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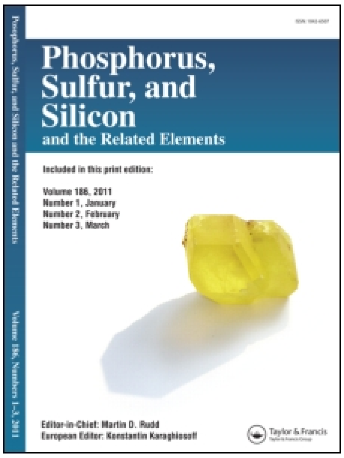

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Stephen Mark Aucott; Alexandra M. Z. Slawin; J. Derek Woollins

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Preparation, Characterisation and Use of $[(^{N\text{-}}Bu_2Sn)S_2N_2]_2$ as a Metathetical Reagent

STEPHEN MARK AUCOTT, ALEXANDRA M. Z. SLAWIN and
J. DEREK WOOLLINS

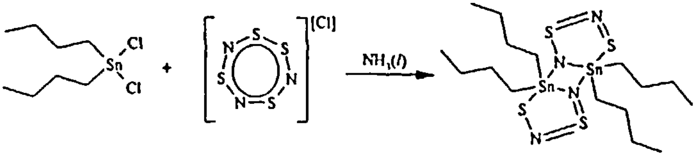
Department of Chemistry, University of St Andrews, Fife, Scotland, KY16 9ST

The dimeric compound $[(^{n\text{-}}Bu_2Sn)S_2N_2]_2$ is readily prepared by addition of $^{n\text{-}}Bu_2SnCl_2$ to a liquid ammonia/$[S_4N_3][Cl]$ reaction mixture. Reaction of $[^{n\text{-}}Bu_2SnS_2N_2]_2$ with mono and dimeric organometallic M(III) (M = Rh, Ir) complexes bearing Cp^* ligands (Cp^* = 1,2,3,4,5-pentamethylcyclopentadienyl) and M(II) (M = Ru, Os) phosphine complexes containing a *cis* arrangement of chlorides gives compounds with MS_2N_2 metallacycles.

Keywords: Tin; Sulfur; Nitrogen; Metathesis; Metallacycles

Introduction

The literature contains a number of examples of molecules which contain SnS_2N_2 rings.[1-4] The reagent most employed in the preparation of these compounds is the potentially explosive tetrasulfur tetranitride (S_4N_4). We have found that large quantities (20-30 g, 70-80%) of $[(^{n\text{-}}Bu_2Sn)S_2N_2]_2$ can be routinely prepared from simple, non-explosive starting materials ie. $^{n\text{-}}Bu_2SnCl_2$ and $[S_4N_3][Cl]$ according to equation 1.



Equation 1

Results and Discussion

X-ray crystallographic analysis of $[(^{n\text{-}}Bu_2Sn)S_2N_2]_2$ reveals that the molecule consists of two identical five-membered ring systems, which are associated via N···Sn interactions to give a four-membered tin-nitrogen ring (Fig 1), both features it shares with $[(\text{Me}_2\text{Sn})\text{S}_2\text{N}_2]_2$[1] and $[(^t\text{Bu}_2\text{Sn})\text{S}_2\text{N}_2]_2$[4].

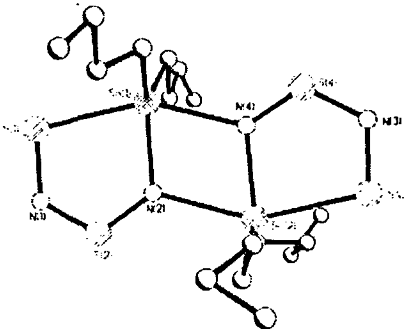
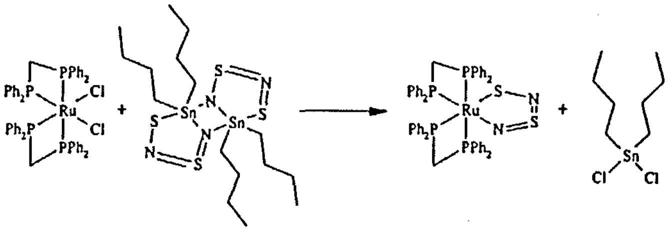


Figure 1 X-ray crystal structure of $[(^n\text{Bu}_2\text{Sn})\text{S}_2\text{N}_2]_2$

Reaction of $[(^n\text{Bu}_2\text{Sn})\text{S}_2\text{N}_2]_2$ with *cis*-$[\text{RuCl}_2(\text{dppm})_2]$, *cis*-$[\text{RuCl}_2(\text{dppe})_2]$ and $[\text{MCl}_2(\text{PP}_3)]$ (M = Ru or Os and (PP_3) = tris[2-(diphenylphosphino)ethyl]phosphine) results in ligand exchange giving $^n\text{Bu}_2\text{SnCl}_2$ and the coressponding Ru or Os MS_2N_2 metallacyclic compound (Equ 2).



Equation 2

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of *cis*-$[\text{Ru}(\text{S}_2\text{N}_2)(\text{dppm})_2]$ and *cis*-$[\text{Ru}(\text{S}_2\text{N}_2)(\text{dppe})_2]$ show three well-separated resonances (Fig 2) of relative intensities 1:1:2 (AMXX' splitting pattern).

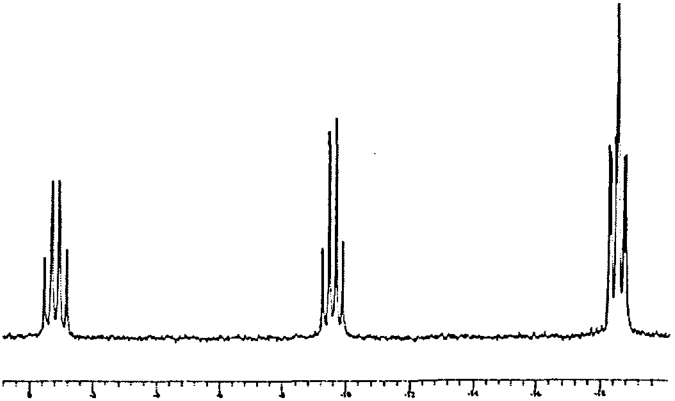


Figure 2 $^{31}P\{^1H\}$ NMR (CD_2Cl_2) of *cis*-$[Ru(S_2N_2)(dppm)_2]$

Preliminary $^{31}P\{^1H\}$ NMR studies of the reaction between $[MCl_2(PP_3)]$ (M = Ru or Os and (PP_3) = tris[2-(diphenylphosphino)ethyl]phosphine) and $[(^nBu_2Sn)S_2N_2]_2$ suggest that in benzene predominantly one isomer is formed, while reaction in either CH_3Cl or CH_2Cl_2 gives equal amounts of both isomers (Fig 3).

Figure 3 Two isomeric forms of $[M(S_2N_2)(PP_3)]$ (M = Ru, Os)

Reaction of $[(^nBu_2Sn)S_2N_2]_2$ with $[Cp^*MCl_2(PPh_3)]$ (M = Rh, Ir) in the presence of $NH_4[PF_6]$ gives highly unusual bimetallic products containing both three and four-coordinate metal centres. The iridium analogue has been crystallographically characterised (Fig 4) and shows that the tri-coordinate $Cp^*IrS_2N_2$ portion of the molecule acts as a neutral ligand and is bound to the tetra-coordinate iridium centre via what is considered the non-basic nitrogen atom in the IrS_2N_2 ring. This is the first reported example of coordination of the S-N=S nitrogen of the $[S_2N_2]^{2-}$ dianion.

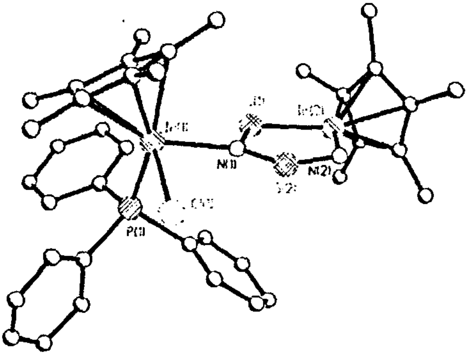


Figure 4 X-ray crystal structure of $[Cp^*IrCl(PPh_3)\{(N_2S_2)IrCp^*)\}][PF_6]$ the PF_6 counterion has been ommited for clarity.

Conclusions

$[(^{n-}Bu_2Sn)S_2N_2]_2$ is accessable via a straightforword (one-pot) synthetic route and has shown its effectiveness as a synthetic $[S_2N_2]^{2-}$ metathesis reagent.

Acknowledgements

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