pd or Pt yields the diarsene compound.⁶⁵ The noncatalytic dehydrogenation process has elegantly been transferred to the synthesis of the parent arsinidene compound $[Cp^*(CO)_2Mn]_2\text{AsH}$ from $Cp^*(CO)_2Mn\text{THF}$ and AsH_3 .^{45,46}

Reactions

Addition of Lewis Bases and Chelate Ligands.

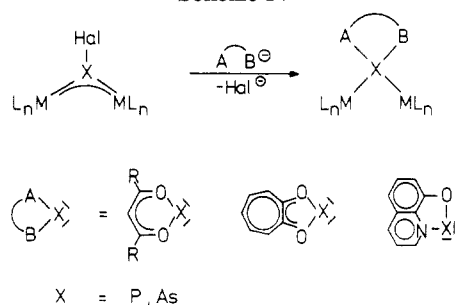
Compounds $[L_nM]_2XR$ behave as Lewis acids. The electron deficiency at the central X atom is only partially removed by the metal- $d\pi$ X- $p\pi$ interaction; the low lying LUMO of the three-center 4π system^{8b} $M\rightarrow X\rightarrow M$ has a large coefficient at the center X (cf. Figure 1). Hence, Lewis bases add to the central atom X to give compounds with tetrahedrally coordinated X atoms (see Scheme III).

In many instances these adducts are thermodynamically stable and may be isolated.^{38,41,42,49,51} In some cases especially with $R-\bar{P}$: bridging units, reversible adduct formation is only observed at low temperatures; it is easily monitored by the change in color^{23,28,30} because the intense long-wavelength absorption of $[L_nM]_2XR$ is quenched by the adduct formation, which destroys the $M\rightarrow X\rightarrow M$ π system.^{23,28,30,38,41,42,49,51} With compounds $[L_nM]_2XHal$, where the halogen function may be substituted, monovalent chelate ligands add and substitute at the same time to give very stable compounds^{30,40,42} (see Scheme IV).

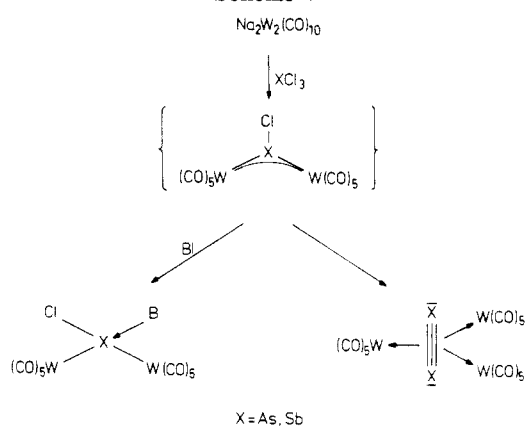
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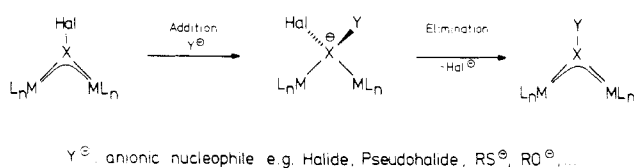
Scheme IV



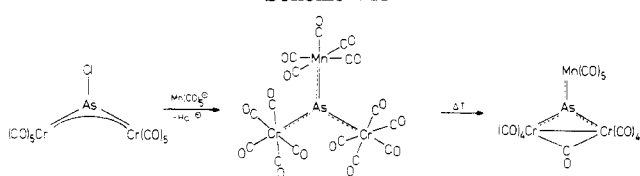
Scheme V



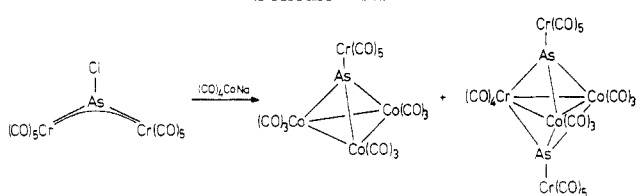
Scheme VI



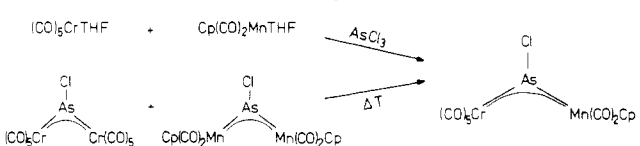
Scheme VII



Scheme VIII



Scheme IX



The chelate compounds as well as the mere base adducts are interesting species since they may be considered as coordinatively stabilized derivatives of Vth (15th) main group species, which are themselves unknown in the free state.⁶⁶

Trapping of $[L_nM]_2XR$ with Lewis bases has been

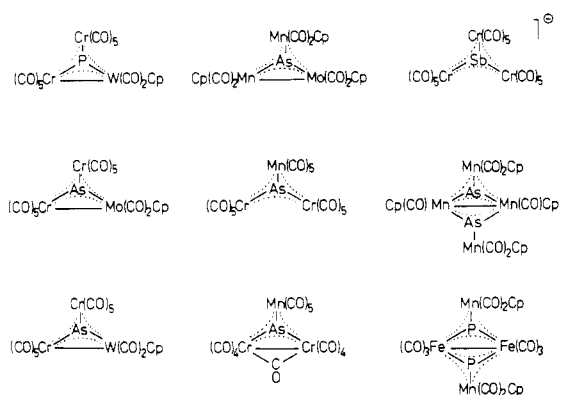


Figure 4. Structurally characterized trigonally planar μ_3 -X compounds.

used to show that reactions of $Na_2W_2(CO)_{10}$ with $AsHal_3$ or $SbHal_3$ involve $[(CO)_5W]_2XHal$ as the primary products⁴⁹ (Scheme V). In the absence of a Lewis base B: the star type $X_2[W(CO)_5]_3$ will be formed⁵⁷ ($X = As, Sb, Bi$) whereas in the presence of B: the adducts are isolated in high yields.⁴⁹

Substitution Reactions. Compounds $[L_nM]_2XHal$ undergo substitution of Hal by nucleophiles in the sense of an addition-elimination sequence (see Scheme VI). When halides or pseudohalides are used as nucleophiles the anionic adducts are so stable in most cases that elimination of Hal^- does not occur.⁴¹ With soft bases like I^- , RS^- as the nucleophiles or in cases where chelate rings are formed (see above) elimination is generally an easy reaction.^{39,42} Substitution of Hal in $[L_nM]_2XHal$ by Lewis acidic reagents like AlR_3 follows a different reaction pathway and is normally a clean reaction, leading to $[L_nM]_2XR$.⁴²

Organometallic Nucleophiles. Organometallic nucleophiles L_nM' also appear to add primarily to the main group center of $[L_nM]_2XHal$.^{32,43} In no case, however, have these adducts been isolated, and even the simple substitution products $[L_nM]_2XM'L_n$, which form after Hal^- elimination, often undergo immediate decarbonylation reactions leading to more condensed species. With the kinetically quite stable $(CO)_5Mn^-$ as the nucleophile, substitution products containing X in a trigonally planar fashion embedded by three metal atoms are stable^{32,43} (see Scheme VII).

In a formal sense, compounds containing X in a trigonally planar coordination and in between three metal atoms, all of which are capable of back bonding into the empty X valence orbital, are related to $[L_nM]_2XR$ species in quite the same way as NO_3^- is related to RNO_2 .

By the methods just described the most extensive series of structurally characterized trigonally planar μ_3 -X compounds (Figure 4) has been obtained.^{20,32,43,67}

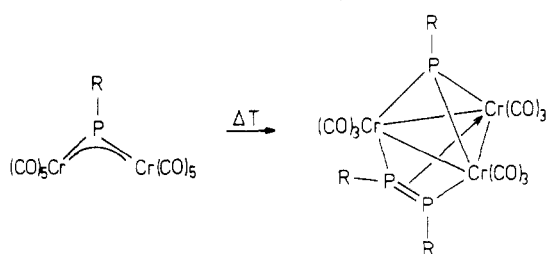
Trigonally planar μ_3 -X bridging appears to be far less common than the pyramidal alternative. In the trigonally planar situation, X has to be involved in using all

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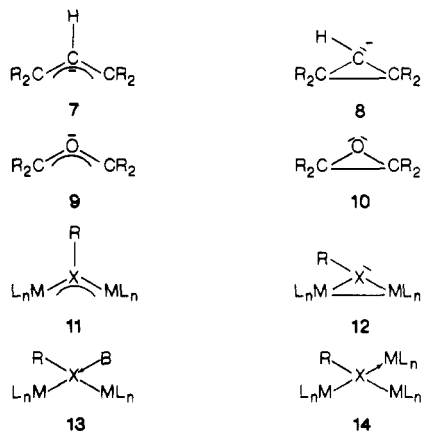
Scheme XIII



coupling may as well explain the formation of $[L_nM]_2(RX=XR)$ from $L_nMXRHal_2$, a verification of this hypothesis comes from the observation, that $[L_nM]_2XR$ compounds and $RX=XR$ derivatives may be transformed into each other (Scheme XII).^{27,52} Compounds $[(CO)_5Cr]_2PR$ are the primary characterizable products from $Na_2Cr_2(CO)_{10}/RPCl_2$ reactions.²⁷ The less stable compounds in this series (e.g., $R = Ph$) slowly transform into diphosphene derivatives with two end-on and one side-on coordinated $Cr(CO)_5$ groups. The reverse type of reaction is observed for distibene compounds which upon treatment with Lewis bases, which act as $W(CO)_5$ scavengers and $[(CO)_5W]_2XR$ stabilizers at the same time, transform into base-stabilized stibinidene compounds (Scheme XII). An example of the transformation of a μ_2 -PR group into a cluster-bound diphosphene is illustrated in Scheme XIII.⁵⁹ A concomitant transformation of μ_2 -PR into cluster bridging μ_3 -PR is observed for this example.

Valence Tautomerism of $[L_nM]_2XR$

Bonding in $[L_nM]_2XR$ is best described in terms of an allylic anion type three-center 4π system^{8b} (see above). It is well-known that the saturated, ring-closed cyclopropyl anion **8** and its valence tautomeric form, the allylic anion **7**, are close in energy on the hyper-surface.

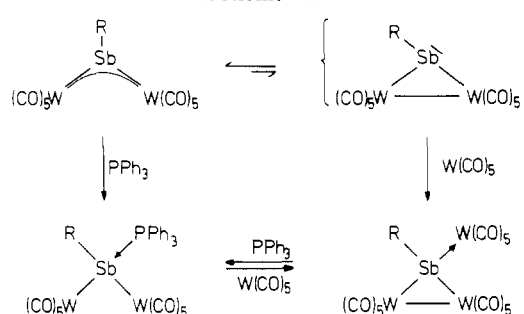


Heteroanalogues of the cyclopropyl anion such as oxiranes **10** react via their ring-opened valence tautomeric form **9**.⁷² With phosphorus as the central atom the same type of rearrangement has been analyzed for organophosphorus species.⁷³ "Inidene" type compounds should not make an exception in this regard. In fact

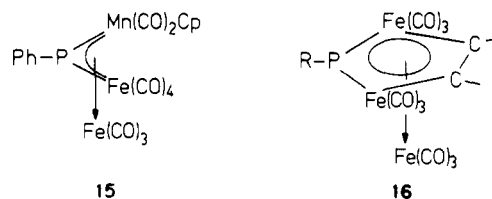
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Scheme XIV



some compounds of type **12**^{62,74} and many derivatives of the ring closed form have become known and have quite some time ago been interpreted in terms of the above valence tautomerism.⁷⁵ As far as the reactivity of X in tautomers **11** and **12** is concerned, the prime difference is that X has a lone pair in **12** and hence behaves as a donor, e.g., **14**, while X is unsaturated in **11** and will act as a Lewis acid (cf. **13**). An almost closed series of transformations between the derivatives of **11** and **12** has been reported for $[(CO)_5W]_2SbR$ ⁵² (Scheme XIV). Typical allylic anion type reactivity of "inidene" complexes **11** has hitherto been constrained to the observation that species **11** may act as allylic type ligands in compounds like **15**⁷⁶ or **16**,¹³ which are generally considered as clusters. Analysis of bonding in clusters along these lines appears to be a rewarding idea.^{13,63}



Concluding Remarks

The coordination chemistry of μ_2 -RX species ($X = P, As, Sb, Bi$) has a number of intriguing aspects. "Inidene" complexes $[L_nM]_2XR$ ($L_nM = 16$ -electron fragments) are examples of the rare trigonally planar coordination of heavier main group elements. This trigonally planar coordination is consistently interpreted in the model of a three-center 4π system $M \leftrightarrow (R)X \leftrightarrow M$ where the empty valence π orbital at the center X is filled by the interaction with filled metal d-type orbitals. This model readily explains the unconventional properties of these compounds, e.g., their structure, their bright color, their exceedingly large NMR shifts, and their propensity to add Lewis bases and form coordinatively stabilized unconventional species such as Ph_3PAsR or $acacAs$. Compounds $[L_nM]_2XHal$ open a systematic way to trimetallic species containing the main group atoms X as trigonally planar coordinated μ_3 -X ligands.

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(77) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III \rightarrow 3 and 13.)

The chemistry of these species is intimately correlated with the chemistry of $RX=XR$ and X_2 ligands. While this aspect concerns species with unconventional multiple bonds, another aspect of RX coordination chemistry is cluster chemistry, where these entities act as stabilizing building blocks.¹³ Since both these views are now taken by many research groups, a rapid de-

velopment of this field may be envisaged.

The enthusiasm of present and former co-workers (names given in references) is gratefully acknowledged as are many helpful discussions with Prof. H. Berke. The financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie has greatly assisted the development of the field.

Clusters: Bridging the Gas and Condensed Phases

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The last decade has seen an explosive burst of activity in studies of clusters with emphasis on their dynamics of formation, chemical properties, photophysics, and structure and stability. Various investigations have dealt with the entire range of systems including very simple van der Waals complexes of rare gases bonded by dispersion forces, more complex clusters where hydrogen bonding and/or partial transfer of charge is important, aggregates involving covalent metallic bonds, and systems comprised of atoms or molecules clustered about ions where electrostatic forces often prevail, but in some cases covalent bonding also contributes to stability. The enormous effort being focused on these systems is due to the many faceted aspects of cluster research pertaining to important fundamental problems such as bonding, energy transfer, and reactivity, as well as to a wide range of applied areas including corrosion, combustion, radiation physics and chemistry, surface analysis, nuclear fission and fusion, and atmospheric and even interstellar chemistry.

Clusters are comprised of an assembly of components, where the aggregated collection displays properties between those of large gas-phase molecules and the bulk condensed state. It is becoming increasingly well recognized that investigations of the formation and properties of weakly bound clusters provide an exciting way of following the molecular details of the course of change of a system from the gaseous to the condensed state, and this is perhaps the largest motivating force

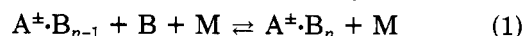
responsible for the increasing attention being paid to this subject. Also, due to the large number of molecules which exist on the surface at any one time, work in this field can provide some insight into the molecular aspects of changing properties of a system as a surface develops.

Although the range of the degree of aggregation of a system that may still be termed "cluster" is not precisely defined, studies grouped under this category commonly involve systems comprised of as few as two and perhaps as many as several thousand entities. In considering the unique distinction of a cluster than an appreciable number of the constituents is present on the surface, it is convenient to note that the proportion of surface constituents falls from approximately 20% to 2% as a cluster grows from 10^3 to 10^6 atoms or molecules.

Ionic System: Cluster Ions

Research on the properties of ion clusters has been particularly valuable and revealing¹ in the field of interphase physics which is concerned with the molecular details of phase transitions (nucleation phenomena), the development of surfaces, and ultimately solvation phenomenon and formation of the condensed state. Clusters are often formed following the bombardment of surfaces with ions,² and studies of the factors influencing their size, stability, and mechanisms of formation also comprise a related active area of research in surface science.

The formation of ion clusters in the gas phase proceeds via a sequence of association reactions between ions and the molecules with which they interact:



Here, A^\pm designates the ion (of either sign) about which molecule B is clustered; M is the third body which serves to stabilize the cluster during the formation process. The importance of measuring intrinsic gas-phase basicities and acidities in order to understand the origin of relative acidities and basicities in solution has been discussed by others.³⁻⁶

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Robert G. Keesee was born in Spokane, WA, and raised in southern California. He received degrees from the University of Arizona (B.S. in chemistry and mathematics, 1975) and the University of Colorado (Ph.D. in physical chemistry, 1979). He was a National Research Council Postdoctoral Fellow at NASA/Ames Research Center, 1979-1981. Since 1982 he has been at The Pennsylvania State University as a Research Assistant Professor of Chemistry. His research interests include the chemical and physical properties of molecular clusters and aerosols, the chemistry of planetary atmospheres, and the interactions of ions with molecules.