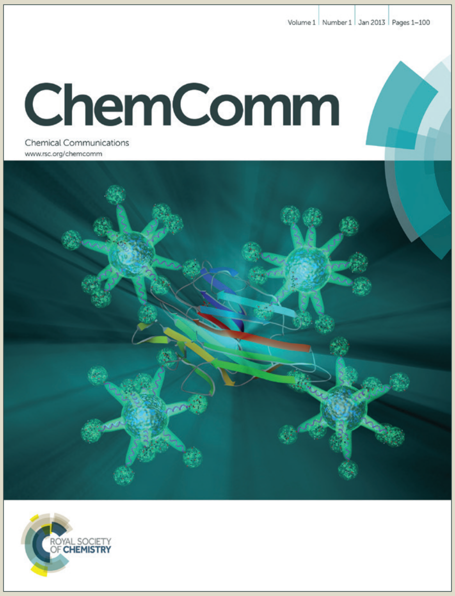
ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Unusual Coordination of Tetrylenes to Molybdenum Carbonyl Fragments

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Felicitas Lips,[a] Joshua D. Queen,[a] James C. Fettinger,[a] Philip P. Power.[a]*

Reactions of the tetrylenes $Ge(SAr^{Me_6})_2$ (1) (Ar^{Me_6} = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)$_2$, and $Sn(SAr^{Me_6})_2$ (2) with $(Mo(CO)_4(NBD)$ (NBD = bicyclo[2.2.1]hepta-2,5-diene) gave three new, unusual complexes $[Mo(THF)(CO)_3\{Ge(SAr^{Me_6})_2\}]$ (3), $[Mo(THF)(CO)_3\{Ge(SAr^{Me_6})_2\}]$ (4) and $[Mo(CO)_4\{Sn(SAr^{Me_6})_2\}]$ (5) which display no significant Ge/Sn−Mo bonding. Instead the ligands are coordinated to molybdenum in a bidentate fashion via the thiolato sulfurs.

Transition metal complexes of divalent group 14 donor ligands (tetrylenes) are a fundamental class of organometallic compounds. The first well characterised stable examples, $W(CO)_5C(OMe)R$ (R = Me, Ph), were reported by Fischer and Maasböl in 1964 and were synthesised by the treatment of $W(CO)_6$ with LiMe or LiPh to generate the carbene ligand.[1] In contrast, their heavier group 14 element congeners, which have been known since the 1970s,[2] are usually obtained by the substitution reaction of the tetrylene[3] with a transition metal complex.[4]

Despite the large number of such complexes now known only a small number of germylene and stannylene complexes in which germanium or tin are substituted by chalcogenolato ligands have been prepared and these are shown in Equations 1-3.[5-7]

$$Fe_2(CO)_9 + E(OAr)_2 \longrightarrow [Fe(CO)_4\{E(OAr)_2\}]^5 + Fe(CO)_5 \quad (1)$$

Ar = C_6H_2-2,6-Bu^t_2-4-Me

$$Cr(CO)_5GeCl_2THF + 2\ (CH_3)_3SiSAr \longrightarrow [Cr(CO)_5\{Ge(SAr)_2\}]^6 + THF + 2\ (CH_3)_3SiCl \quad (2)$$

Ar = C_6H_2-2,4,6-Me_3

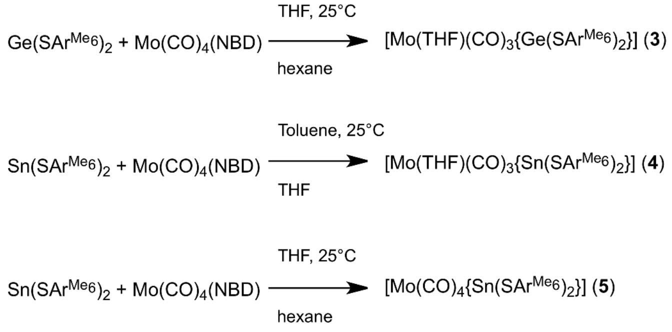
$$Cr(CO)_5THF + E(SAr)_2 \longrightarrow [Cr(CO_5)\{E(SAr)_2\}]^7 + THF \quad (3)$$

Ar = C_6H_2-2,4,6-Bu^t_3

no structural data reported

Thus, the reaction of the aryloxides $E(OAr)_2$ (E = Ge, Sn; Ar = C_6H_2-2,6-Bu^t_2-4-Me) with $Fe_2(CO)_9$ yielded $[Fe(CO)_4\{Ge(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2\}]$ and $[Fe(CO)_4\{Sn(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2\}]$ which displayed short Fe−Ge (2.240(2) Å) and Fe−Sn (2.408(l) Å) bonds and almost coplanar EO_2 and $Fe(CO)_{ax}E$ arrays consistent with good π-acceptor and poor σ-donor behaviour (Eq.1).[5] The arylthiolato germylene carbonyl complex pentacarbonyl[bis(mesitylthio)germylene]chromium(0) $[Cr(CO)_5\{Ge(SAr)_2\}]$ (Ar = C_6H_2-2,4,6-Me_3) (the first well-characterised chalcogenolato substituted heavier element tetrylene complex) was prepared by the reaction of $[Cr(CO)_5GeCl_2(THF)]$ and silyl thioethers.[6] The Cr−Ge bond length 2.361(2) Å is shorter than that predicted from the sum of the single bond covalent radii (2.43 Å),[8] as a result of a strong Cr−Ge π-interaction (Eq. 2).[6] The thiolato stannylene complex $[Cr(CO)_5\{Sn(SAr)_2\}]$ was obtained from the reaction of $Sn(SAr)_2$ [Ar = C_6H_2-2,4,6-Bu^t_3] with $Cr(CO)_5(THF)$, however, no structural data have been reported (Eq.3).[7]

Herein, we report the reaction of the tetrylenes $Ge(SAr^{Me_6})_2$ (Ar^{Me_6} = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)$_2$, **1**)[8] and $Sn(SAr^{Me_6})_2$ (**2**)[8] with bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylmolybdenum(0) ($Mo(CO)_4(NBD)$) (NBD = bicyclo[2.2.1]hepta-2,5-diene) to yield the complexes $[Mo(THF)(CO)_3\{Ge(SAr^{Me_6})_2\}]$ (**3**) and $[Mo(THF)(CO)_3\{Sn(SAr^{Me_6})_2\}]$ (**4**). From the reaction of $Sn(SAr^{Me_6})_2$ (**2**) with $Mo(CO)_5(THF)$, complex **5** $[Mo(CO)_4\{Sn(SAr^{Me_6})_2\}]$ could be isolated in low yield after extraction in hexane. It was also obtained in higher yield by the reaction of $Sn(SAr^{Me_6})_2$ (**2**) with $Mo(CO)_4(NBD)$ in THF and extraction in hexane (Scheme 1).



$$Ge(SAr^{Me_6})_2 + Mo(CO)_4(NBD) \xrightarrow[\text{hexane}]{\text{THF, 25°C}} [Mo(THF)(CO)_3\{Ge(SAr^{Me_6})_2\}]\ (\mathbf{3})$$

$$Sn(SAr^{Me_6})_2 + Mo(CO)_4(NBD) \xrightarrow[\text{THF}]{\text{Toluene, 25°C}} [Mo(THF)(CO)_3\{Sn(SAr^{Me_6})_2\}]\ (\mathbf{4})$$

$$Sn(SAr^{Me_6})_2 + Mo(CO)_4(NBD) \xrightarrow[\text{hexane}]{\text{THF, 25°C}} [Mo(CO)_4\{Sn(SAr^{Me_6})_2\}]\ (\mathbf{5})$$

Scheme 1. Illustration of the synthesis of compounds **3**-**5**.

ChemComm Accepted Manuscript

This journal is © The Royal Society of Chemistry 2012

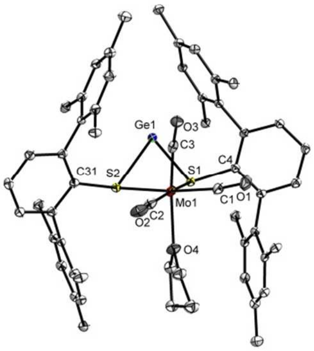


Figure 1. Thermal ellipsoid plot (30 %) of the molecular structure of **3**. H atoms are not shown. Selected bond distances (Å) and angles (deg.): Mo1−C(1-3) 1.949(4), 1.960(5), 1.975(5); Mo1−O4 2.269(3); Mo1−S(1,2) 2.5902(10), 2.6240(9); Ge1−S(1,2) 2.3986(10), 2.4305(9); S(1,2)−C(4,31) 1.803(4), 1.791(4), C(1,2,3)–O(1,2,3) 1.166(6), 1.157(5), 1.168(5), Mo1····Ge1 2.7034(5). S1-Mo1-S2 70.69(3), S1-Ge1-S2 77.31(3), angle between S1-Ge1-S2 and S1-Mo1-S2 planes is 84.478°.

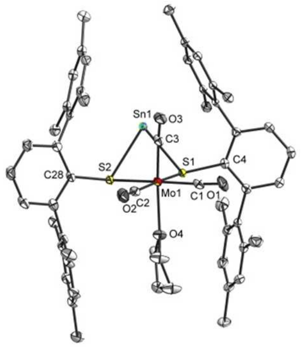


Figure 2. Thermal ellipsoid plot (50 %) of the molecular structure of **4**. H atoms are not shown. Selected bond distances (Å) and angles (deg.): Mo1−C(1-3) 1.944(3), 1.949(3), 1.970(3); Mo1−O4 2.270(2); Mo1−S(1,2) 2.6082(7), 2.6119(7); Sn1−S(1,2) 2.6279(7), 2.6303(7); S(1,2)−C(4,28) 1.798(3), 1.801(3); C(1,2,3)–O(1,2,3) 1.156(4), 1.157(4), 1.170(4); Mo1····Sn1 2.9050(3). S1-Mo1-S2 73.19(2), S1-Sn1-S2 72.58(2), angle between S1-Sn1-S2 and S1-Mo1-S2 planes is 87.139°.

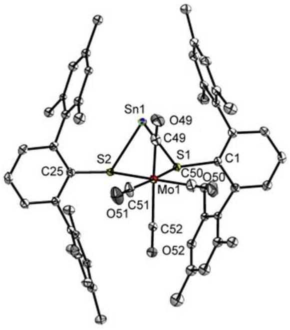


Figure 3. Thermal ellipsoid plot (30 %) of the molecular structure of **5**. H atoms are not shown. Selected bond distances (Å) and angles (deg.): Mo1−C(49-52) 1.982(3), 1.988(3), 2.003(4), 2.101(4); Mo1−S(1,2) 2.6194(10), 2.6235(9); Sn1−S(1,2) 2.595(2), 2.597(3); S(1,2)−C(1,25) 1.787(3), 1.793(3); C(49-52)–O(49-52) 1.150(5), 1.145(4), 1.148(4) , 1.123(5); Mo1····Sn(1,2) 2.9633(10), 2.9542(19). S1-Mo1-S2 68.22(8), S1-Sn1-S2 68.98(6), angle between S1-Sn1-S2 and S1-Mo1-S2 planes is 86.859°.

The products were characterised by ^{1}H, ^{13}C{^{1}H}, ^{119}Sn (**4**), IR spectroscopy, and by X-ray crystallography. No coordination of the transition metal to the group 14 element was observed in **3**-**5**. Instead the sulfur atoms of the thiolate substituents bind to molybdenum and the group 14 metal atoms remain uncomplexed. The coordination of $Ge(SAr^{Me6})_2$ and $Sn(SAr^{Me6})_2$ to the molybdenum carbonyl fragments thus differs greatly from that observed in $E(OAr)_2$ (E = Ge, Sn; Ar = C_6H_2-2,6-Bu^t_2-4-Me)[5] and in $[Cr(CO)_5\{Ge(SAr)_2\}]$ (Ar = C_6H_2-2,4,6-Me_3)[6] where the group 14 element is coordinated to the transition metal. The difference is due to the steric bulk of the thiolato terphenyl ligands and the dispersion forces between the terphenyl substituents.

The structural details of **3**-**5** are illustrated in Figures 1-3. It can be seen that the molybdenum atom in **3**-**5** is six-coordinate. In **3** and **4** the molybdenum atom is complexed by two sulfur atoms, three carbon atoms of the carbonyl ligands and one oxygen atom of a THF ligand. In complex **5**, however, the molybdenum atom is coordinated to two sulfur atoms and four carbonyl carbon atoms. Selected distances and angles are compared in Table 1. The Mo−S bonds in **3** (2.5902(10), 2.6240(9) Å) and **4** (2.6082(7), 2.6119(7) Å) are marginally longer than the sum of the single bond covalent radii of molybdenum and sulfur (2.59 Å).[9] The Mo−C bond distances to the carbonyl ligands in **3** and **4** are in the normal range for six-coordinate molybdenum carbonyl complexes.[10] As a result of the coordination of the sulfur atoms to molybdenum, the S-E-S (E = Ge, Sn) angles within the coordinated tetrylene ligand fragment become significantly narrower. Thus in **3** the S-Ge-S angle (77.31(3)°) is 11.37° narrower than the 88.68(2)° observed in the precursor germylene **1**.[8] Similarly, the S-Sn-S angle 72.58(2)° in **4** is 12.97 ° narrower than the 85.555(3)° in the uncomplexed stannylene **2**.[8] It is also narrower than the 73.09(2)° for the S-Sn-S angle in the thiolato stannylene $Sn(SAr^{Pr^i_8})_2$ which has the bulkiest terphenyl substituted ligand $SAr^{Pr^i_8}$ ($Ar^{Pr^i_8}$ = $(C_6H$-2,6$(C_6H_2$-2,4,6-$Pr^i{}_3)_2$-3,5-$Pr^i{}_2)$), and the narrowest S-Sn-S angle of all known thiolato stannylenes. The angles between the central aryl rings of the thiolate ligands and the S-E-S planes are 11.190°, 18.873° in **3** and 11.268, 13.114° in **4**. The complexation of the molybdenum to the thiolato sulfur atoms results in a significant lengthening of the E−S bond distances. In **3**, the Ge-S bond lengths of 2.3986(10) and 2.4305(9) Å are *ca.* 0.08 Å, longer than the average Ge−S distance of 2.265(1) Å in the germylene $Ge(SAr^{Me6})_2$. The same trend is observed in **4** where the Sn−S distances (2.6279(7), 2.6303(7) Å) are ca. 0.15 Å longer than in the precursor stannylene (2.479(5) Å). The lengthening is caused in part by a disruption in the Ge−S and Sn−S π-bonding. In contrast, the S−C bond distances in **3** (1.791(4) and 1.803(4) Å) and in **4** (1.798(3) and 1.801(3) Å) are only slightly longer than those in $Ge(SAr^{Me6})_2$ (1.785(1) Å) and $Sn(SAr^{Me6})_2$ (1.7815(9) Å). The Mo--Ge (2.7034(5) Å) and Mo--Sn (2.9050(3) Å) distances are near the upper limit of the known range of Mo−Ge and Mo−Sn bond lengths. However it is doubtful that they have significant Mo−Ge or Mo−Sn bonding because of orbital overlap considerations.

Table 1. Comparison of selected distances (Å) and angles (°) of **3**-**5** (E = Ge, Sn)

Compound	**Mo−S**	**Mo−C**	**Mo−O**	**S−E**	**S−C**	**Mo----E**	**S-E-S**
(**3**) $[Mo(THF)(CO)_3\{Ge(SAr^{Me6})_2\}]$	2.607(10)*	1.961(5)*	2.269(3)	2.415(10)*	1.797(4)*	2.7034(5)	77.31(3)
(**4**) $[Mo(THF)(CO)_3\{Sn(SAr^{Me6})_2\}]$	2.610(7)*	1.954(3)*	2.270(2)	2.629(7)*	1.800(3)*	2.9050(3)	72.58(2)
(**5**) $[Mo(CO)_4\{Sn(SAr^{Me6})_2\}]$	2.622(13)*	2.019(4)*	–	2.596(3)*	1.790(3)*	2.959(15)*	68.64(5)*

* = Averaged Value

ChemComm Accepted Manuscript

This journal is © The Royal Society of Chemistry 2012

Complexes **3** and **4** feature angles between the S1-E-S2 and the S1-Mo1-S2 planes of 84.478° in **3** and 87.139° in **4** showing that the sulfur atoms interact through the lone pair orbital that was π-bonding with respect to the tetrel atom (E).[22]

Complex **5** has longer Mo−S and Mo−C bonds and shorter Sn−S and S−C bonds than those in **4**. This is consistent with decreased electron density at molybdenum as a result of the replacement of a THF by a CO ligand. The average S-Sn-S angle 68.64(5)° is 16.91° narrower than that in the free ligand (85.555(3)°) and the central aryl rings of the terphenyl ligand are almost coplanar (angles between the central aryl rings and the S-E-S plane are 2.106°, 4.862°). The Mo--Sn distance (2.9542(19) Å) is slightly longer than in **4** (2.9050(3) Å). Complex **5** also has a near right angle between the S1-E-S2 and the S1-Mo1-S2 planes (86.859°), like **4**.

IR spectroscopy of complexes **3** and **4** revealed υ(CO) frequencies at 1948 (s, sharp), 1855 (s, sharp), 1820 (s, sharp) cm^{-1} for **3** and 1945 (s, broad), 1845 (s, broad), 1785 (s, broad) for **4**. Complex **5** showed υ(CO) frequencies at 1990 (s, broad), 1915 (s, broad), 1842 (s, broad), 1810 (s, broad) cm^{-1} which are higher in comparison to those of **4** which is in accord with the more electron rich nature of the molybdenum atom in **4** due to the replacement of one of the π-acidic CO ligands with a σ-donating THF molecule. The frequencies in **3**-**5** are also lower than those in the $Mo(CO)_4(NBD)$ complex[11] and, in comparison to $Mo(CO)_4(PR_3)_2$ complexes,[12] consistent with stronger σ-donor and weaker π-acceptor interactions of the $E(SAr^{Me6})_2$ ligands in compounds **3**-**5**.

^{119}Sn NMR spectroscopy of **4**·THF revealed a signal at −101.70 ppm that is shifted to higher field in comparison to that of the free ligand $Sn(SAr^{Me6})_2$ (δ = 786.22 ppm in CD_2Cl_2). Compound **5** resonates at an even higher field at −542.14 ppm in comparison to that of $Sn(SAr^{Me6})_2$ with appears at 763.8 ppm in C_6D_6 solvent. The dramatic shifts upfield can be rationalized in terms of an increase of the electron withdrawing character of the thiolato ligands as a result of their complexation to molybdenum. This increase leads to a stabilization of the tin non-bonding pair, and consequent upfield chemical shift.[13] The effect is enhanced further in **5** by the presence of an extra carbonyl π-acidic ligand at molybdenum which is expected to increase S→Mo electron donation further.

Coordination of molybdenum by sulfur atoms related to that in **3**-**5** has been observed in $[(CO)_4MS_2CC(PPh_3)_2]$ (M = Cr, Mo, W)[14] and in $[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_2(CO)_3(PMe\text{-}Ph_2)]$ which was prepared from $[MoH(SC_6H_3Pr^i_3\text{-}2,4,6)_3(PMePh_2)]$ and CO in THF. However the latter complex has a phosphine instead of a THF ligand.[15] A molybdenum bis-arylthiolato complex $Mo\{SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2\}_2(\eta^1\text{-}CH_3CN)_2(\eta^2\text{-}CH_3CN)_2$ with acetonitrile ligands has been obtained from the π-sandwiched bis-arylthiolato complex $Mo\{\eta^5\text{-}SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2\}\{\eta^7\text{-}SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2\}$ in acetonitrile.[16] Group 6 carbonyl complexes bearing THF co-ligands as in **3** and **4** are rare. The only known, structurally characterised examples are $[Cr(THF)(CO)_5]$,[17] $[HO\text{–}(N\cap N)]Mo(CO)_3(THF)]$,[18] [*trans*-$Mo(THF)(CO)_3\{CNArDipp_2\}_2$] (Dipp = $C_6H_3\text{-}2,6\text{-}Pri_2$),[19] and $[Mo(DAD)(CO)_3(THF)]$ (DAD = N,N′-bis(2,6-dimethylphenyl)butane-2,3-diimine).[20]

Treatment of the germylene $Ge(Ar^{Me6})_2$[21] and the stannylene $Sn(Ar^{Me6})_2$[21] – in which the Ar^{Me6} substituent is directly bonded to molydenum − with $Mo(CO)_4(NBD)$ resulted in no reaction. Attempted extension of the synthetic approach in Scheme 1 to silicon or lead thiolato derivatives[22] also afforded no reaction in the case of silicon. At present, $Pb(SAr^{Me6})_2$ has not been isolated.[23]

In summary, three transition metal carbonyl tetrylene complexes with an unexpected coordination of the molybdenum atom to the sulfur atoms of the thiolate ligands of tetrylenes have been synthesised and characterised. Further investigations on the unusual coordination mode are ongoing.

We are grateful to the U. S. Department of Energy Basic Energy Sciences (DE-FG02-07ER46475, P. P. P.). F. L. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Research Fellowship.

Notes and References

[a] Department of Chemistry, University of California at Davis, One Shields Avenue, Davis, CA 95616. E-mail for P. P. P.: pppower@ucdavis.edu

Electronic Supplementary Information (ESI) available: Full experimental and spectroscopic as well as crystallographic details. CCDC 984312-984314 for CIFs for compounds **3**, **4** and **5**. For ESI in electronic format see DOI: XXX].

1 E. O. Fischer, A. Maasböl, *Angew. Chem. Int. Ed.,* 1964, **3**, 580.
2 J. D. Cotton, P. J. Davidson, D. E. Goldberg, M. F Lappert, K. M. Thomas, *J. Chem. Soc., Chem. Commun.,* 1974, 893.
3 Y. Mizuhata, T. Sasamori, N. Tokitoh *Chem. Rev.,* 2009, **109**, 3479.
4 a) W. Petz, *Chem. Rev.,* 1986, **86**, 1019; b) M. F. Lappert, R. S. Rove, *Coord. Chem. Rev.,* 1990, **100**, 267. c) V. Y Lee, A. Sekiguchi, *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and P: From Phantom Species to Stable Compound,* Wiley, 2010.
5 P. B. Hitchcock, M. F. Lappert, S. A. Thomas, A. J. Thorne, A. J. Carty, N. J. Taylor, *J. Organomet. Chem.*, 1986, **315**, 27.
6 P. Jutzi, W. Steiner, E. König, G. Huttner, A. Frank, U. Schubert, *Chem. Ber.*, 1978, **111**, 606.
7 P. B. Hitchcock, M. F. Lappert, B. J. Samways, E. L. Weinberg, *J. Chem. Soc., Chem. Commun.,* 1983, 1492.
8 B. D. Rekken, T. M. Brown, J. C. Fettinger, F. Lips, H. M. Tuononen, R. H. Herber, P. P. Power, *J. Am. Chem. Soc.,* 2013, **135**, 10134.
9 P. Pyykkö, M. Atsumi, *Chem. Eur. J.,* 2009, **15**, 86.
10 a) W. Levason, L. P. Ollivere, G. Reid, N. Tsoureas, M. Webster, *J. Organomet. Chem.,* 2009, **694**, 2299; b) J. A. Connor, G. A. Hudson, *J. Chem. Soc., Dalton Trans.,* 1975, **11**, 1025.
11 D. J. Darensbourg, J. E. Tappan, H. H. Nelson III, *Inorg. Chem.,* 1977*,* **3**, 534.
12 a) K. Maitra, V. J. Catalano, J. H. Nelson, *J. Am. Chem. Soc.,* 1997, **119**, 12560; b) W. A. Herrmann, C. W. Kohlpaintner, E. Herdtweck, P. Kiprof, *Inorg. Chem.,* 1991, **30**, 4271; c) M. J. M. Vlaar, S. G. A. van Assema, F. J. J. de Kanter, M. Schakel, A. L. Spek, M. Lutz, K. Lammertsma, *Chem. Eur. J.,* 2002, **8**, 58.
13 Wrackmeyer, B. *Ann. Rep. NMR Spectrosc.* 1999, **38**, 203.
14 W. Petz, C. Kutschera, M. Heitbaum, G. Frenking, R. Tonner, B. Neumüller, *Inorg. Chem.,* 2005, **44**, 1263.
15 T. E. Burrow, D. L. Hughes, A. J. Laugh, M. J. Maguire, R. H. Morris, R. L. Richards, *J. Chem. Soc., Dalton Trans.,* 1995, 1315.
16 T. Komuro, T. Matsuo, H. Kawaguchi, K. Tatsumi, *J. Am. Chem. Soc.,* 2003, **125**, 2070.
17 U. Schubert, P. Friedrich, O. Orama, *J. Organomet. Chem.,* 1978, **144**, 175.
18 K. Heinze, *J. Chem. Soc., Dalton Trans.*, 2002, 540.
19 T. B. Ditri, B. J. Fox, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Inorg. Chem.,* 2009, **48**, 8362.
20 B. Oelkers, A. Venker, J. Sundermeyer, *Inorg. Chem.*, 2012, **51**, 4636.

ChemComm Accepted Manuscript

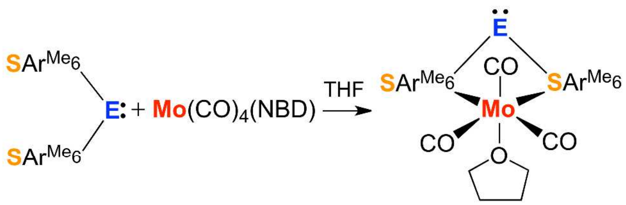
21 R. S. Simons, L. Pu, M. M. Olmstead, P. P. Power, *Organometallics,* 1997, **16**, 1920.

22 B. D. Rekken, T. M. Brown, J. C. Fettinger, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.,* 2012, **134**, 6504.

23 B. D. Rekken, T. M. Brown, M. M. Olmstead, J. C. Fettinger, P. P. Power, *Inorg. Chem.,* 2013, **52**, 3054.

TOC

Reactions of tetrylenes Ge(SAr^{Me_6})$_2$ and Sn(SAr^{Me_6})$_2$ with [Mo(CO)$_4$(NBD)] (NBD=bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)) yield compounds with unusual coordination of the molybdenum carbonyl fragment to the sulfur atoms of the thiolato ligand.



E = Ge, Sn
Ar^{Me6} = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)$_2$
NBD = bicyclo[2.2.1]hepta-2,5-diene

ChemComm Accepted Manuscript

This journal is © The Royal Society of Chemistry 2012