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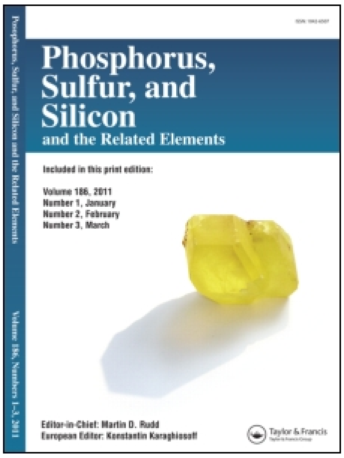

Phosphorus, Sulfur, and Silicon and the Related Elements

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To cite this Article Banister, Arthur J. and May, Iain(1994) 'Metal Insertion into the Sulfur-Sulfur Bond of the Phenyl Dithiadiazolyl, ', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 447 — 448

To link to this Article: DOI: 10.1080/10426509408021897

URL: http://dx.doi.org/10.1080/10426509408021897

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Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 447–448
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METAL INSERTION INTO THE SULFUR-SULFUR BOND OF THE PHENYL DITHIADIAZOLYL, $\mathrm{Ph\overline{CNSSN}}$.

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Abstract Complexation reactions of phenyl dithiadiazolyl with various transition metal complexes are reviewed.

INTRODUCTION

A recent development in the chemistry of dithiadiazolyls is their reaction with various metal complexes. In this process ring opening through the S-S bond enables either one or two metals to insert, in chelating or bridging fashion respectively. Complexes are now known which incorporate Fe, Ni, Pd or Pt into the heterocyclic ring.

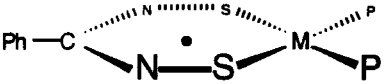
DISCUSSION

Complexation has proved difficult, due in part to the instability of the free radical, $\mathrm{Ph\overline{CNSSN}}$, in solution and the frequent formation of highly insoluble impure products. However, three types of complex have been synthesised incorporating 1,2 or 3 metal centres (see table).

In the monometallic complexes, M(SNCPhNS-*S,S*)(P)$_2$ (FIG 1.), the dithiadiazolyl simply chelates the metal. The two metal centre complexes, [Fe$_2$(CO)$_6$(μ-SNCPhNS-*S,S*)] (FIG 2.) and [Ni$_2$(C$_5$H$_5$)$_2$(μ-SNCPhNS-*S,S*)] consist of the SNCPhNS group bridging 2 metals in a classical butterfly arrangement. Such bridging again occurs in the trimetallic complexes of general formula M$_3$(μ-SNCPhNS-*S,S*)$_2$(P)$_4$ (FIG.2.) (where M = Pd or Pt and P = PPh$_3$ or $^1/_2$PPh$_2$C$_2$H$_4$PPh$_2$); the two dithiadiazolyl groups now bridge three metal centres.

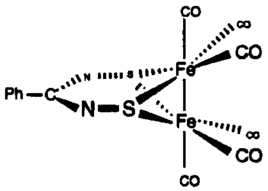
In all cases the starting metal complex is oxidised by the $\mathrm{Ph\overline{CNSSN}}$ ring system (formal covalent bonds are established to the metal). The monometallic and dimetallic complexes retain the free radical , yielding intresting e.s.r. spectra and magnetic properties in the former. The trimetallic complexes are formed from the decomposition of one metal centre complexes, presumbly through a further two metal centre intermediate. These complexes show a unique type of bonding as indicated by the absence of free radical character

STARTING COMPLEX	DITHIADIAZOLYL COMPLEX	REF
$Fe_2(CO)_9$	$[Fe_2(CO)_6(\mu\text{-SNCPhNS-}S,S)]$	1
$[Ni(C_5H_5)CO]_2$	$[Ni_2(C_5H_5)_2(\mu\text{-SNCPhNS-}S,S)]$	2
$Pd(PPh_3)_4$	$Pd_3(\mu\text{-SNCPhNS-}S,S)_2(PPh)_4$	3,6
$Pd(Ph_2PC_2H_4PPh_2)_2$	$Pd(SNCPhNS\text{-}S,S)(Ph_2PC_2H_4PPh_2)$	4
$Pd(Ph_2PC_2H_4PPh_2)_2$	$Pd_3(\mu\text{-SNCPhNS-}S,S)_2(Ph_2PC_2H_4PPh_2)_2$	4
$Pt(PPh_3)_4$	$Pt(SNCPhNS\text{-}S,S)(PPh)_2$	5,6
$Pt(PPh_3)_4$	$Pt_3(\mu\text{-SNCPhNS-}S,S)_2(PPh)_4$	5,6
$Pt(Ph_2PC_2H_4PPh_2)_2$	$Pt(SNCPhNS\text{-}S,S)(Ph_2PC_2H_4PPh_2)$	5



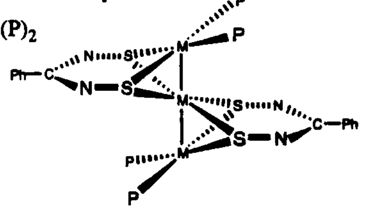
$M(SNCPhNS\text{-}S,S)(P)_2$

FIG 1.



$Fe_2(CO)_6(\mu\text{-SNCPhNS})$

FIG 2.



$M_3(\mu SNCPhNS\text{-}S,S)_2(P)_4$

FIG 3.

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