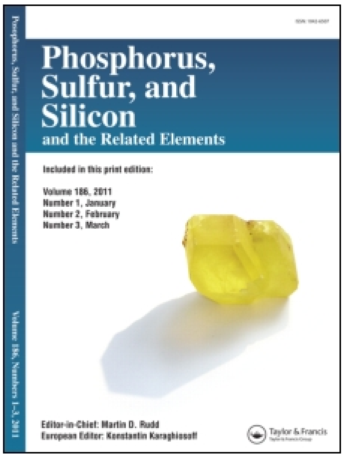


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Phosphinowethanide Complexes/Metalla-Phospha Heterocycles

Hans H. Karsch[a]
[a] Anorganisch-chemisches Institut, Technische Universität München, Garching

To cite this Article Karsch, Hans H.(1992) 'Phosphinowethanide Complexes/Metalla-Phospha Heterocycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 64: 1, 77 — 84

To link to this Article: DOI: 10.1080/10426509208041131

URL: http://dx.doi.org/10.1080/10426509208041131

Phosphorus, Sulfur, and Silicon, 1992, Vol. 64, pp. 77–84
Reprints available directly from the publisher
Photocopying permitted by license only

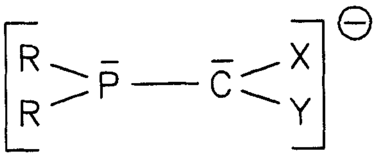
PHOSPHINOMETHANIDE COMPLEXES/METALLA-PHOSPHA HETEROCYCLES

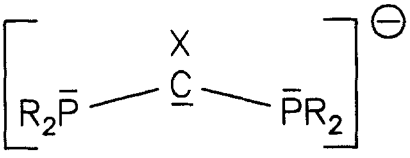
HANS H. KARSCH
Anorganisch-chemisches Institut, Technische Universität München,
D-8046 Garching

Abstract An overview of recent results in the field of heterocycles with incorporated phosphinomethanide moieties is provided in this article. Monophosphinomethanides and Diphosphinomethanides interact with main group, transition or lanthanoide metal centers to give complexes with chelating ligands of the type M(CP), M(PCP) and M(PCP)M. Insertion of sulfur or selenium into the metal-phosphorus bond is feasible, leading to novel heterocycles. Likewise, insertion of CO into the metal-carbon bond may be achieved, and again, after rearrangement, novel type heterocycles can be obtained. The interaction of at least two phosphinomethanide ligands at a metal center may promote oxidative coupling (C-C, P-C, or P-P), methyl transfer, and various kinds of metalation reactions at a C-H functionality. The products again represent novel classes of metalla-phospha heterocycles. The reaction course and thus the type of heterocycles obtained may be tuned by the substitution pattern of the phosphinomethanides and by the choice of the coordination center. Coupling of two M(PCP)M fragments may lead to heterocycles of the type $c\text{-}M_4(PCP)_2$.

INTRODUCTION

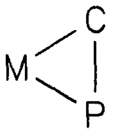
The element phosphorus ranks in the periodic table of elements by its diagonal relationship to carbon. Phosphinomethanides I are unique in representing the only meaningful species, where the reactivity of both elements can be investigated in a comparative manner: both elements are linked together directly and both elements have the same valence electron and coordination number.


I

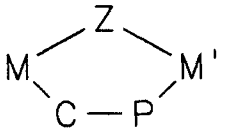

II

RESULTS

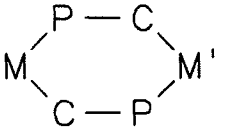
In fact, the coordination to metal centers is tunable by the appropriate choice of substituents. Heteroelement substituents at the formal carbanion (X,Y = SiMe$_3$, PR$_2$) reduce the nucleophilicity of the carbon ("α-effect") and enhance that of phosphorus ("phospha-β-effect*") to an extent, that both may compete for the electrophile. As a consequence, three-, five- or six membered heterocycles III-VI are obtained.



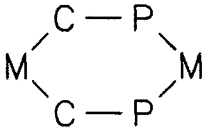
III



IV

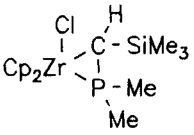


V

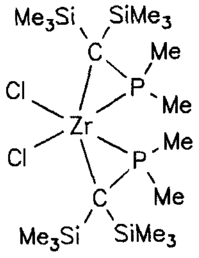


VI

Whereas type III heterocycles are now quite common with d^1-d^8 metal centers,[1] with zirconium metal centers (d^0), the first complexes of type III could be achieved by the strategy mentioned above. Examples are 1[2] and 2[3]:

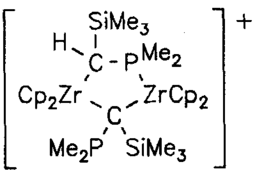


1

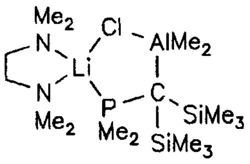


2

Examples for type IV are provided by complexes 3[2] and 4,[4];

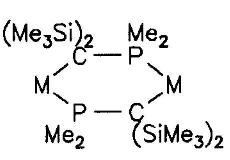


3

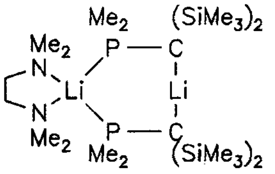


4

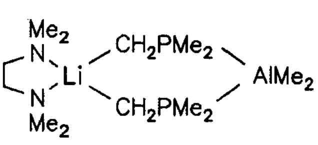
for V by **5**,[5] **6**,[6], and **7**,[7], for VI by **8**[8] and **9**[9]:



5: M = Me_2Al
6: M = Li
7: M = (THF)Li

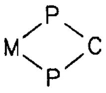


8

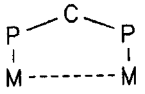


9

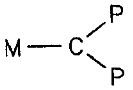
Also with diphosphinomethanides of type II, substituent effects are important. The most common coordination mode is a chelating one of type VII, but also a bridging coordination type VIII, and η^1-C (type IX) or η^2-C,P (type X) coordinations are feasible. Moreover, a hetero-π-allylic type of coordination, either inter- or intramolecular (type XI and XII), are possible.



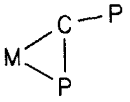
VII



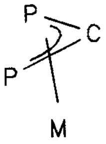
VIII



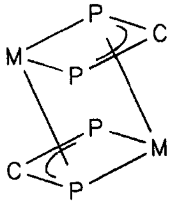
IX



X

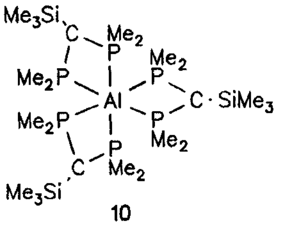


XI

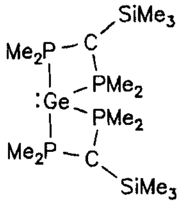


XII

Type VII coordination is found e.g. in $Al[(Me_2P)_2C(SiMe_3)]_3$, **10**,[10] $Ge[(Me_2P)_2C(SiMe_3)]_2$, **11** and related compounds of Si, Sn, Pb in oxidation states II and IV, in $[(TMEDA)_2Li][Cl_3Zr[C(PPh_2)_2(SiMe_3)]$, **12**,[12] or in $(THF)Lu[(Me_2P)_2(C(SiMe_3)]_3$, **13**.[13] Type VIII coordination, besides in some transition metal complexes is mainly found in a series of low-valent germanium complexs, which are derived from the bis-germylene complex $\{Ge[(Me_2P)_2C(SiMe_3)]\}_2$, **14**.[14] Type IX, clearly not heterocyclic, is exemplified by $Ge[(Ph_2P)_2CH]_2$, **15**,[15] and related compounds. For type XI, only one example is known:

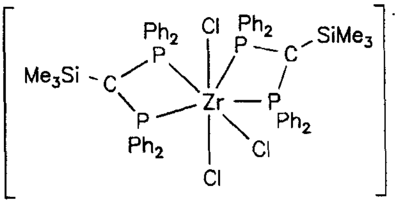


10

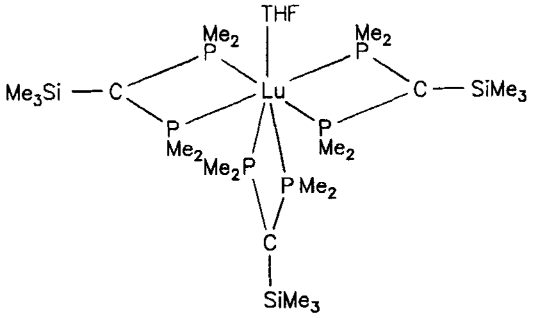


11

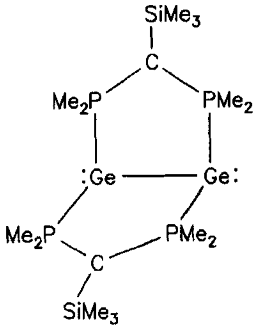
$[Li(TMEDA)_2]^+$



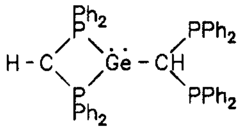
12



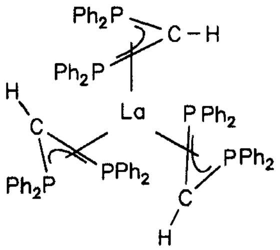
13



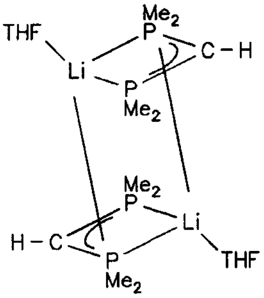
14



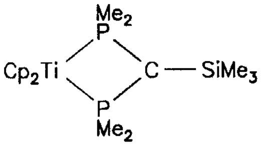
15



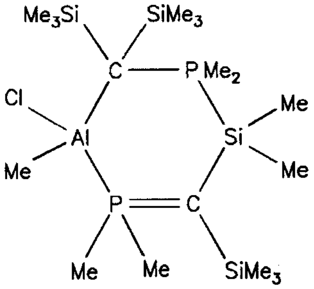
16



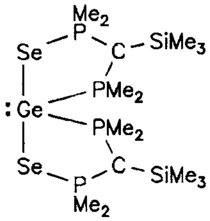
17



18



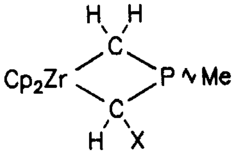
19



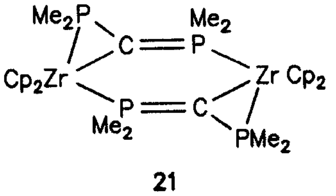
25

$La[(Ph_2P)_2CH]_3$, **16**,[16] whereas type XII is found in some structures of lithium phosphinomethanides, e.g. $[(THF)Li[(Me_2P)_2CH]]_2$, **17**.[17]

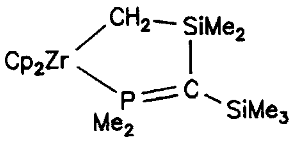
The interaction of at least two phosphinomethanide ligands at one metal center either may lead to oxidative coupling products of the phosphinomethanides, i.e. C-C, P-C, and P-P coupling, depending again on the substitution pattern and the metal. With titanium(IV) as oxidant, some cyclic complexes may be isolated as intermediates and/or final products e.g. $Cp_2Ti[(Me_2P)_2C(SiMe_3)]$, **18**,[18] which characterizes these reactions as metal centered processes. The interaction of two $[(Me_2P)C(SiMe_3)_2]^-$ ligands at an aluminum center leads to a surprising methyl transfer from Si to Al and $(Cl)(Me)\overline{AlC(SiMe_3)_2P(Me)_2Si(Me)_2C(SiMe_3)P}(Me)_2$, **19**[4] is isolated in high yield. At zirconocene metal centers, two phosphinomethanides interact in a way, that one ligand metalates the other one and, depending again on the substituents, different metalation products are obtained, e.g. **20**,[19] **21**,[19] or **22**.[19]



20

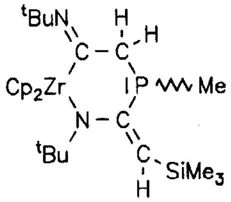


21

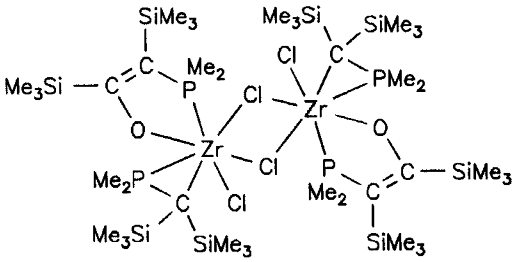


22

Insertion of ^tBuNC into the Zr-C bonds in **20** gives **23**,[19]



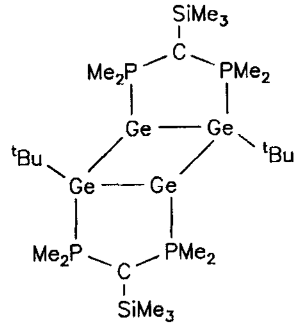
23



24

whereas CO insertion into **2** gives rise to **24**.[19] Both reactions include a 1,2 shift of a PMe or $SiMe_3$ group, respectively. Insertion of S or Se into the Ge-P bonds in **11** can occur four times, giving rise to spirocycles with 4/5, 5/5, 5/6 and 6/6 membered rings. An example for a 5/5 spirocycle is $\mathrm{Ge[\overline{SeP(Me)_2C(SiMe_3)P}(Me)_2]_2}$, **25** which contains an almost linear Se-Ge-Se bond and which can be regarded as a phosphinomethanide stabilized $[\mathrm{Se{-}Ge{-}Se}]^{2+}$ moiety.[20]

Though highly nucleophilic, the phosphinomethanide ligands in metallacycles of the kind described in this paper are susceptible to attack and replacement of the phosphinomethanide ligand by other nucleophiles in certain cases. An example is provided by the reaction of **14** with two equivalents of $\mathrm{Li^tBu}$, which under elimination of $\mathrm{Li[(Me_2P)_2C(SiMe_3)]}$ leads to the novel homocycle **26**.[21]



26

CONCLUSION

Mono- and Diphosphinomethanides react with electrophilic metal centers giving a variety of cyclic complexes, which constitute a novel class of heterocycles. The substitution pattern of the phosphinomethanides at a given metal center and/or the choice of the appropriate metal center allow for a wide range of structural variations, including coupling reactions and transformation by insertion of other species. Moreover, unusual coordination numbers and oxidation states of the metals are stabilized by these ligands. A systematic extension of this work to other substituents and/or metals seems feasible and would allow for a broad access to novel heterocycles.

REFERENCES

1. For an overview of first examples see: H.H. Karsch, Chem. Ber. 117, 783 (1984).
2. H.H. Karsch, G. Grauvogl, B. Deubelly, and G. Müller, Organometallics, submitted.
3. H.H. Karsch, G. Grauvogl, P. Bissinger, O. Kumberger, and G. Müller, Organometallics, submitted.
4. H.H. Karsch, K. Zellner, and G. Müller, Organometallics, in press
5. H.H. Karsch, K. Zellner, J. Lachmann, and G. Müller, J. Organomet. Chem. 409, 109 (1991).
6. H.H. Karsch, K. Zellner, P. Mikulcik, J. Lachmann, and G. Müller, Organometallics 9, 190 (1990).
7. H.H. Karsch, K. Zellner, S. Gamper, and G. Müller, J. Organomet. Chem., in press.
8. H.H. Karsch, A. Appelt, B. Deubelly, K. Zellner, J. Riede, and G. Müller, Z. Naturforsch. 43b, 1416 (1988).
9. H.H. Karsch, A. Appelt, and G. Müller, Organometallics 4, 1624 (1985).
10. H.H. Karsch, A. Appelt, J. Riede, and G. Müller, Organometallics 6, 316 (1987).
11. H.H. Karsch, B. Deubelly, G. Hanika, J. Riede, and G. Müller, J. Organomet. Chem. 344, 153 (1988).
12. H.H. Karsch, G. Grauvogl, P. Bissinger, O. Kumberger, and G. Müller, Organometallics, submitted.
13. H.H. Karsch, G. Ferazin, O. Steiglmann, unpublished work.
14. H.H. Karsch, B. Deubelly, J. Riede, and G. Müller, Angew. Chem. 99, 705 (1987).
15. H.H. Karsch, A. Appelt, and G. Hanika, J. Organomet. Chem. 312, C1(1986).
16. H.H. Karsch, A. Appelt, and G. Müller, Ange. Chem. 98, 832 (1986)
17. H.H. Karsch, G. Grauvogl, P. Mikulcik, and G. Müller, J. Organomet. Chem., submitted.
18. H.H. Karsch, G. Grauvogl, B. Deubelly, and G. Müller, unpublished work.
19. H.H. Karsch, G. Grauvogl, Organometallics, submitted.
20. H.H. Karsch, G. Baumgartner, S. Gamper, J. Lachmann, and G. Müller, Chem. Ber., submitted.