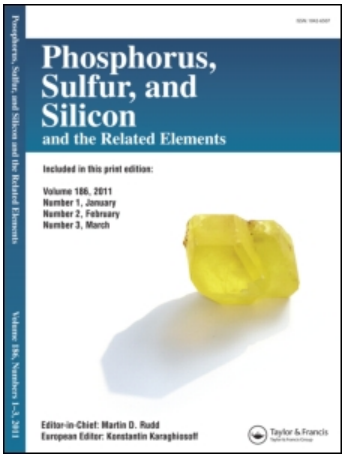

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Multiple Bonding Between Main-Group And Transition Elements

Alan H. Cowley[a]
[a] Department of Chemistry, The University of Texas at Austin, Aurtin, Texas, U.S.A.

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MULTIPLE BONDING BETWEEN MAIN-GROUP AND TRANSITION ELEMENTS

ALAN H. COWLEY

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

The reaction of $(Me_3Si)_2CHBiCl_2$ with $K_2[W(CO)_5]$ results in tungsten/bismuth cluster compounds. The reaction of $(Me_3Si)_2CHSbCl_2$ with $Na_2[Fe(CO)_4]$ affords an η^2-distibene complex which, in turn, reacts with $Fe_2(CO)_9$ to produce $Fe_2\{\mu\text{-}SbCH(SiMe_3)_2\}(CO)_8$, a "closed" (*i.e.* metal-metal bonded) stibinidene complex. The reaction of (2,4,6-*t*-$Bu_3C_6H_2$)PCl_2 with $Na[Co_2(\mu_2\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ produces (2,4,6-*t*-$Bu_3C_6H_2$)-$P[Co(CO)(\eta\text{-}C_5H_5)]_2$, an "open" phosphinidene complex. The factors affecting the "open" or "closed" nature of dimetallic phosphinidene (or heavier congeneric) complexes are discussed. The discussion is extended from sixteen-electron to fifteen- or fourteen-electron organometallic fragments. The synthesis of $Co_2\{\mu\text{-}P(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}(CO)_6$, a three-membered ring with Co—P multiple bonding is discussed. Finally, the reaction of the phosphaketene, (2,4,6-*t*-$Bu_3C_6H_2$)P=C=O, with $Fe_2(CO)_9$ is described.

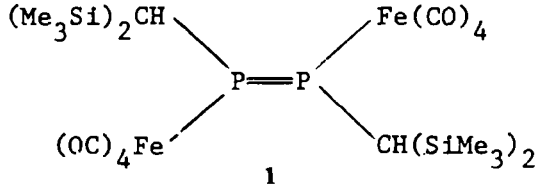
The "double-bond ring" notwithstanding,[1] several compounds have now been prepared which involve multiple bonding on the part of heavier main-group elements.[2] A listing of such compounds appears in Table I. Prior to this development, a large number of compounds featuring multiple bonding between transition metals has been isolated.[3] The focus of the present work is to explore the consequences of multiple bonding between main-group and organometallic fragments. Such compounds, analogues of *e.g.* metal carbenes, carbynes, and nitrenes, are of potential interest for several reasons:

(i) The multiple bonding takes place between distinctly different reaction centers, hence novel patterns of reactivity are anticipated.

(ii) As in the case of main-group/main-groups systems, considerable interest is associated with the stereochemical and electronic structural aspects of these multiple bonds.

(iii) These compounds represent potential sources of novel hybrid main-group/transition element clusters *via e.g.* thermolysis or photolysis reactions. A unifying concept in this area is the isolobal principle[4] which emphasizes the similarities in the frontier orbitals of organic, main-group, and transition metal fragments. Table II illustrates the electronic equivalence of several such moieties.

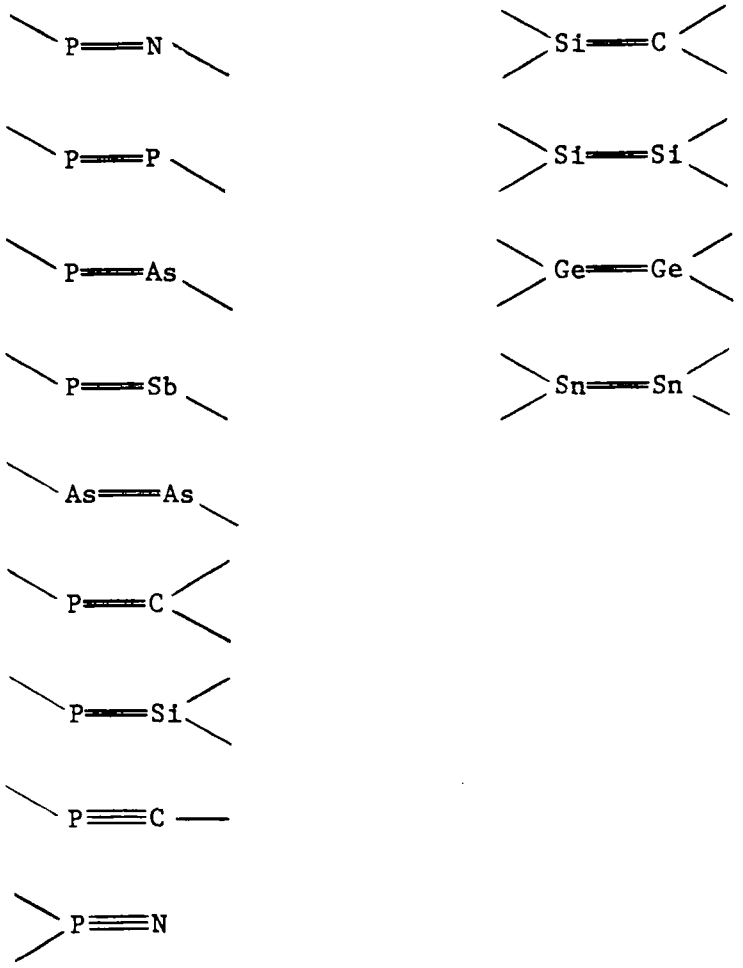
Our introduction to this field commenced with attempts to prepare compounds with unsuspended antimony-antimony or bismuth-bismuth double bonds. Power *et al.*[5] reported that the reaction of $(Me_3Si)_2CHPCl_2$ with $Na_2[Fe(CO)_4]$ affords the diphosphene complex, **1**. Arguing that both organic and organometallic moieties



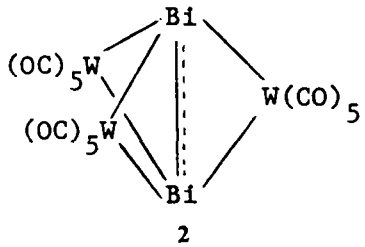
1

TABLE I

STABLE MULTIPLE-BONDED MAIN-GROUP SYSTEMS



would be necessary to effect kinetic stabilization of Sb=Sb or Bi=Bi bonds, we treated bulky dihalostibines and dihalobismuthines with organometallic dianions. The reaction of $(Me_3Si)_2CHBiCl_2$ with $K_2[W(CO)_5]$ results in two tungsten-bismuth cluster compounds **2** and **3**, which are separable by column chromatography.[6,7] Both



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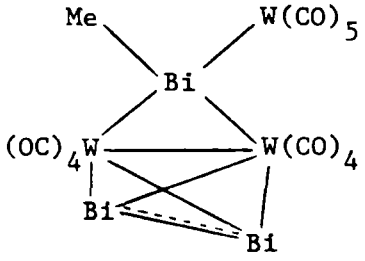


3

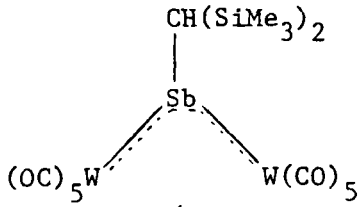
TABLE II

SOME ISOLOBAL RELATIONSHIPS

Main-Group Fragment	Organometallic Fragment
R_2C, R_2Si, RN, RP, O, S	$Cr(CO)_5$, $Mn(CO)_2(\eta\text{-}C_5H_5)$, $Fe(CO)_4$, $Co(CO)(\eta\text{-}C_5H_5)$, $Pt(PR_3)_2$, $Cr(CO)(NO)(\eta\text{-}C_5H_5)$
RC, RSi, N, P	$Mo(CO)_2(\eta\text{-}C_5H_5)$, $W(O\text{-}t\text{-}Bu)_3$, $Co(CO)_3$, $Mn(CO)_4$

2 and **3**, which have been characterized by X-ray crystallography, can be regarded as dibismuth complexes; however, at this point the nature of the bonding between the Bi atoms is not clear. Interestingly, the bismuth-bismuth bond distances are similar in both compounds (2.815(1) Å in **2** and 2.795(3) Å in **3**) and correspond to a bond order of approximately two. Note also that a $(Me_3Si)_2CHBi$ group is converted into a bridging methylbismuthinidene (MeBi). Presumably, this transformation occurs *via* successive nucleophilic attacks of the Me_3Si groups, followed by protonation of the resulting carbanions. Other conversions of this type include $(Me_3Si)_3C \rightarrow (Me_3Si)_2CH$[8] and $(Me_3Si)_2CH \rightarrow Me_3SiCH_2$.[9]

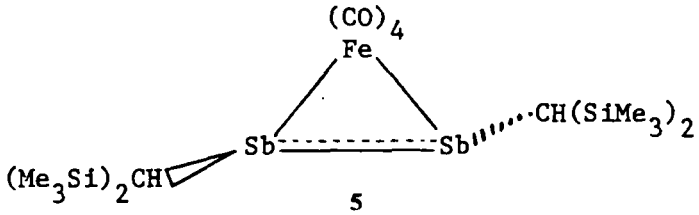
The reaction of $(Me_3Si)_2CHSbCl_2$ with $K_2[W(CO)_5]$ followed a different course to that of the bismuth analogue and resulted in the "open" stibinidene complex, **4**.[10]



4

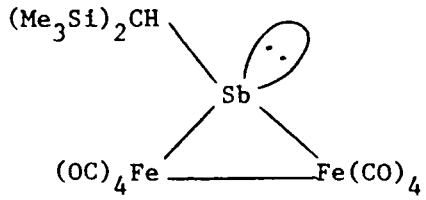
Several other complexes of this genre have been reported previously.[11] Like the other "inidene" (RE, E = P, As, Sb, Bi) complexes, **4** adopts a trigonal planar geometry at the main-group center.

The reaction of $(Me_3Si)_2CHSbCl_2$ with $Na_2[Fe(CO)_4]$ produced the distibene complex **5** as the primary product. The Sb—Sb bond length (2.774(1)Å) is shorter



5

than those of Sb—Sb single bonds and thus consistent with a modicum of multiple bonding. In terms of the isolobal principle, the bonding in **5** resembles that in *e.g.* $(\eta^2\text{-}C_2H_4)Fe(CO)_4$. Treatment of **5** with $Fe_2(CO)_9$ in *n*-hexane affords **6** and minor yields of the cluster, **7**.



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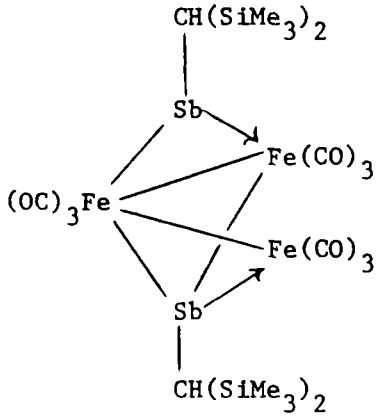
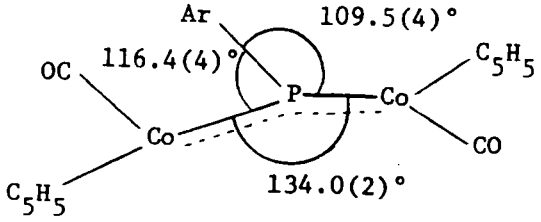


7

Compound **6** is particularly interesting because it represents the first "closed" complex of a bridging "inidene" moiety. The Fe—Fe distance (2.801(1)Å) is somewhat longer than normal; however the presence of an Fe–Fe bond can be implied from the pronounced pyramidality at the antimony center. What are the factors that are responsible for the "open" or "closed" structure preference? Two generalizations were apparent. First, all the "open" structures occur with Group 6B or 7B organometallic fragments while **6**, the only "closed" structure, involves a Group 8B fragment. Secondly, all the compounds with "open" structures would imply heptacoordinate metals if the structures were "closed", while in **6** the Fe is hexacoordinate. Recognizing these generalizations, we sought to prepare other "closed" complexes by employing potentially hexacoordinate fragments involving later transition elements. Somewhat surprisingly, however, the major product of the reaction of $ArPCl_2$ (Ar = 2,4,6-*t*-$Bu_3C_6H_2$) with $Na[Co_2(\mu_2\text{-}CO)_2\text{-}(\eta\text{-}C_5H_5)_2]$ is **8** which features an "open" structure.[12]



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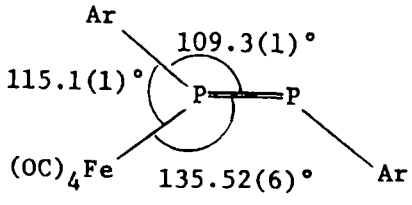

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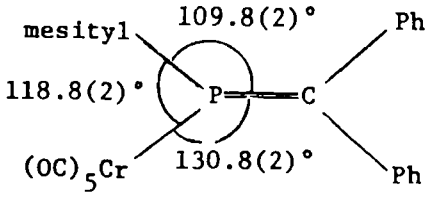
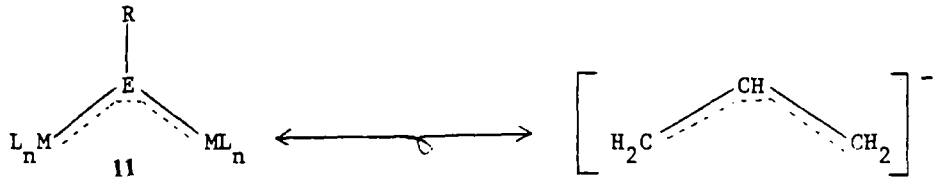


10

The difference in the P—Co bond lengths in **8** is virtually insignificant (2.115(4) and 2.105(3)Å). Interestingly, however, there are appreciable distortions of the angles at phosphorus which resemble those for η^1-diphosphene (**9**)[13] and η^1-phosphaalkene (**10**)[14] complexes.

The reactivities of "open" and closed complexes are quite distinct. Thus, like other "open" complexes, **4** functions as a Lewis acid toward *e.g.* Me_3P, whereas **6**, which possesses a lone pair of electrons at antimony, behaves as a Lewis base toward *e.g.* H^+ and Me^+. In terms of isolobal relationships, the "open" complexes are related to the allyl anion, while their "closed" analogues are related to cyclopropane. The ER fragment may therefore be termed *ambilobal*, being isolobal with either CH^- or CH_2 in **11** or **12**, respectively.



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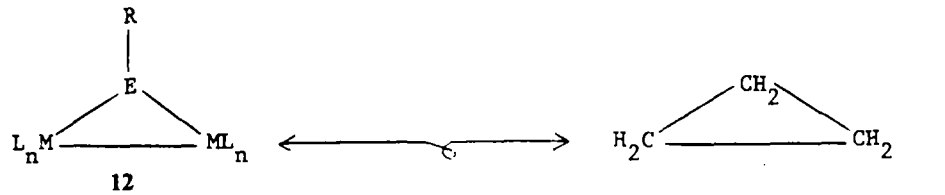
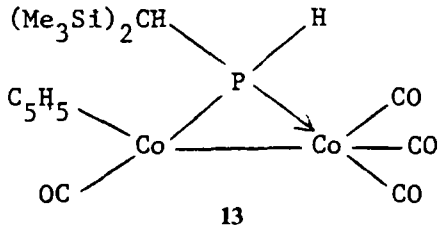


12

E = P, As, Sb, Bi $\quad ML_n$ = 16e$^-$ organometallic fragment

A major point to emerge from our studies is that the products are markedly dependent on the nature of the bulky group. Thus, in contrast to the (2,4,6-*t*-$Bu_3C_6H_2$)PCl_2 reaction described above, treatment of $(Me_3Si)_2CHPCl_2$ with $Na[Co_2(\mu_2\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ results in **13**.[9]



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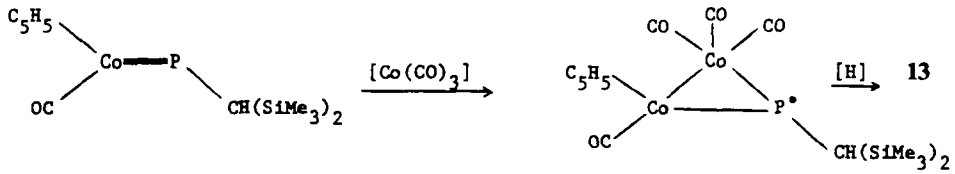
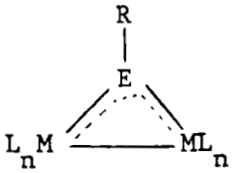
We do not have any evidence regarding the mechanism of formation of **13**; however, it is possible that this compound arises *via* the addition of a $Co(CO)_3$ unit



across the cobalt—phosphorus double bond of an initially formed terminal phosphinidene complex, followed by hydrogen abstraction from the solvent (THF), *viz.* The most plausible source of the $Co(CO)_3$ unit is the $[Co(CO)_4]^-$ anion which is always present in solutions of $Na[Co_2(\mu_2\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$.[15]

It occurred to us that the bonding dichotomy discussed above for sixteen-electron organometallic fragments should also occur for fifteen- or fourteen-electron fragments as represented below.

15e⁻ FRAGMENTS



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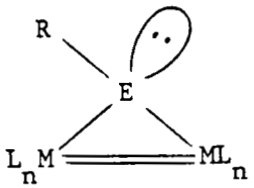
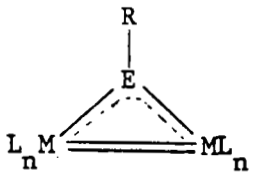


15

14e⁻ FRAGMENTS



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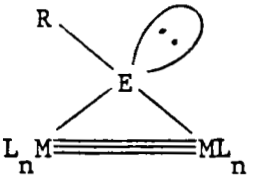
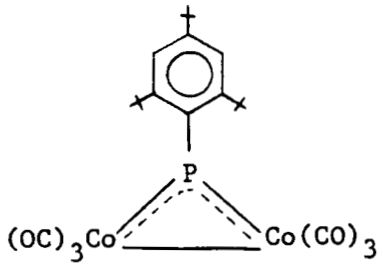


17

So far, we have found an example of structure **14**. Compound **18** was prepared by the reaction of $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)PCl_2$ with $K[Co(CO)_4]$ in THF solution.[16] An

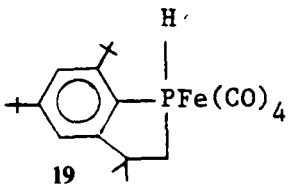


18

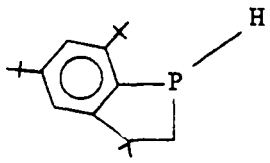
X-ray crystallographic study revealed that each molecule of **18** resides on a site of C_{2v} symmetry. The sum of angles at phosphorus is 360° within experimental error; moreover, the P—Co bond length (2.047(6)Å) is short and consistent with the hypothesis of multiple bonding between these atoms.[17] As expected, the ^{31}P NMR chemical shift of **18** appears at low field (+664 ppm). From the point of view of

fragment analysis, **18** can be construed as the product of addition of a phosphinidene unit to a Co≡Co bond. If one recognizes the isolobal relationship between C≡C and metal-metal triple bonds, an interesting parallel emerges between **18** and phosphirenes. Note, however, that the latter adopt structure **15**.[18] It should also be remarked that with less bulky substituents, phosphinidenes form larger clusters such as $Co_3(\mu_3\text{-PPh})(CO)_9$[19] and $Co_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})_2(CO)_8$.[20] In the case of **18**, the approach of additional $Co(CO)_n$ moieties is inhibited by *o-t*-Bu groups. Structures akin to **18** may therefore be involved in the cluster building process.

Attention is now turned to the attempted synthesis of stable terminal phosphinidene complexes. The intermediacy of $PhPW(CO)_5$ has been demonstrated elegantly by Mathey and co-workers.[21] Furthermore, there have been two recent reports[22] describing evidence for cationic phosphinidene species of the type $[RPML_n]^+$ (which can also be regarded as metallophosphenium ions). One of our approaches to this problem involves the reaction of the phosphaketene, $(2,4,6\text{-}t\text{-}Bu_3C_5H_2)P{=}C{=}O$[23] with a variety of organometallic reagents. For example, reaction of the phosphaketene with $Fe_2(CO)_9$ in toluene affords **19**.[24] It has not yet proved possible to isolate single crystals of **19** which are appropriate for X-ray crystallography. However, the proposed structure is consistent with all spectroscopic evidence. Moreover, **19** can be synthesized independently by treatment of **20** with $Fe_2(CO)_9$. The most reasonable



19



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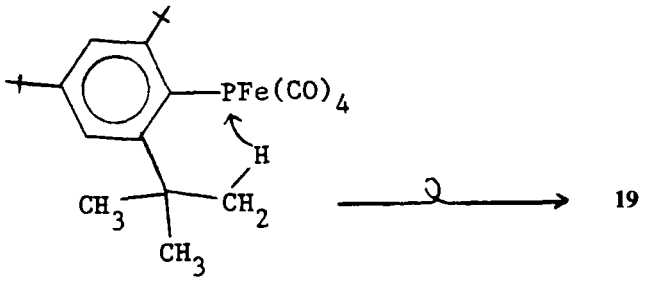

21

mechanism of formation of **19** involves the terminal phosphinidene complex, **21**, which rearranges to the observed product *via* intramolecular insertion of the phosphorus atom into a C—H bond of an *o-t*-Bu group. Precedent exists for such insertion reactions[25]; moreover, they are known to occur when the phosphorus center is two- or three-coordinate and electropositive. Free-radical pathways to **19** are considered unlikely because no P—D bond formation was observed when the reactions were conducted in toluene-d_8.

ACKNOWLEDGMENT

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