Stable Systems with a Triple Bond to Silicon or Its Homologues: Another Challenge

Peter Jutzi*

Already early in the last century scientists observed that rules developed for the organic chemistry of carbon were not applicable for the element silicon. According to F. S. Kipping it was not possible to generate stable compounds comparable to olefins or ketones bearing a Si=C or a Si=O double bond.[1] E. Wiberg mentioned the nonexistence of the disilene $H_2Si{=}SiH_2$, which is comparable to ethylene. He pointed out that in general the elements of the second row show no tendency to form double bonds as found for their first-row counterparts. They achieve the noble gas configuration by polymerization generating larger structures.[2] In that context E. Wiberg refered to the "not well-known double-bond rule", which strictly speaking still holds for basic systems.[3]

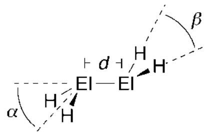
However, the introduction of substituents that were capable of kinetic and/or thermodynamic stabilization led already in the 1970s to many exceptions to this rule.[4] By the end of the century one had, through the use of well chosen substituents (by actual "design" of the substituents) and from the results of high level calculations, a comprehensive understanding of both the double-bond systems incorporating elements of Groups 13, 14, and 15 and of their often energetically preferred isomeric counterparts. Excellent reviews are available which describe this subject very extensively.[5]

Besides the double-bond systems, the triple-bond systems have recently become—as a final challenge—the focus of interest.[6] Herein a short report is given on the latest results on the triple-bond systems R_2El_2 and $[L_nMElR]$ (El = Si, Ge), which can be regarded as compounds analogous to alkynes and carbyne complexes, respectively. For a better awareness of the recent developments, the current understanding in the field of double-bond systems is summarized by using the compounds R_4El_2 and $[L_nMElR_2]$, which are analogous to alkenes and carbene complexes, respectively, as examples.

Disilenes, -germenes, -stannenes, and -plumbenes R_4El_2

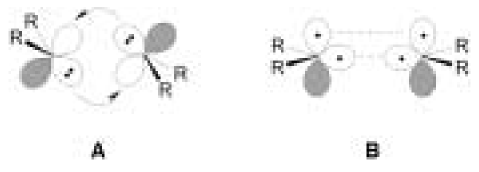
Theoretical papers have discussed the geometric changes in the ground state between the stable ethene molecule and the highly reactive homologues H_4El_2 (El = Si, Ge, Sn, Pb), which are unknown or experimentally difficult to prepare.[7, 8] Density functional theory (DFT) calculations revealed the expected planar configuration for the ethene molecule, whereas for all the other molecules a *trans* bent configuration with pyramidalization at the element center was calculated (Table 1).[9] The angle α increases and the angle H-El-H decreases with increasing atomic number. The ratio of double-bond length to single-bond length (d/δ) also increases with increasing atomic number. The factor d/δ results from the calculated distances for single (δ(El–El)) and double bonds (d(El=El)).

Table 1. Structural data for H_4El_2 molecules from DFT calculations.[9]



El	C	Si	Ge	Sn	Pb
α [°]	0	36.1	47.3	51.0	53.6
β [°]	116.5	112.4	109.5	105.8	107.7
$d_{El=El}$ [(Å]	1.323	2.150	2.245	2.569	2.819
δ_{El-El} [(Å]	1.511	2.322	2.413	2.721	2.931
d/δ	0.876	0.926	0.930	0.944	0.962

There are several models to explain the different bonding.[5, 8, 9] A simple approach predicts a distortion from the planar geometry when the corresponding fragment ElR_2 has a singlet ground state. The formation of *trans* bent double-bond systems can then be described by two donor–acceptor interactions between the filled s orbitals and the empty p orbitals of two singlet ElR_2 units (**A** in Scheme 1). Classic planar double-bond systems are formed by the interaction of two ElR_2 units in the triplet ground state (**B**).

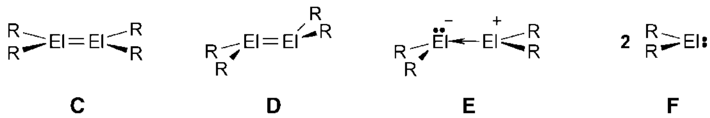


Scheme 1. Construction of R_4El_2 structures from singlet (**A**) and triplet R_2El fragments (**B**).

---

[*] Prof. Dr. P. Jutzi
Fakultät für Chemie
Universität Bielefeld
33615 Bielefeld (Germany)
Fax: (+49)521-1066026
E-mail: peter.jutzi@uni-bielefeld.de

Through the design of the substituent R, today a large number of compounds of the type R_4El_2 are known, which are kinetically or thermodynamically stabilized.[5] These compounds are stable under normal conditions and their structures are known in solution and in the solid state. The different types of structure **C**–**F** are shown in Scheme 2. All the tin and lead compounds, which are known so far,[10] along with some silicon and germanium compounds, dissociate in solution forming species of the type **F**. This behavior expresses clearly the "inert pair effect" of the involved s electron pair. The energetic differences between the structures **C** and **D** are often very small, particularly for silicon, where the variation of the substituents causes interesting effects.[5b] In general, for structures with extremely bulky substituents a discrepancy is noted between the experimentally observed and the theoretically predicted structures.

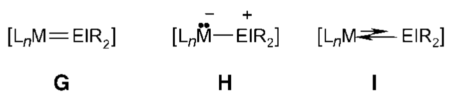


Scheme 2. Structural types of R_4El_2 compounds.

Silylene, Germylene, Stannylene, and Plumbylene Transition Metal Complexes

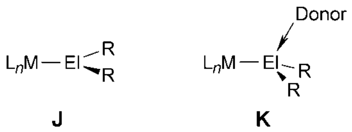
About ten years after the discovery of the Fischer carbene complexes of the type $[L_nMCR_2]$, the first complexes with GeR_2, SnR_2, and PbR_2 ligands were described.[11] In contrast to the situation in carbene complex chemistry, one had the advantage of the existence of stable ElR_2 units, which could be used for successful ligand exchange reactions. After the discovery of stable silylenes, this strategy was then applied for the preparation of silylene complexes $[L_nMSiR_2]$ (the same was true for carbene complexes). Cationic silylene complexes of the type $[L_nMSiR_2]^+$ can be prepared by removing an anionic substituent X^- from the corresponding silyl complex $[L_nMSiR_2X]$.[12] Variation of substituents at the Group 14 element as well as variations of the metal unit meanwhile have led to a huge number of stable complexes with ligands which are analogous to carbenes.[13]

As for the Fischer carbene complexes, the Dewar–Chatt–Duncanson model can be applied to explain the bonding (Scheme 3).[14] The strength of the π-back bond expressed by the mesomeric structure **G** determines the double-bond character of the M–El bond. For example, high double-bond character has been found in cationic silylene complexes. In many other complexes, in particular those with SnR_2 or PbR_2 ligands, the donor–acceptor bond is clearly preferred (mesomeric structure **H**). It is easier to formulate double bonds than to establish them; thus, cautious authors describe the bonding in the form of **I**! The controversial discussion about multiple bonds in gallium chemistry shows that caution is appropriate.[15]



Scheme 3. Description of the bonding in $[L_nMElR_2]$ complexes.

In the case of the carbon homologues, besides complexes with a planar arrangement at the Group 14 element (**J** in Scheme 4), several complexes are known that show a distorted tetrahedral arrangement (**K**); this is caused by the coordination of an additional donor group. The apparent acidic character of the ElR_2 fragment in **K** confirms the importance of the resonance structure **H** in describing the bonding.



Scheme 4. Donor-free and donor-stabilized complexes.

A special type of germylene complex is represented by the compounds $[RH_4C_5(CO)_2Mn{=}Ge{=}Mn(CO)_2C_5H_4R]$ (R = Me, H).[16] Here, two carbenoid metal centers are bound to one germanium atom; calculations reveal even a partial triple-bond character for the Mn–Ge bonds.[17]

The Problem of the Si≡Si Triple Bond

In 1991 an experiment that postulated a different structure for disilyne (H_2Si_2) than for acetylene, generated considerable interest: the microwave spectrum of a SiH_4 plasma at −196 °C indicated a bridged structure.[18] The bonding parameters of H_2Si_2 are shown in Figure 1; the Si–H distance is approximately 12% longer than normal and typical for a three-center–two-electron bond. Thus, older calculations were confirmed which showed that H_2Si_2 has a double-bridged structure in the ground state and that a compound with a structure analogous to acetylene does not even correspond to a minimum on the potential surface![9, 19]

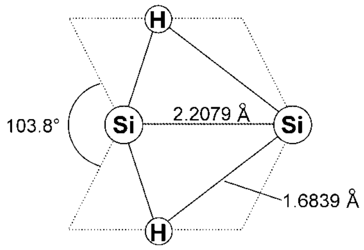


Figure 1. Structure of H_2Si_2

The energetic array of the calculated structures for the H_2Si_2 molecule along with those for the H_2Ge_2 molecule is shown in Figure 2.[8] These structures can be explained through the different orientation of the HEl fragments in the doublet state ($^2\pi$) which lead to different interactions and structures. The $ns^2np^1np^1$ configuration expresses the low tendency for hybridization.[20]

Larger structural changes can be expected by the introduction of other substituents. Calculations predict a stabilization of a bent triple-bond structure for bulky σ-donor

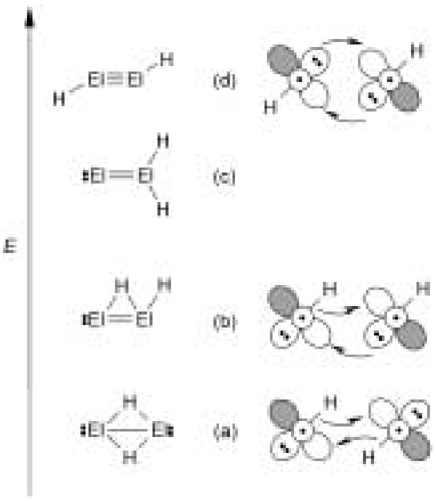
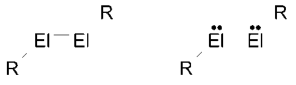


Figure 2. Energetic array of H_2El_2 structures (El = Si, Ge) and their construction from HEl units.

substituents such as tBu$_3$Si (**L** in Scheme 5) (see below for experiments on this topic).[21] In contrast, π-donor substituents should lead to a single-bond structure **M**.[8] The latter is undoubtedly preferred for the heavier homologues tin and lead, if the steric demand of the substituents doesn't cause a different structure.



L **M**

Scheme 5. Structural possibilities for R_2El_2 compounds.

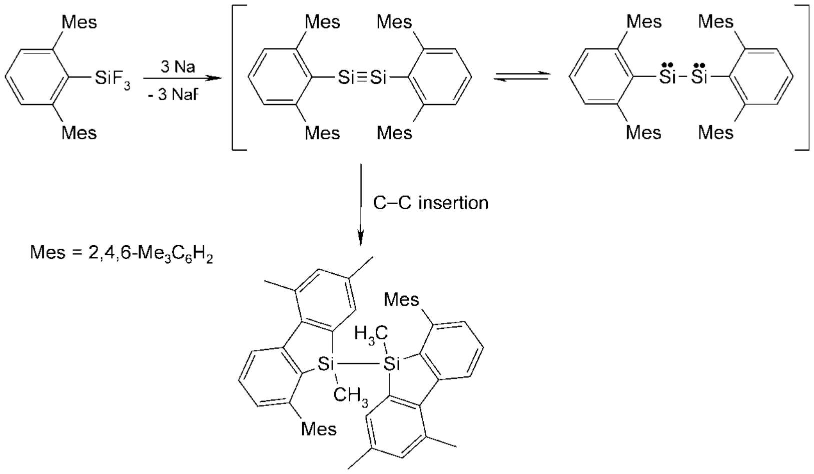
Preparative work with the thrilling aim of stabilizing Si≡Si triple bonds under normal conditions is perhaps close to a breakthrough. Currently, the research group of N. Wiberg is dealing with the question of whether it is possible to stabilize a disilyne, which is discussed as an intermediate in the tetrasilatetrahedran synthesis (Scheme 6), by using bulkier silyl groups.[22]

$$\left(t\mathrm{Bu_3Si{-}SiBr_2}\right)_2 \xrightarrow[-4\,\mathrm{Br}]{} \left[t\mathrm{Bu_3Si{-}Si{\equiv}Si{-}Si}t\mathrm{Bu_3}\right] \xrightarrow{\times 2} (t\mathrm{Bu_3SiSi})_4$$

Scheme 6. Tetrasilatetrahedrane synthesis.

Experiments in the research group of R. West on the reduction of special aryltrifluorosilanes showed that the generated disilyne (or its structural isomer), which is formed as intermediate, is such a reactive molecule that it even inserts into C–C bonds (Scheme 7).[23] The attempt for future work is to prevent this "interfering" reaction by designing special substituents.

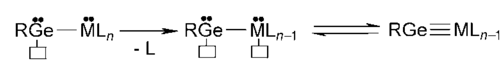
At this point the experimental evidence of formal triple bonds to silicon by matrix isolation spectroscopy (HSi≡N,[24] HN≡Si[25] and $C_6H_5N{\equiv}Si$[26]), by neutralization reionization (NR) mass spectrometry (HC≡SiX (X = F,Cl)[27]), as well as by photoelectron spectroscopy ($C_6H_5N{\equiv}Si$[28]) should be mentioned.



Scheme 7. C–C insertion of an intermediary disilyne.

The First Stable Germylyne Transition Metal Complexes

After the successful synthesis of metallogermylenes,[29] there was at least an obvious strategy for the preparation of germylyne complexes: it was necessary to create a situation at the transition metal comparable to that at the germanium center; through the neighborhood of the two centers, which both possess a lone pair of electrons as well as a free coordination site, the electronic interactions should be such so as to allow the formation of up to a triple bond (Scheme 8).



$$\mathrm{R\ddot{G}e{-}\ddot{M}L}_n \xrightarrow[-\mathrm{L}]{} \mathrm{R\ddot{G}e{-}\ddot{M}L}_{n-1} \rightleftharpoons \mathrm{RGe{\equiv}ML}_{n-1}$$

Scheme 8. Strategy for the preparation of transition metal germylyne complexes.

However, in the case of the ferriogermylene [(2,4,6-tBu$_3$C$_6$H$_2$)GeFe(CO)$_2$C$_5$Me$_5$] one observes an insertion of the germylene unit into one of the C–H bonds of the aryl ligand instead of the desired CO loss.[29] In contrast, the experiments in the research group of P. P. Power are leading in the right direction: treatment of extremely bulky aryl(chloro)germylenes with cyclopentadienyl(tricarbonyl)metalates of chromium, molybdenum, and tungsten gave the first stable germylyne complexes **1**–**5**, which could be isolated as red crystals (Table 2).[30] In the case of the synthesis of **1**, **2**, and **4** there is a spontaneous loss of CO, while in the course of the preparation of **3** and **5** it was possible to isolate and characterize the metallogermylenes as stable intermediates; CO loss is then observed on thermal or photochemical treatment.

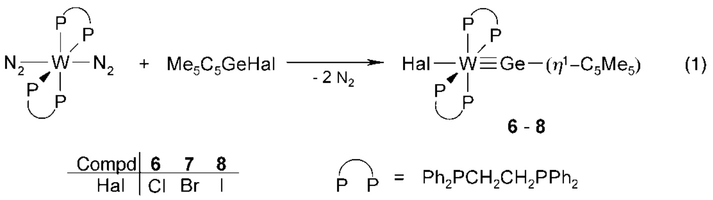
Table 2. Data of **1**–**5**.

$$\mathrm{ArGeCl} + \mathrm{Na[M(CO)_3Cp]} \xrightarrow[-\mathrm{NaCl},\ -\mathrm{CO}]{} \underset{\mathbf{1-5}}{[\mathrm{ArGe{\equiv}M(CO)_2Cp}]}$$

Compd.	M	Aryl	d_{Ge-M} [Å]	∢M-Ge-C [°]
1	Mo	2,6-(2,4,6-$Me_3C_6H_2$)$_2$$C_6H_3$	2.271(1)	172.2(2)
2	W	2,6-(2,4,6-$Me_3C_6H_2$)$_2$$C_6H_3$	2.2767(14)	170.9(3)
3	Cr	2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$	2.1666(4)	175.99(6)
4	Mo	2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$	2.272(8)	174.25(14)
5	W	2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$	–	–

Compounds **1**–**5** were characterized by NMR, UV/Vis, and IR spectroscopy and except for **5** by X-ray diffraction. The $Ge\equiv M$ bonds are usually about 0.4 Å shorter than the corresponding Ge–M single bonds. As expected, the $Ge\equiv M-C$(aryl) arrangements are almost linear (Table 2). Apparently, in these complexes the triple bond is shielded in an excellent way by these tailor-made aryl ligands.

A completely different approach to stable germylyne complexes was recently presented by the research group of A. C. Filippou.[31] Here the synthetic strategy was based on the easy loss of dinitrogen molecules from a double dinitrogen-substituted metal complex, on the formal oxidative addition of a RGeHal unit at the corresponding metal center, and on the concomitant reorganization of the electronic system leading to the formation of a triple bond. Treatment of the tungsten complex *trans*-[W(dppe)$_2$(N$_2$)$_2$] (dppe = 1,2-bis(diphenylphosphanyl)ethane) with germanium(II) compounds of the type Me$_5$C$_5$GeHal gave the stable germylyne complexes **6**–**8** as orange or red-brown powders [Eq. (1)]. These compounds are also fully characterized by spectroscopic means. The X-ray structure analysis of crystalline **6** · toluene confirms the existence of a distorted octahedral complex with *trans* configuration of the chlorine and the germylyne ligand; the $Ge\equiv W$ distance is 2.302(1) Å, and the $C-Ge\equiv W$ arrangement is again almost linear with an angle of 172.2°.



Density functional calculations show that the triple bond should be described in a classical way. The germylyne ligand is a weaker σ donor than a carbyne ligand, but a comparable π acceptor. The synthetic route used by Filippou et al. is very promising because of the existence of many dinitrogen complexes that could be used as starting compounds to prepare germylyne complexes. In addition the Me$_5$C$_5$ substituent is generally accepted as a good leaving group in main group chemistry,[32] which will also be beneficial for reactivity studies on substitutions at the germanium center.

The most recent results in the area of compounds with real or formal triple bonds to silicon or its homologues illustrate that one can expect extremely interesting results in the near future.

---

[1] F. S. Kipping, *Proc. R. Soc. London A* **1937**, *159*, 139.

[2] O. Stecher, E. Wiberg, *Chem. Ber.* **1942**, *75*, 2003.

[3] *Holleman-Wiberg*, *Lehrbuch der Anorganischen Chemie*, 22nd and 23rd ed., **1943**, p. 207, 291, 292, 346.

[4] a) P. Jutzi, *Angew. Chem.* **1975**, *87*, 269; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 232; b) P. Jutzi, *Chem. Unserer Zeit* **1981**, *15*, 149.

[5] a) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463; b) M. Driess, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 828; c) J. Escudie, H. Ranaivonjatovo, *Adv. Organomet. Chem.* **1999**, *44*, 113.

[6] A different type of triple bond is well established and can be formed in π complexes of the type R$_5$C$_5$El$^+$ (El = Ge, Sn, Pb): P. Jutzi, N. Burford, *Chem. Rev.* **1999**,*99*, 969.

[7] Mass spectrometric evidence for Si$_2$H$_4$: K. Tonokura, T. Murasaki, M. Koshi, *Chem. Phys. Lett.* **2000**, *319*, 507.

[8] R. S. Grev, *Adv. Organomet. Chem.* **1991**, *33*, 125.

[9] H. Jacobsen, T. Ziegler, *J. Am. Chem. Soc.* **1994**, *116*, 3667.

[10] M. Stürmann, W. Saak, H. Marsmann, M. Weidenbruch, *Angew. Chem.* **1999**, *111*, 145; *Angew. Chem. Int. Ed.* **1999**, *38*, 187.

[11] a) W. Petz, *Chem. Rev.* **1986**, *86*, 1019; b) M. F. Lappert, R. S. Rove, *Coord. Chem. Rev.* **1990**, *100*, 267; c) T. D. Tilley, *Comm. Inorg. Chem.* **1990**, *10*, 37; d) P. D. Lickiss, *Chem. Soc. Rev.* **1992**, 271.

[12] S. K. Grumbine, G. P. Mitchell, D. A. Straus, T. Don Tilley, A. L. Rheingold, *Organometallics* **1998**, *17*, 5607.

[13] Recent work: silylene complexes;[12] germylene complexes: K. Ueno, K. Yamaguchi, H. Ogino, *Organometallics* **1999**, *18*, 4468; J. E. Bender IV, A. J. Shusterman, M. M. Banaszak Holl, J. W. Kampf, *Organometallics* **1999**, *18*, 1547; stannylene complexes: M. Weidenbruch, A. Stilter, W. Saak, K. Peters, H. G. von Schnering, *J. Organomet. Chem.* **1998**, *560*, 125; J. J. Schneider, N. Czap, D. Bläser, R. Boese, J. Ensling, P. Gütlich, C. Janiak, *Chem. Eur. J.* **2000**, *6*, 468.

[14] C. Boehme, G. Frenking, *Organometallics* **1998**, *17*, 5801.

[15] a) R. Dagani, *Chem. Eng. News* **1998**, *76*(11), 31; b) R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1095.

[16] a) W. Gäde, E. Weiss, *J. Organomet. Chem.* **1981**, *213*, 451; b) J. D. Korb, I. Bernal, R. Hörlein, R. Serrano, W. A. Herrmann, *Chem. Ber.* **1985**, *118*, 340.

[17] N. M. Kostic, R. F. Fenske, *J. Organomet. Chem.* **1982**, *233*, 337.

[18] M. Bogey, H. Bolvin, C. Demynck, J. L. Destombes, *Phys. Rev. Lett.* **1991**, *66*, 413.

[19] H. Lischka, H. J. Kohler, *J. Am. Chem. Soc.* **1983**, *105*, 6646.

[20] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272.

[21] K. Kobayashi, S. Nagase, *Organometallics* **1997**, *16*, 2489.

[22] N. Wiberg, *Coord. Chem. Rev.* **1997**, *163*, 217.

[23] a) R. Pietschnig, R. West, D. R. Powell, *Organometallics* **2000**, *19*, 2724; b) R. Pietschnig, R. West, *Abstr. Pap. 33rd Organosilicon Symposium* (Saginaw, Michigan, USA) **2000**, pp. B5.

[24] G. Maier, J. Glatthaar, *Angew. Chem.* **1994**, *106*, 486; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 473.

[25] J. F. Ogilvie, S. Cradock, *J. Chem. Soc. Chem. Commun.* **1966**, 364.

[26] J. G. Radziszewski, D. Littmann, V. Balaji, L. Fabry, G. Gross, J. Michl, *Organometallics* **1993**, *12*, 4816.

[27] M. Karni, Y. Apeloig, D. Schröder, W. Zummack, R. Rabezzana, H. Schwarz, *Angew. Chem.* **1999**, *111*, 344; *Angew. Chem. Int. Ed.* **1999**, *38*, 332.

[28] H. Bock, R. Dammel, *Angew. Chem.* **1985**, *97*, 128; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 111.

[29] a) R. S. Simmons, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 1196; b) P. Jutzi, C. Leue, *Organometallics* **1994**, *13*, 2898.

[30] L. Pu, B. Twamley, S. T. Haubrich, M. M. Olmstead, B. V. Mork, R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 650.

[31] A. C. Filippou, A. I. Philippopoulos, P. Portius, D. U. Neumann, *Angew. Chem.* **2000**, *112*, 2281; *Angew. Chem. Int. Ed.* **2000**, *39*, 2778.

[32] P. Jutzi, G. Reumannn, *J. Chem. Soc. Dalton Trans.* **2000**, 2237.