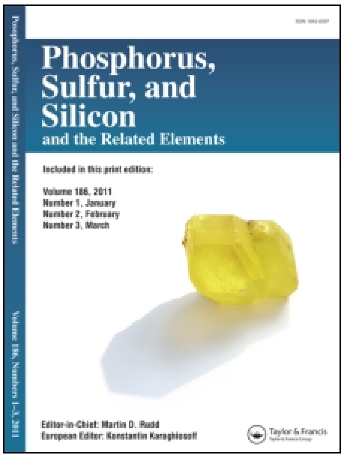


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Supramolecular Self-Assembly Through Secondary Bonds in Organotellurium Chemistry

Ionel Haiduc[a]; Julio Zukerman-schpector[b]
[a] Facultatea de Chimie, Universitatea “Babes-Bolyai”, Cluj-Napoca, Romania [b] Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil

To cite this Article Haiduc, Ionel and Zukerman-schpector, Julio(2001) 'Supramolecular Self-Assembly Through Secondary Bonds in Organotellurium Chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 171: 1, 171 — 185
To link to this Article: DOI: 10.1080/10426500108046632
URL: http://dx.doi.org/10.1080/10426500108046632

Phosphorus, Sulfur, and Silicon, 2001, Vol. 171, pp. 171-185
Reprints available directly from the publisher
Photocopying permitted by license only

Supramolecular Self-Assembly Through Secondary Bonds in Organotellurium Chemistry

IONEL HAIDUC[a] and JULIO ZUKERMAN-SCHPECTOR[b]

[a]*Facultatea de Chimie, Universitatea "Babes-Bolyai", RO-3400 Cluj-Napoca, Romania and* [b]*Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905 São Carlos, SP, Brazil*

The solid state structures of organotellurium compounds, associated through secondary bonds, are presented in the light of supramolecular chemistry principles. Supramolecular self-assembly through secondary bonds occurs in organotellurium-nitrogen, -oxygen, -sulfur and -halogen compounds and leads to the formation of discrete supermolecules (*e.g.* dimers or tetramers) or infinite supramolecular arrays.

Keywords: supramolecular chemistry; self-assembly; secondary bonds; organotellurium(IV) compounds

BASIC CONCEPTS OF SUPRAMOLECULAR CHEMISTRY

Supramolecular chemistry is "*the chemistry of molecular*

***assemblies and of the intermolecular bond*". It is "*the chemistry beyond the molecule*" and deals with "*organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces*".[1,2]

There are two types of subjects in supramolecular chemistry: a) the *supramolecular assemblies* or systems, also called supramolecular arrays, *i.e.* "*polymolecular entities that result from the spontaneous association of a large undefined number of components*", and b) *supermolecules*, i.e. "*well-defined discrete oligomolecular species that result from the intermolecular association of a few components*".[3]

The supramolecular structures are formed through self-assembly; this is a spontaneous process of intermolecular association, resulting in discrete or extended polymolecular assemblies held together by non-covalent bonds.[1] When the resulting supramolecular species display a high degree of order (usually in the solid state) the term *self-organization* is frequently used.

Organometallic compounds provide numerous examples of supramolecular architectures formed by assembling molecular units *(tectons)* connected through noncovalent intermolecular forces (dative, secondary, ionic or hydrogen bonds).[4] The term *tecton* was introduced to describe the molecular units of supramolecular structures assembled through non-covalent forces. Thus, the *tecton* has been defined as "*any molecule whose interactions are dominated by particular associative forces that induce self-assembly of an organized network*".[5,6] This is intended to replace the term *synthon,* which was used to describe both fragments of covalent molecules (built by synthetic procedures of organic chemistry) and molecular building blocks of supermolecules (self-assembled through non-covalent interactions). The *synthons* were defined as "*structural units within supermolecules which can be formed and/or assembled by known or conceivable synthetic operations involving intermolecular interactions*". [7] The same meaning can be assigned to the term *tecton*.

This review will deal only with supramolecular architecures of organotellurium compounds formed through non-covalent forces known as *secondary bonds or soft-soft interactions.*[8-10] These are characterized by interatomic distances longer than covalent bonds but shorter than van der Waals interatomic distances. Such interactions are weaker than two electron covalent or dative bonds, but are strong enough to influence the coordination geometry of the atoms involved and to connect the atoms, either intramolecularly or intermolecularly, and to induce self-assembly with formation of organized supramolecular solid state structures.

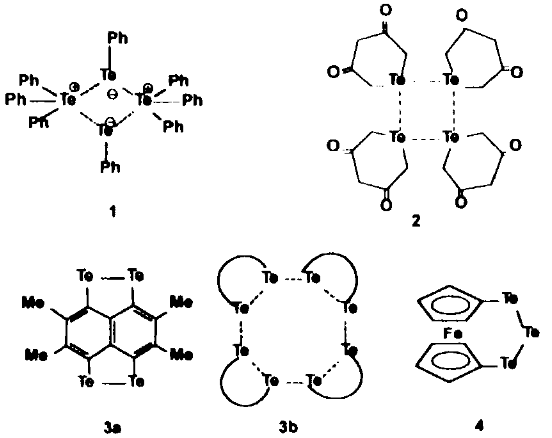
In molecular solids at least three levels of structural organzation can be distinguished: i) a *primary structure*, at the molecular level (the atoms connected in a molecule), ii) a *secondary structure*, consisting of supramolecular assemblies resulted from intermolecular connections of the molecular tectons, and iii) a *tertiary structure*, determined by the crystal packing of the secondary structures or supramolecular entities.[4] In some cases the supermolecules are interconnected in larger blocks and their packing is a *quaternary* level of structural organization.

In organo-tellurium chemistry the supramolecular self-assembly through secondary bonds is very common. These are found in organotellurium-nitrogen, -oxygen, -sulfur and halogen compounds and lead to the formation of discrete (*e.g.* dimeric or tetrameric) supermolecules or infinite supramolecular arrays (chains, 2D sheets, 3D networks). Selected examples are illustrated here. No attempt is made to provide an exhaustive presentation. Few of these structures discussed have been previously described as supramolecular. The survey is by no means exhaustive.The supramolecular structures of organotellurium-sulfur compounds have been previously reviewed.[11]

SELF-ASSEMBLY THROUGH TELLURIUM-TELLURIUM SECONDARY BONDS

In several compounds tellurium atoms are found at distances shorter than the sum of Van der Waals radii (4.40 Å) in secondary structures based upon Te···Te weak interactions. Examples include triphenyltelluronium phenyltelluride (**1**) (Te···Te 3.323-3.596 Å),[12] 1-telluracyclohexane-3,5-dione (**2**) (Te···Te 3.95-4.18 Å),[13] 2,3,6,7-tetramethylnaphto-bis[1,2]tellurole (**3**) (Te···Te 4.019 Å)[14] (Scheme 1) and 1,1'-tritelluraferrocenophane (**4**).[15] The packing of molecules of the latter (Fig.1) clearly shows an arrangement based upon Te···Te secondary bonds.

No doubt, there are other compounds with Te···Te interatomic distances smaller than the sum of Van der Waals radii not yet identified as supramolecular.



SCHEME 1

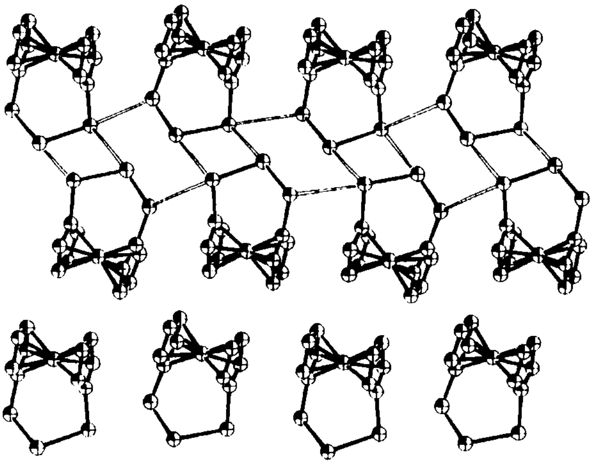
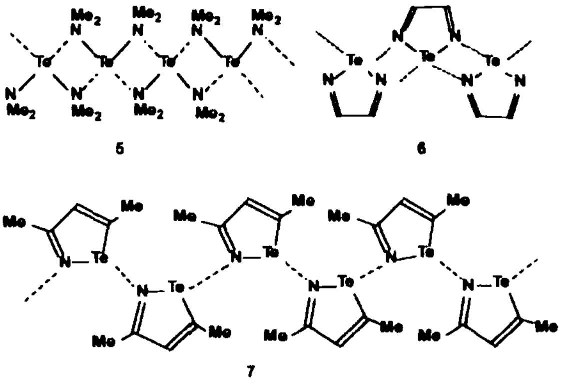


FIGURE 1. The molecular packing of compound (4) in the crystal, showing intermolecular Te···Te secondary bonds

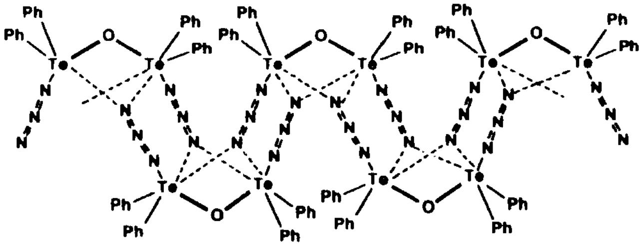
SELF-ASSEMBLY THROUGH TELLURIUM-NITROGEN SECONDARY BONDS

Not many organotellurium-nitrogen compounds have been structurally investigated, but supramolecular self-organization through Te···N secondary bonds has been observed in bis(dimethylamino) tellurium(II) (**5**) (Te-N 2.05 Å, Te···N 2.96 Å),[16] telluradiazole (**6**) (Te-N 2.005 Å, Te···N 2.764 Å),[17] 3,5-dimethyltellurazole (**7**) (Te···N 2.640-2.774 Å) [18] (which form chain-like supramolecular arrays, Scheme 2), and in the dimeric di-*tert*-butyl-benzotelluradiazole (Te-N 2.004 Å, Te···N 2.628 Å).[19] The more sterically crowded $Te[N(SiMe_3)_2]_2$ is monomeric.[20] This shows that steric factors play an important role in determining the association of molecular tectons into supramolecular structures based upon secondary bonds.



SCHEME 2

An interesting supramolecular architecture (shown in Fig. 2 along with a line diagram for clarity) is found in 1,3-diazido-1,1,3,3-tetraphenylditelluroxane,[21] $(N_3)Ph_2Te\text{-}O\text{-}TePh_2(N_3)$.



Te-N	2.396 A
Te···N	3.138 A
	3.174 A
Te-O	1.972 A
Te-O-Te	126.2°

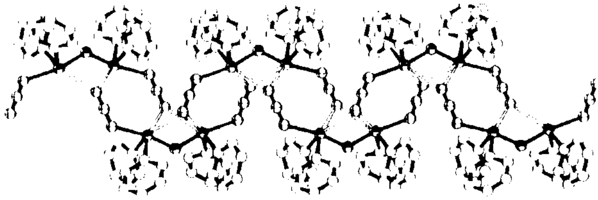
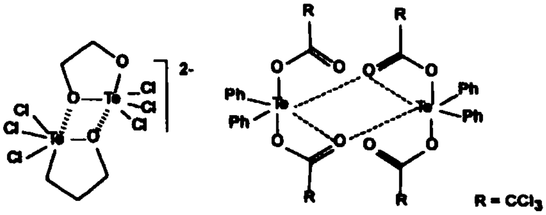


FIGURE 2. The crystal structure of $(N_3)Ph_2TeOTePh_2(N_3)$. Above: line diagram; below: ZORTEP drawing (redrawn from deposited X-ray diffraction data)

The structure consists of double chains connected through interpenetrating head-to-tail azido bridges, which form eight-membered Te_2N_6 quasicyclic units and Te_2ON_2 clusters.

SELF-ASSEMBLY THROUGH TELLURIUM-OXYGEN SECONDARY BONDS

A few structurally characterized oxygen-containing organo tellurium derivatives, such as carboxylates, *e.g.* dimethyltellurium(IV) dibenzoate,[22] diphenyltellurium(IV) bis(trichloroacetate), $Ph_2Te(OOCCCl_3)_2$ (**8**) (Te-O 2.149 and 2.163 Å; Te⋯O 3.060-3.250 Å)[23] or heterocyclic compounds such as trichloro(ethane-1,2-diolato-O,O') tellurate anion $[OCH_2CH_2OTeCl_3]^{2-}$ (**9**) (Te-O 1.946 and 1.968 Å; Te⋯O 2.764 Å) [24] (Scheme 3) are associated, suggesting that an open eye should be kept upon compounds with oxygen binding sites as potential supramolecular tectons.

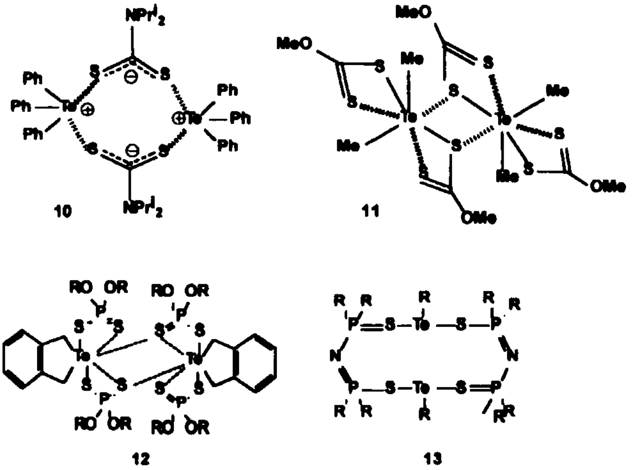


8 **9**

SCHEME 3

SELF-ASSEMBLY THROUGH TELLURIUM-SULFUR SECONDARY BONDS

There are numerous organotellurium-sulfur compounds associated through Te⋯S secondary bonds, in either dimeric or polymeric structures. Dimers (Scheme 4) include dithiocarbamates [*e.g.* **(10)** Te⋯S 3.095 and 3.145 Å],[25] xanthates [*e.g.* **(11)** Te-S 2.680 Å, Te⋯S 3.352 Å in the bridge and Te-S 2.566 Å, Te⋯S 3.303 Å in the chelating ligand],[26] dithiophosphates [*e.g.* **(12)** Te-S 2.621-2.627 Å, Te⋯S 3.393-3.447 Å][27] and imidodiphosphinates [*e.g.* **(13)** Te-S 2.557 Å, Te⋯S 2.843 Å].[28]

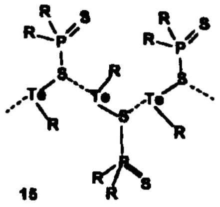


SCHEME 4

Several organotellurium(II) dithiophosphates, *e.g.* **(14)**[29] [Ar = Ph, 4-$MeOC_6H_4$ and 4-$EtOC_6H_4$, P-S 2.439 Å, P⋯S 3.309 Å] form chain-like supramolecular arrays through intermolecular Te⋯S secondary bonds from bridging ligands (Scheme 5) involving both sulfur atoms. Another pattern was found with the diphenyldithio phosphinato ligand, which forms zig-zag chains with a different type of bridge, involving only one sulfur atoms, as shown in **(15)** (Te⋯S 3.383

Å in the low temperature yellow form and Te⋯S 3.422 Å in the room temperature red form).[30]

14



15

The dithioisocyanato derivative (SCN)Ph_2Te-O-TePh_2(NCS),[31] forms a double chain supramolecular array, with interpenetrating SCN double bridges, which connect the chains through Te⋯S secondary bonds, as shown in Fig. 3. The structure is similar to that of the corresponding diazide, shown above.

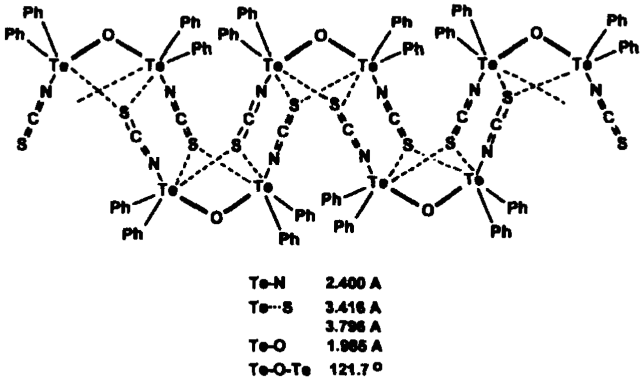
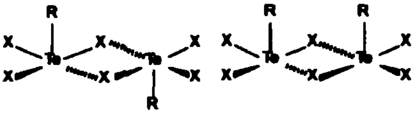


FIGURE 3. The supramolecular structure of (SCN)Ph_2Te-O-TePh_2 (NCS)

SELF-ASSEMBLY THROUGH TELLURIUM-HALOGEN SECONDARY BONDS

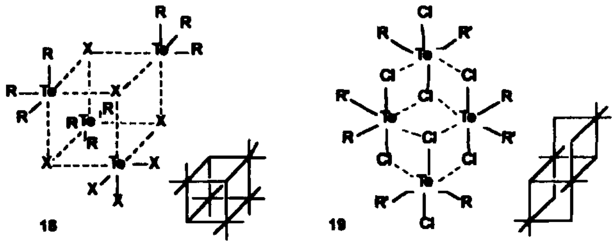
Probably the best structurally investigated are the organotellurium halides and numerous x-ray crystal structure determinations are available. Many of the compounds reported are associated in supramolecular architectures formed with bridging halogens. The monoorganotellurium(IV) trihalides tend to form dimers and all halogens can act as bridges, as shown in Scheme 6. Both *trans*- (**16**) and *cis*- (**17**) forms with two bridging halogens were found, *e.g.* *trans*-$[(C_6F_5)_2TeF(\mu\text{-}F)]_2$,[32] *cis*-$[(4\text{-}PhOC_6H_4)_2TeCl(\mu\text{-}Cl)]_2$ (**17**),[33] and *cis*- and *trans*-$[ArTeBr(\mu\text{-}Br)]_2$ and $[ArTeBr(\mu\text{-}I)]_2$ (Ar = $4\text{-}MeOC_6H_4$ and $4\text{-}EtOC_6H_4$).[34]



trans **16**   cis **17**

SCHEME 6

Some tetrameric structures, such as the cubane $[Et_3TeI]_4$ (**18**)[35] or incomplete dicubanes (**19**) [R = R' = $4\text{-}MeOC_6H_4$,[36] R = Ph, R' = $4\text{-}BrC_6H_4$,[37] and RR' = $2,2'\text{-}C_6H_4OC_6H_4$][38] (Scheme 7) are reminiscent of the structure of inorganic tetrameric $[TeCl_4]_4$, which is also a cubane.[39]

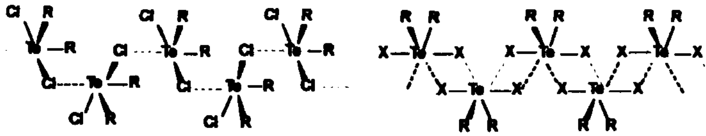


18

19

SCHEME 7

Chain-like supramolecular arrays are frequently formed in diorganotellurium(IV) dihalides. Single halogen bridges are present in diphenyltellurium(IV) dichloride, Ph_2TeCl_2 (**20**) [Te-Cl 2.482 Å (non-bridging) and 2.529 Å (bridging); Te$\cdots$Cl 3.677 Å][40] but more frequent is the double halogen bridge motif (**21**) observed in diphenyltellurium difluoride, Ph_2TeF_2 (Te-F 2.115 Å; Te$\cdots$F 3.208 Å),[41] diiodophenoxa tellurine (R_2 = 2,2'-$C_6H_4OC_6H_4$, X = I)[42] and diiododibenzo tellurophene (R_2 = 2,2'-$C_6H_4C_6H_4$)[43] (Scheme 8).



20

21

SCHEME 8

The "simplest" dihalides, Me_2TeX_2 (X = Cl,[44] Br,[45] I[46]) deserve a comment. All three are made up of Te_2X_2 dinuclear units, connected in various ways in bi- or tridimensional nets. The four members of the diphenyltellurium(IV) dihalide series, Ph_2TeX_2, with

X = F, Cl, Br and I, have also been structurally characterized by single crystal X-ray diffraction. Each one has a different crystal structure: the fluoride forms double bridge chains and the chloride forms single bridge chains, but in the dibromide the molecular tectons are connected in bidimensional sheets [47] and the diiodide forms a complex 3D network made of ψ-octahedra (six-coordinate tellurium) and ψ-pentagonal bipyramids (7-coordinate tellurium), in which dimeric units Te_2I_2 can be distinguished.[48]

It is obvious from the above presentation that most if not all organotellurium halides can be expected to be associated in solid state and should be regarded as potential supramolecular architectures.

CONCLUSION AND OUTLOOK

The data presented in this review demonstrate the great propensity of tellurium to form secondary bonds with nitrogen, oxygen, sulfur and halogens. These can serve to connect organotellurium molecular tectons into supramolecular architectures. In many cases the supramolecular architecture is ignored in published crystal structure reports and thus important and interesting information is lost. The understanding of the chances offered by secondary bonds and the exploration of intermolecular interactions leading to supramolecular self-organization in the solid state, could provide a fertile area of future investigations in the crystal engineering of organotellurium compounds.

ACKNOWLEDGEMENT

We gratefully acknowledge the assistance of Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Brazil, which supported financially the work presented here and a Visiting Professorship to IH.

References

[1] J.M. Lehn, *Angew. Chem.* **100**, 91 (1988); *Angew. Chem., Int. Ed. Engl.* **27**, 89 (1988).

[2] J.M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH Weinheim (1995).

[3] J.M. Lehn, J.L. Atwood, J.E.D. Davies, D.D. MacNicol and F. Vögtle (Editors), *Comprehensive Supramolecular Chemistry*, Pergamon Press, Oxford (1996).

[4] I. Haiduc and F.T. Edelmann, *Supramolecular Organometallic Chemistry*, Wiley-VCH, Weinheim, New York (1999).

[5] S. Simard, D. Su and J.D. Wuest, *J. Am. Chem. Soc.* **113**, 4696 (1991).

[6] M.C.T. Fyfe and J.F. Stoddart, *Acc, Chem. Res.* **30**, 393 (1997).

[7] G.R. Desiraju, *Angew. Chem.* **107**, 2541 (1995); *Angew. Chem. Int. Ed. Engl.* **34**, 2311 (1995).

[8] N.W. Alcock, *Advan. Inorg. Chem. Radiochem.* **15**, 1 (1972).

[9] N.W. Alcock, *Bonding and Structure. Structural Principles* in *Inorganic and Organic Chemistry*, Ellis Horwood, New York, London, p. 195 (1993).

[10] P. Pyykkö, *Chem. Rev.* **97**, 597 (1997).

[11] I. Haiduc, R.B. King and M.G. Newton, *Chem. Rev.* **94**, 301 (1994).

[12] J. Jeske, W.W. du Mont and P.G. Jones, *Angew. Chem., Int. Ed. Engl.* **35**, 2653 (1996).

[13] C.L. Raston, R.J. Secomb and A.H. White, *J. Chem. Soc., Dalton Trans.*, 2307 (1976).

[14] E. Arai, H. Fujiwara, H. Kobayashi, K. Takimiya, O. Otsubo and F. Ogura, *Inorg. Chem.* **37**, 2850 (1998).

[15] T.A. Hamor, N. Al-Salim and W.R. McWhinnie, *J. Organomet. Chem* **310**, C 5 (1986).

[16] R.E. Allan, H. Gornitzka, J. Kärscher, M.A. Paver, M.A. Rennie, C.A. Russell, P.R. Raithby, D. Stalke, A. Steiner and D.S. Wright, *J. Chem. Soc., Dalton Trans.*, 1727 (1996).

[17] V. Bertini, P. Dapporto, F. Luchesini, A. Sega and A. De Munno, *Acta Cryst.* C **40**, 653 (1984).

[18] G. De Munno and F. Luchesini, *Acta Cryst.* C **48**, 1437 (1992).

[19] T. Chivers, X.L. Gao and M. Parvez, *Inorg. Chem.* **35**, 9 (1996).

[20] M. Bjorgvinsson, H.W. Roesky, F. Paner, D. Stalke and G.M. Sheldrick, *Inorg. Chem.* **29**, 5140 (1990).

[21] P. Magnus, N.B. Roe, W. Lynch and C. Hulme, *J. Chem. Soc., Chem. Comm.* 1609 (1995).

[22] P.C. Srivastava, A. Sinha, S. Bajpai, H.G. Schmidt and M. Noltemeyer, *J. Organomet. Chem.* **575**, 261 (1999).

[23] N.W. Alcock, J. Culver and S.M. Roe, *J. Chem. Soc., Dalton Trans.* 1477 (1992).

[24] M.R. Sundberg, R. Uggla, T. Laitalainen and J. Bergman, *J. Chem. Soc., Dalton Trans.*, 3279 (1994).

[25] J.E. Drake and M.L.Y.N. Wong, *J. Organomet. Chem.* **377**, 43 (1989).

[26] M. Wieber, E. Schmidt and C. Burschka, *Z. Anorg. Allg. Chem.* **525**, 127 (1985).

[27] D. Dakternieks, R. Di Giacomo, R.W. Gable and B.F. Hoskins, *J. Am. Chem. Soc.* **110**, 6753 (1988).

[28] S. Husebye, K. Maartmann-Moe and O. Mikalsen, *Acta Chem. Scand.* **44**, 802 (1990).

[29] (a) D. Lang and M. Wieber, *private communication* (1993); (b) S. Husebye, K. Maartmann-Moe and O. Mikalsen, *Acta Chem. Scand.* **43**, 868 (1989); (c) S. Husebye, K. Maartmann-Moe and O. Mikalsen, *Acta Chem. Scand.* **44**, 464 (1990).

[30] A. Silvestru, I. Haiduc, K.H. Ebert and H.J. Breunig, *Inorg. Chem.* **33**, 1253 (1994); *J. Organomet. Chem.* **482**, 253 (1994).

[31] C.S. Mancinelli, D.D. Titus and R.F. Ziolo, *J. Organomet. Chem.* **140**, 113 (1977).

[32] J. Aramini, R.J. Batchelor, C.H.W. Jones and F.W.B. Einstein, *Can. J. Chem.* **65**, 2643 (1987).

[33] M. De Matheus, L. Thorres, J.F. Piniella, J.L. Brianso and C. Miravitles, *Acta Cryst.* **C 47**, 703 (1991).

[34] P.H. Bird, V. Kumar and B.C. Pant, *Inorg. Chem.* **19**, 2487 (1980).

[35] R.K. Chadha and J.E. Drake, *J. Organomet. Chem.* **299**, 331 (1986).

[36] R.K. Chadha and J.E. Drake, *Acta Cryst.* **C 40**, 1349 (1984).

[37] R.K. Chadha, J.E. Drake and M.A. Khan, *Acta Cryst.* **C 39**, 45 (1983).

[38] J.D. Korp, I. Bernal, J.C. Turley and G.E. Martin, *Inorg. Chem.* **19**, 2556 (1980).

[39] B. Buss and B. Krebs, *Angew. Chem., Int. Ed. Engl.* **9**, 463 (1970).

[40] N.W. Alcock and W.D. Harrison, *J. Chem. Soc., Dalton Trans.*, 251 (1982).

[41] F.J. Berry and A.J. Edwards, *J. Chem. Soc., Dalton Trans.*, 2306 (1980).

[42] J.D. McCullough, *Inorg. Chem.* **12**, 2669 (1973).

[43] J.D. McCullough, *Inorg. Chem.* **14**, 1142 (1975).

[44] R.F. Ziolo and J.M. Troup, *J. Am. Chem. Soc.* **105**, 229 (1983).

[45] P.C. Srivastava, S. Bajpai, H.G. Schmidt and M. Noltemeyer, *J. Organomet. Chem.* **575**, 261 (1999).

[46] L.Y. Chan and F.W.B. Einstein, *J. Chem. Soc., Dalton Trans.*, 316 (1972).

[47] G.D. Christopherson and J.D. McCullough, *Acta Cryst.* **11**, 249 (1958).

[48] N.W. Alcock and W.D. Harrison, *J. Chem, Soc., Dalton Trans.*, 869 (1984).

[49] R.K. Chadha, J.E. Drake and J.L. Hencher, *Can, J. Chem.* **61**, 1222 (1983).