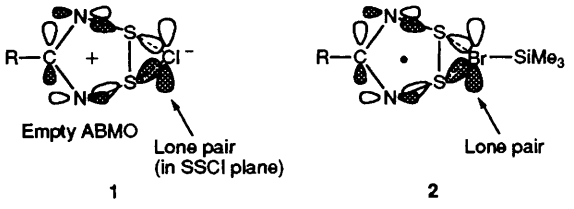
4-Phenyl-1,2,3,5-dithiadiazolyl: a Novel Coupling Reagent for the Formation of E–E Bonds (E = C, P, Si)

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

$[PhC\overline{NSSN}]_2$ 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 $[PhC\overline{NSSN}]X$ (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, $RC\overline{N_2S_2}^{\bullet}$, 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 $[RC\overline{NSSN}][AsF_6]$ or $[RC\overline{NSSN}]_2[SnCl_6]$. However, it is only recently[4] that phenyl dithiadiazolyl, $[PhC\overline{NSSN}]^{\bullet}$, which is dimeric in the solid state,[5] has been used as a formal reducing agent. $[PhC\overline{NSSN}]_2$ reacts[4] with the sulfur–nitrogen salts S_5N_5Cl and S_4N_3Cl to give $[PhC\overline{NSSN}]Cl$, S_4N_4 and other dithiadiazolylium salts (formed by trapping of intermediate sulfur–nitrogen radical



fragments): $[PhC\overline{NSSN}][S_3N_3]$, $[(PhC\overline{NSSN})_2Cl][S_3N_3]$ and $[PhC\overline{NSSN}][S_3N_2]Cl$.

As a continuation of this work, we have examined the reactivity of $[PhC\overline{NSSN}]_2$ towards other E–Hal (rather than S–Cl) bonds and now report the use of $[PhC\overline{NSSN}]_2$ 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 Me_3SiCl and $[PhC\overline{NSSN}]_2$, reaction of $[PhC\overline{NSSN}]_2$ with Me_3SiBr in toluene provided an immediate red precipitate of $[PhC\overline{NSSN}]Br$ (IR and elemental analysis comparable with an authentic sample[1]) and 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 (≥2:1) of Ph_2PCl to $[PhC\overline{NSSN}]_2$ in CH_2Cl_2 at room temp. rapidly provided a yellow precipitate of $[PhC\overline{NSSN}]Cl$ (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 $[Ph_2P–PPh_2]$[13] [$\delta(CH_2Cl_2)$ = +16] and some unconverted Ph_2PCl (plus minor quantities of oxidation and hydrolysis products). Further stirring for 24 h and cooling to 0 °C yielded further quantities of $[PhC\overline{NSSN}]Cl$ (87% recovered yield). Addition of alkali metals (such as Li, K or Mg) to $PhPCl_2$ has previously been shown[14] to produce cyclophosphanes, $(PhP)_n$ (n = 4, 5, 6). However, in the presence of an excess of metal, cyclic salts[15] of the type $K_2[PPh]_3$ or linear salts[15] such as $Li_2[PhP(PPh)_nPPh]$ may be formed. Such reactions are complex and, for example, the ^{31}P NMR spectrum of a solution of $(PhP)_n$ containing lithium showed over ten resonances.[15] Reaction of a slight stoichiometric excess of $[PhC\overline{NSSN}]_2$ with $PhPCl_2$ in toluene produced an immediate yellow precipitate ($[PhC\overline{NSSN}]Cl$, 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 $(PhP)_n$ $^{31}P[(PPh)_4]$, δ = +9},[16] plus further minor resonances, which may be attributable to the formation of anions of the type $[PhC\overline{NSSN}]_2[PPh]_n$ where the phospho-anion may be either cyclic or linear in nature.

Thus $[PhC\overline{NSSN}]_2$ 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 $[PhC\overline{NSSN}]_2$ in the dehalogenation

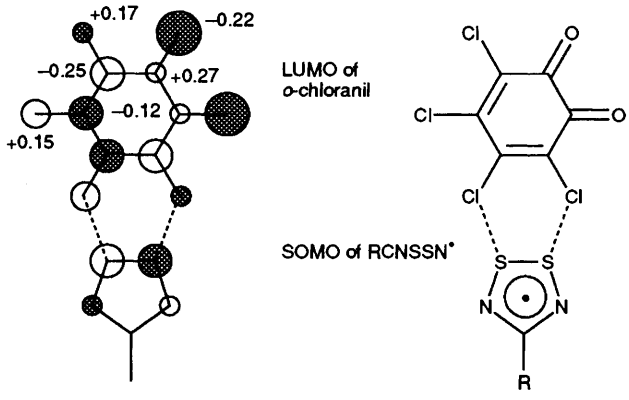
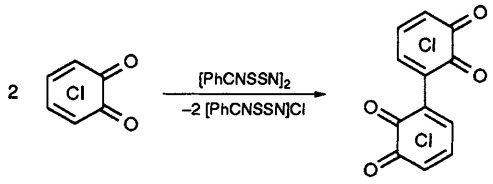


Fig. 1 Orbital symmetry and charge distribution in *ortho*-chloranil and phenyl-1,2,3,5-dithiadiazolyl



of activated C–Hal bonds. In the simplest case, oxalyl chloride $(COCl)_2$ reacted with $[PhC\overline{NSSN}]_2$ in toluene to give an instant yellow precipitate of $[PhC\overline{NSSN}]Cl$ (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 $[PhC\overline{NSSN}]_2$ to precipitate $[PhC\overline{NSSN}]Br$ and form butane-2,3-dione (MeCO.COMe) (GC mass spectrometry 86.3%).

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 $[PhC\overline{NSSN}]_2$ in toluene over a period of 3 days to produce a yellow precipitate of $[PhC\overline{NSSN}]Cl$ under a red solution. Evaporation of the soluble fraction, followed by SO_2 extraction (to remove $[PhC\overline{NSSN}]Cl$ and some unconverted $[PhC\overline{NSSN}]_2$) 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, $C_{12}O_4Cl_6$ (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 $[PhC\overline{NSSN}]Cl$ 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 C_2Cl_2 fragment (adjacent to CO) as that observed for the singly occupied molecular orbital (SOMO) of the $[PhC\overline{NSSN}]^{\bullet}$ 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 $[PhC\overline{NSSN}]_2$ 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

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