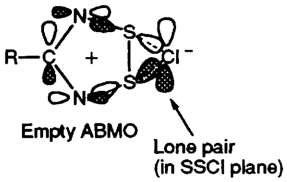
4-Phenyl-1,2,3,5-dithiadiazolyl: a Novel Coupling Reagent for the Formation of E–E Bonds (E = C, P, Si)

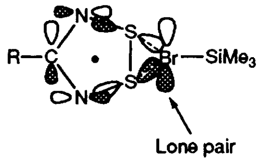
Neil Adamson, Arthur J. Banister,* Ian B. Gorrell, Anthony W. Luke and Jeremy M. Rawson
Department of Chemistry, Durham University, South Road, Durham, UK DH1 3LE

$[\mathrm{Ph\overline{CNSSN}}]_2$ reacts under mild conditions with molecules containing bonds of the types P–Cl (Ph_2PCl and $PhPCl_2$), Si–Br (Me_3SiBr) and activated C–Cl or C–Br (*ortho*-chloranil or MeCOBr) with the formation of $[\mathrm{Ph\overline{CNSSN}}]X$ (X = Cl or Br) and the corresponding E–E (E = P, Si or C) bonded compounds; the application of dithiadiazolyl radicals as coupling reagents is discussed in the context of the strength of the E–Hal bond.

Halogenation of dithiadiazolyl radicals, $\mathrm{R\overline{CN_2S_2}}^{\bullet}$, by diatomic halogens[1] (Cl_2, Br_2 or I_2) or halides,[1] such as $SOCl_2$ and SO_2Cl_2, gives the corresponding dithiadiazolylium halide salts in high yield, although oxidation by fluorinating agents has led to more complex products.[2] Oxidation of these radicals is also readily achieved with reagents such as $Se_4(AsF_6)_2$,[1] AsF_5[3] or $SnCl_4$[1] to give $[\mathrm{R\overline{CNSSN}}][AsF_6]$ or $[\mathrm{R\overline{CNSSN}}]_2[SnCl_6]$. However, it is only recently[4] that phenyl dithiadiazolyl, $[\mathrm{Ph\overline{CNSSN}}]^{\bullet}$, which is dimeric in the solid state,[5] has been used as a formal reducing agent. $[\mathrm{Ph\overline{CNSSN}})_2$ reacts[4] with the sulfur–nitrogen salts S_5N_5Cl and S_4N_3Cl to give $[\mathrm{Ph\overline{CNSSN}}]Cl$, S_4N_4 and other dithiadiazolylium salts (formed by trapping of intermediate sulfur–nitrogen radical



1



2

fragments): $[\mathrm{PhCNSSN}][\mathrm{S_3N_3}]$, $[(\mathrm{PhCNSSN})_2\mathrm{Cl}][\mathrm{S_3N_3}]$ and $[\mathrm{PhCNSSN}][\mathrm{S_3N_2}]\mathrm{Cl}$.

As a continuation of this work, we have examined the reactivity of $[\mathrm{PhCNSSN}]_2$ towards other E–Hal (rather than S–Cl) bonds and now report the use of $[\mathrm{PhCNSSN}]_2$ as an 'organically soluble metal' for the formation of E–E bonds. Various reagents are available for effecting symmetrical coupling reactions by halogen abstraction *e.g.* Pd-catalysed systems using electrolysis,[6] tin compounds,[7] cyclooctadiene nickel(0)[8] and finely divided metals.[9] However, many of these are either highly toxic (pyrophoric lead[10]) or expensive (diiodosamarium[11]) and consequently other novel reagents are of special interest.

Although no reaction was observed between $\mathrm{Me_3SiCl}$ and $[\mathrm{PhCNSSN}]_2$, reaction of $[\mathrm{PhCNSSN}]_2$ with $\mathrm{Me_3SiBr}$ in toluene provided an immediate red precipitate of $[\mathrm{PhCNSSN}]\mathrm{Br}$ (IR and elemental analysis comparable with an authentic sample[1]) and $\mathrm{Me_3Si{-}SiMe_3}$ (b.p. 111–116 °C, *cf.* lit. value 112–114 °C[12]). As yet the mechanism of reaction is unknown but in view of three-centre (SSCl) interaction in dithiadiazolylium halides, **1**, a similar transition state, **2**, seems likely (the unpaired electron of the radical is in an out-of-plane molecular orbital).

The differing bond energies associated with the Si–Hal bond (Si–Br, 310 kJ mol^{-1} and Si–Cl, 481 kJ mol^{-1}, *cf.* P–Cl, 326 kJ mol^{-1})[12] led us to examine the reactivity of other E–Hal bonds. Some qualitative reactions with P–Cl bonds established that dechlorination also occurs at phosphorus.

Additon of a slight molar excess ($\geqslant 2:1$) of $\mathrm{Ph_2PCl}$ to $[\mathrm{PhCNSSN}]_2$ in $\mathrm{CH_2Cl_2}$ at room temp. rapidly provided a yellow precipitate of $[\mathrm{PhCNSSN}]\mathrm{Cl}$ (IR and elemental analysis comparable with an authentic sample[1]) under a pale-yellow solution. The ^{31}P NMR spectrum after 3 h indicated the formation of $[\mathrm{Ph_2P{-}PPh_2}]$[13] [$\delta(\mathrm{CH_2Cl_2}) = +16$] and some unconverted $\mathrm{Ph_2PCl}$ (plus minor quantities of oxidation and hydrolysis products). Further stirring for 24 h and cooling to 0 °C yielded further quantities of $[\mathrm{PhCNSSN}]\mathrm{Cl}$ (87% recovered yield). Addition of alkali metals (such as Li, K or Mg) to $\mathrm{PhPCl_2}$ has previously been shown[14] to produce cyclophosphanes, $(\mathrm{PhP})_n$ (n = 4, 5, 6). However, in the presence of an excess of metal, cyclic salts[15] of the type $\mathrm{K_2[PPh]_3}$ or linear salts[15] such as $\mathrm{Li_2[PhP(PPh)}_n\mathrm{PPh]}$ may be formed. Such reactions are complex and, for example, the ^{31}P NMR spectrum of a solution of $(\mathrm{PhP})_n$ containing lithium showed over ten resonances.[15] Reaction of a slight stoichiometric excess of $[\mathrm{PhCNSSN}]_2$ with $\mathrm{PhPCl_2}$ in toluene produced an immediate yellow precipitate ($[\mathrm{PhCNSSN}]\mathrm{Cl}$, 72% recovered yield) under a deep-red solution. The ^{31}P NMR spectrum of the extremely air-sensitive solution showed a complex multiplet in the region δ 3–9 indicative of formation of isomers of $(\mathrm{PhP})_n$ $^{31}\mathrm{P[(PPh)_4]}$, $\delta = +9\}$,[16] plus further minor resonances, which may be attributable to the formation of anions of the type $[\mathrm{PhCNSSN}]_2[\mathrm{PPh}]_n$ where the phospho-anion may be either cyclic or linear in nature.

Thus $[\mathrm{PhCNSSN}]_2$ appears to be capable of breaking E–Hal bonds in excess of *ca.* 300 kJ mol^{-1}. We, therefore, undertook a study of the chemistry of $[\mathrm{PhCNSSN}]_2$ in the dehalogenation of activated C–Hal bonds. In the simplest case, oxalyl chloride $(\mathrm{COCl})_2$ reacted with $[\mathrm{PhCNSSN}]_2$ in toluene to give an instant yellow precipitate of $[\mathrm{PhCNSSN}]\mathrm{Cl}$ (92%) and this was accompanied by the evolution of gas (presumed to be CO). Similar reactions were also observed with other groups containing halogen atoms α to carbonyl group, *e.g.* MeCOBr reacted with $[\mathrm{PhCNSSN}]_2$ to precipitate $[\mathrm{PhCNSSN}]\mathrm{Br}$ and form butane-2,3-dione (MeCO.COMe) (GC mass spectrometry 86.3%).

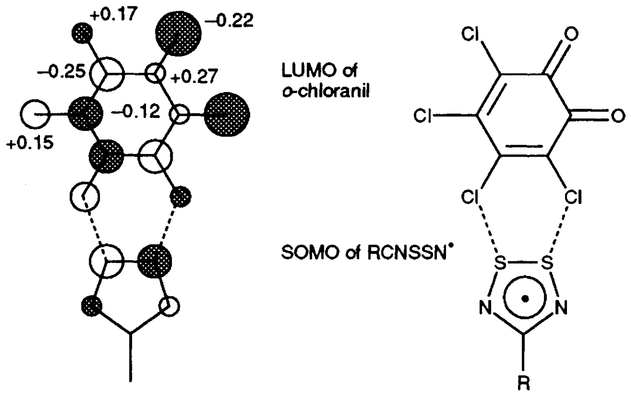
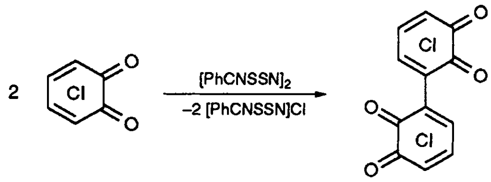


Fig. 1 Orbital symmetry and charge distribution in *ortho*-chloranil and phenyl-1,2,3,5-dithiadiazolyl



We also found that in some cases C–Hal bonds β to a carbonyl group were activated sufficiently for halogen abstraction to take place. *Ortho*-chloranil reacted with $[\mathrm{PhCNSSN}]_2$ in toluene over a period of 3 days to produce a yellow precipitate of $[\mathrm{PhCNSSN}]\mathrm{Cl}$ under a red solution. Evaporation of the soluble fraction, followed by $\mathrm{SO_2}$ extraction (to remove $[\mathrm{PhCNSSN}]\mathrm{Cl}$ and some unconverted $[\mathrm{PhCNSSN}]_2$) yielded a bright-red powder, thermally stable to above 300 °C. Elemental analysis and mass spectrum of this compound indicated that dimerisation had occurred to give a coupled product, $\mathrm{C_{12}O_4Cl_6}$ (68%). When this reaction was repeated in benzene, a ^{13}C NMR spectrum of the soluble fraction showed residual *ortho*-chloranil peaks only (δ 131.7, 141.9 and 167.8). The $[\mathrm{PhCNSSN}]\mathrm{Cl}$ and chloranil coupled species had precipitated.

PM3 molecular orbital calculations[17] on *ortho*-chloranil (minimised from the geometry taken from crystal data[18]) indicate that the lowest unoccupied molecular orbital (LUMO) has the same orbital symmetry around the $\mathrm{C_2Cl_2}$ fragment (adjacent to CO) as that observed for the singly occupied molecular orbital (SOMO) of the $[\mathrm{PhCNSSN}]^{\bullet}$ radical (Fig. 1). Moreover, the stronger C–Cl bond polarisation for the β-Cl than the γ-Cl would indicate that coupling should take place through the carbon atoms *ortho* to the carbonyl group, Scheme 1.

This series of reactions show that $[\mathrm{PhCNSSN}]_2$ can act as a coupling agent under mild conditions in the synthesis of some Si–Si, P–P and C–C compounds. The formation of more reactive dithiadiazolyl radicals[19] (*e.g.* with substituents that stabilise the dithiadiazolylium cation) should facilitate the activation of stronger E–Hal bonds.

We thank the SERC for a studentship (A. W. L.) and post-doctoral funding (J. M. R.), the EC for financial support (I. B. G.) and Mr T. G. Hibbert for assistance with syntheses.

Received, 24th December 1992; Com. 2/06851F

References

1 A. J. Banister, N. R. M. Smith and R. G. Hey, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1181.

2 I. B. Gorrell, PhD Thesis, University of Durham, 1991; A. J. Banister and J. M. Rawson, in *The Chemistry of Inorganic Ring Systems*, ed. R. Steudel, Elsevier Press, Amsterdam, ch. 17, 1992.

3 S. Parsons, J. Passmore, M. J. Schriver and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1991, 369.

4 A. J. Banister, M. I. Hansford, Z. V. Hauptman, S. T. Wait, A. W. Luke, W. Clegg and K. A. Jørgensen, *J. Chem. Soc., Dalton Trans.*, 1990, 2793.

5 A. Vegas, A. Perez-Salazar, A. J. Banister and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1980, 1812.

6 S. Torii, H. Tanaka and K. Morisaki, *Tetrahedron Lett.*, 1985, **26**, 1655.

7 A. M. Echavarren and J. K. Stille, *J. Am. Chem. Soc.*, 1987, **109**, 5478.

8 M. F. Semmelhack, P. Helquist, L. D. Jones, L. Keller, L. Mendelson, L. S. Ryono, J. G. Smith and R. D. Stauffer, *J. Am. Chem. Soc.*, 1981, **103**, 6460.

9 M. Sainsbury, *Tetrahedron*, 1980, **36**, 3327.

10 L. Mészáros, *Tetrahedron Lett.*, 1967, **49**, 4951.

11 P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693.

12 *Handbook of Chemistry and Physics*, ed. R. Weast, CRC Press Inc., Boca Raton, Florida, 70th edn. (1989–90).

13 J. E. Huheey, *Inorganic Chemistry*, Harper and Row, Cambridge, 3rd edn., 1983.

14 J. G. Verkade and L. D. Quin, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Florida, USA, 1987.

15 W. A. Henderson, M. Epstein and F. S. Seichter, *J. Am. Chem. Soc.*, 1963, **85**, 2462.

16 K. Issleib and E. Fluck, *Angew. Chem., Int. Ed. Engl*, 1966, **5**, 587.

17 A. H. Cowley and R. P. Pinnell, *Top. Phosph. Chem.*, 1967, **4**, 1.

18 M. J. S. Dewar and W. J. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899; J. J. P. Stewart, *Quantum Chemistry Program Exchange*, No. 455, (MOPAC), 1984.

19 G. Zanotti and A. Del Pra., *Acta. Crystallogr. Sect. B*, 1978, **34**, 2997.

20 1,2,3,4-dithiadiazolyl radicals are stronger reducing agents than their analogous 1,2,3,5-dithiadiazolyl radicals by *ca.* 0.3 V; see for example, C. M. Aherne, A. J. Banister, I. B. Gorrell, A. W. Luke, M. I. Hansford, Z. V. Hauptman and J. M. Rawson, *J. Chem. Soc., Dalton Trans.*, 1993, 967.