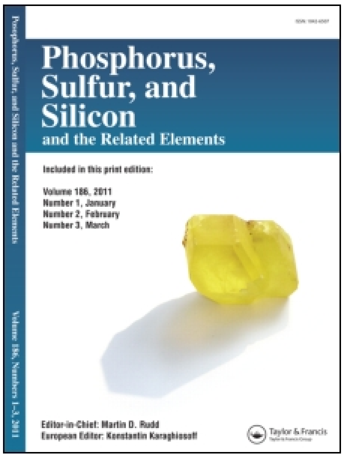


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Structures of Metal Carbonyl Cowlexes of P(III)-N-S Rings and the Ligand Properties of P(V)-N-S Rings

Tristram Chivers[a]; Kaveripatnam S. Dhathathreyan[a]; Cees Lensink[a]; Stephen W. Liblong[a]
[a] Department of Chemistry, The University of Calgary, Calgary, A1berta, Canada

To cite this Article Chivers, Tristram , Dhathathreyan, Kaveripatnam S. , Lensink, Cees and Liblong, Stephen W.(1989) 'Synthesis and Structures of Metal Carbonyl Cowlexes of P(III)-N-S Rings and the Ligand Properties of P(V)-N-S Rings', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 1, 85 — 95

To link to this Article: DOI: 10.1080/10426508908039696

URL: http://dx.doi.org/10.1080/10426508908039696

Phosphorus, Sulfur and Silica, Vol. 41, pp. 85–95
Reprints available directly from the publisher
Photocopying permitted by license only

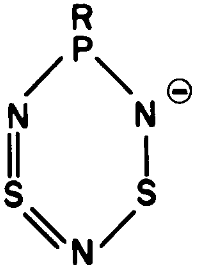
SYNTHESIS AND STRUCTURES OF METAL CARBONYL COMPLEXES OF P(III)-N-S RINGS AND THE LIGAND PROPERTIES OF P(V)-N-S RINGS.

TRISTRAM CHIVERS, KAVERIPATNAM S. DHATHATHREYAN, CEES LENSINK and STEPHEN W. LIBLONG
Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

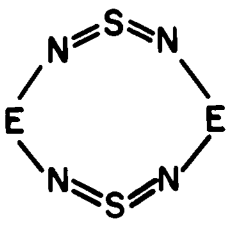
Abstract The preparation and structures of the first examples of unsaturated phosphorus(III)-nitrogen-sulphur rings, as metal carbonyl complexes, are described and comparisons are made with the corresponding arsenic(III) compounds. The ligand properties of phosphorus(V)-nitrogen-sulphur rings are also discussed.

INTRODUCTION

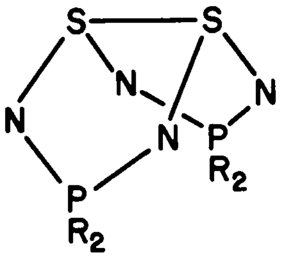
The RP(III) group is isolectronic with a sulphur atom as a substituent in a binary S-N ring. Thus it is reasonable to propose the possibility of ring systems such as 1 and 2 (E=RP) as phosphorus (III) analogues of $S_3N_3^-$ and S_4N_4, respectively. In addition to the versatile ligand properties of these heterocycles, their molecular and electronic structures are of interest in view of the possible involvement of the phosphorus lone pair in delocalized ring bonding.



1



2



3

Prior to the work described herein, such heterocycles were unknown although the first example of an As(III)-N-S ring, **2** (E=MeAs), was reported in 1971.[1] Subsequently, X-ray structural studies of **2** (E=PhAs,[2] MesAs,[2] ^{t}BuAs[3]) revealed a boat conformation for the ring with d(S-N) = 1.51-1.52Å and <AsNS = 128-132°. The ligand **2** (E=RAs) can be incorporated into metal carbonyl complexes either as a monodentate[4] or as a bidentate chelating ligand bonded to one or two metal centres.[4-6] Neither the structural parameters nor the conformation of the ring are changed significantly upon coordination.

The first part of this paper describes the synthesis and structural characterization of the first metal complexes of **1** and **2**. The ligand properties of the phosphorus(V)-nitrogen-sulphur ring, **3** are discussed in the second part.

SYNTHESIS OF METAL CARBONYL COMPLEXES OF P(III)-N-S RINGS

Metal carbonyl complexes of R_2PNSO ligands are readily obtained by metathetical reactions (Eq. 1).[7,8]

$$ML_n(R_2PCl) + KNSO \xrightarrow[-40°C]{CH_3CN} ML_n(R_2PNSO) + KCl \qquad (1)$$

Treatment of these complexes with potassium t-butoxide promotes condensation to give the corresponding sulphur diimide complexes (Eq. 2).[8]

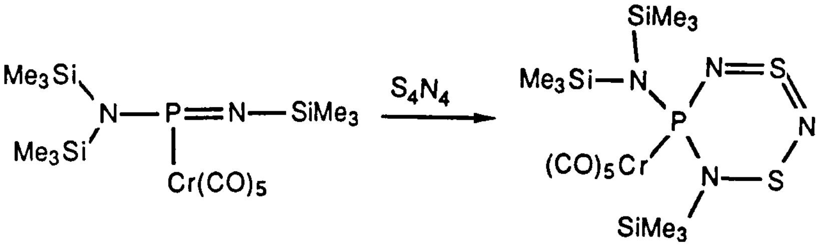
$$2ML_n(R_2PNSO) \xrightarrow{KO^tBu} L_nMP(R)_2NSN(R)_2PML_n \qquad (2)$$

The attempted extension of this synthetic method to metal carbonyl complexes of $RP(NSO)_2$ led to the direct formation of binuclear complexes of the eight-membered ring $P_2^{III}N_4S_2$, **2** (E=PR) (Eq. 3).[9]

$$2Cr(CO)_5(RPCl_2) + 2KNSO^- \xrightarrow{-2KCl} (CO)_5Cr[RP(NSN)_2PR]Cr(CO)_5 \qquad (3)$$

(4a, R=$^iPr_2N$, trans, 3%)
(4b, R=^tBu, cis, 21%)

By contrast Herberhold et al. have recently reported that treatment of $Cr(CO)_5(^tBuPCl_2)$ with K_2SN_2 in acetonitrile produces $Cr(CO)_5[P(Bu^t)NSNSNH]$, a complex of a protonated derivative of 1.[10] We have developed an alternative approach to complexes of this six-membered ring that involves a double 1,4-cycloaddition of a P=N bond to two S_2N_2 units of S_4N_4 followed by symmetrical rupture of the eight-membered S_4N_4 ring (cf. ref. 11).



(4)

5a

The product 5a (δ ^{31}P + 151 .0 ppm) is obtained as a yellow oil, which is converted to the more easily crystallized derivative $Cr(CO)_5(P(Me_3SiNH)NSNSNH)$, 5b (δ ^{31}P + 110.9 ppm) upon treatment with isopropanol.

STRUCTURES OF METAL CARBONYL COMPLEXES OF P(III)-N-S RINGS

The structures of 4a and 4b as determined by X-ray crystallography are shown in Figures 1 and 2, respectively.

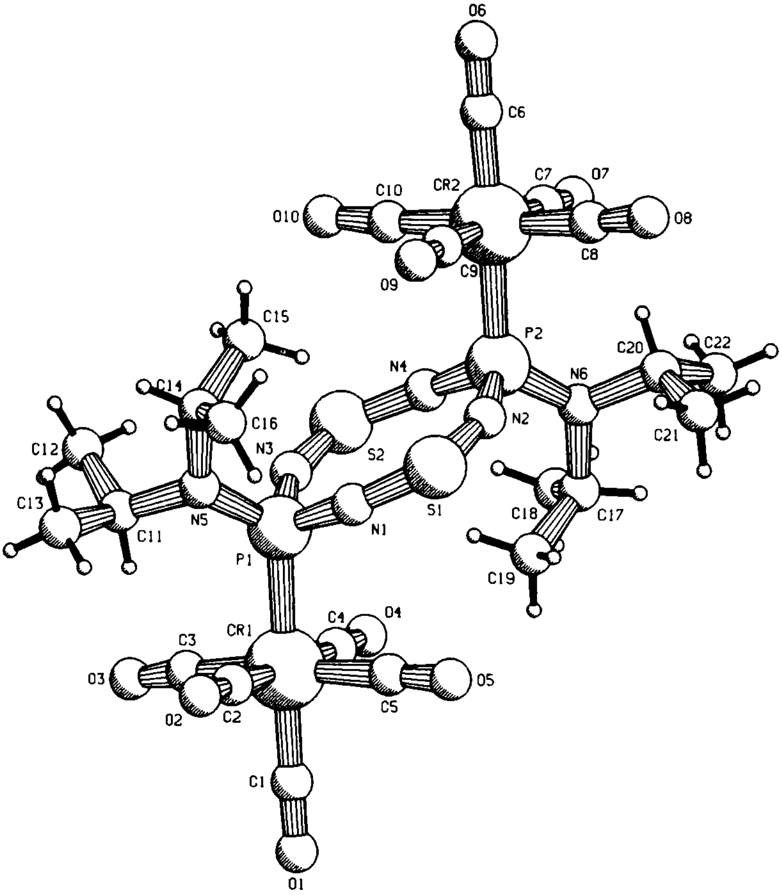


FIGURE 1. Structure of **4a**

The *trans* derivative **4a** possesses a non-crystallographic inversion centre inside the ring, which is essentially planar with small distortions towards a chair conformation. The phosphorus atoms are 0.08Å out of and on opposite sides of the best $P_2^{III}N_4S_2$ plane. By contrast, the *cis* derivative **4b** is distorted from planarity towards a boat conformation with P(1) and P(2) above the plane by 0.188 and 0.204Å, respectively, and S(1) and S(2) below the plane of the ring by 0.122 and 0.108Å, respectively. The bond angles at nitrogen of 150-153° for 4a and 146-155° for 4b are unusually large compared to the values found for 2 (E=RAs)[2,3] and metal complexes of 2,[4-6] presumably as a consequence of the near planarity of the rings in 4a and 4b. Nevertheless the values of the S-N bond lengths of 1.50-1.52Å and the bond angles of 124-125° at sulphur in 4a and 4b are typical for cyclic sulphur diimides. Thus the overall structures appear to be those of cyclic sulphur diimides with almost planar conformations enforced by the bulky groups on phosphorus.

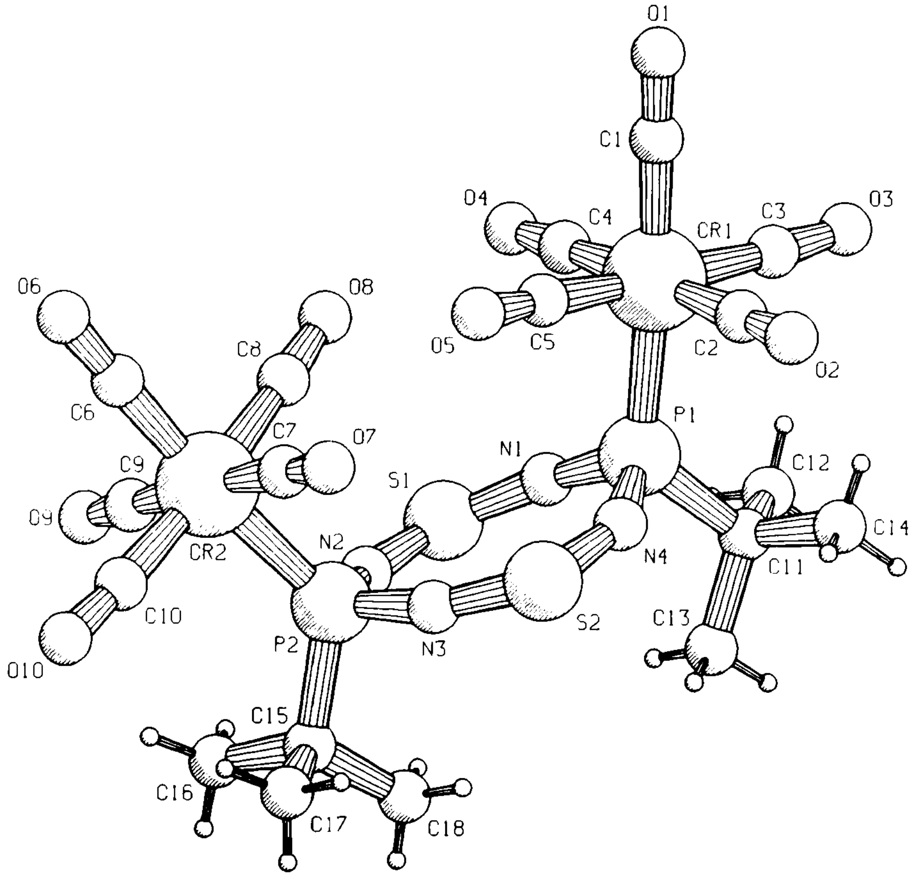


FIGURE 2. Structure of 4b

The $P^{III}S_2N_3$ in 5b has two short (ca. 1.56Å) and two long (1.66 and 1.67Å) S-N bonds[12] suggesting a strong tendency towards localized sulphur diimide bonding as represented for 5a in Eq. 4.

The preparation of 4a, 4b and 5b demonstrates that it is possible to obtain the ring systems 1 and 2 stabilized by coordination to a metal. The structures of the metal carbonyl complexes reveal localized sulphur diimide bonding within the P(III)-N-S rings. The isolation of the free ligands and an assessment of the involvement of the phosphorus lone pair in delocalized ring bonding has yet to be achieved.

LIGAND PROPERTIES OF THE 1,5-$P_2^{V}N_4S_2$ RING

The almost planar $P_2^{III}N_4S_2$ rings in 4a and 4b are stabilized by coordination of the phosphorus lone pairs to metal centres. By contrast, the corresponding P^{V} rings, 3 (R=Me,Ph) have folded structures with cross-ring S-S bonds of ca. 2.5Å.[13,14] In the absence of lone pair electrons on phosphorus, the ligand properties of the 1,5-$P_2^{V}N_4S_2$ ring will be limited to the nitrogen or sulphur centres.

Our studies of the Lewis base behaviour of the $P^{V}N_3S_2$ and 1,3-$P_2^{V}N_4S_2$ rings have shown that Lewis or Bronsted acids coordinate preferentially to a nitrogen atom between a phosphorus and a sulphur atom.[15,16] In the formation of Lewis base adducts of 3 no ambiguity exists over the site of coordination since all four nitrogen atoms are chemically equivalent. However, the effect of adduct formation on ring conformation, particularly with regard to the loss or retention of the cross-ring S-S interaction, and the possible formation of diadducts, for which there are three structural isomers, are of interest.

As indicated in Figure 3, the σ and σ* orbitals of the cross-ring S-S bonds in the $P^{V}_{2}N_{4}S_{2}$ ring are isolobal with the π and π* orbitals of a typical olefin.[17] Thus it is reasonable to surmise that these heterocycles might form η^2-S,S' complexes with metals, e.g. Pt, in which the bonding would be comparable to that found in the classic metal-olefin complexes.[18]

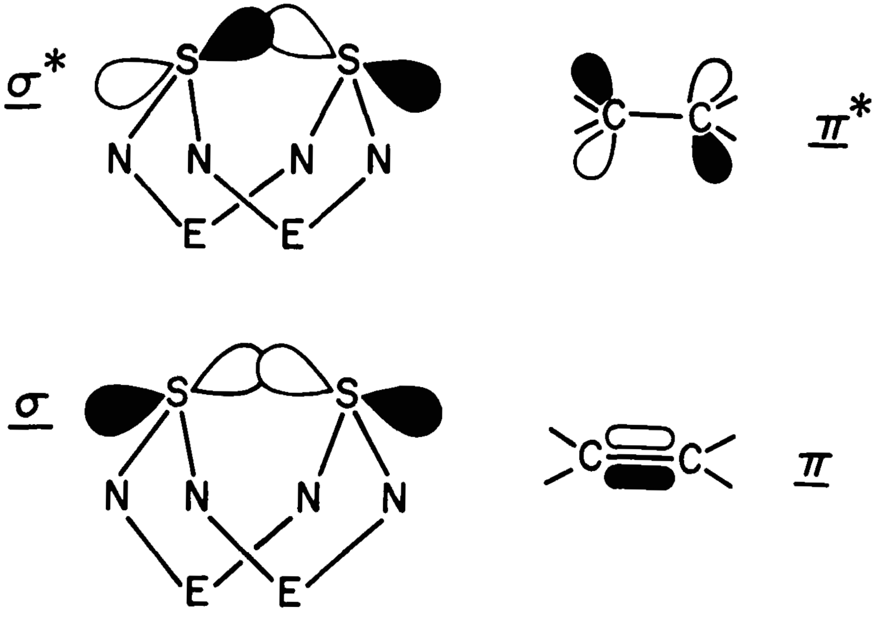


FIGURE 3. The σ and σ* orbitals of the cross-ring S-S bond in 3.

Lewis Base Behaviour of the 1,5-$P^V_2N_4S_2$ Ring

The monoadduct of 3 (R=Ph) with BCl_3 and monoprotonated and monomethylated derivatives are readily obtained as moisture-sensitive, pale yellow solids. The ^{31}P NMR spectra of the monoadducts show two doublets ($^4J_{PP}$ = 16-24 Hz) with chemical shifts in the range 83-95 ppm and 124-129 ppm (cf. 114 ppm for the free ligand).[11] The X-ray structure of the methylated derivative is illustrated in Figure 4. The folded conformation of the $P^V_2N_4S_2$ ring is retained and the cross-ring S-S interaction is shortened by ca. 0.1Å. Coordination also causes a lengthening of the P-N and, especially, the S-N bonds involving the coordinated nitrogen to 1.67 and 1.68 from 1.62 and 1.60Å, respectively.

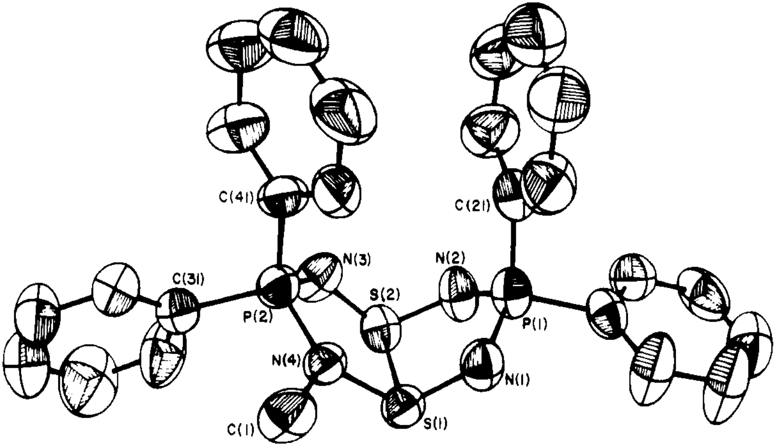
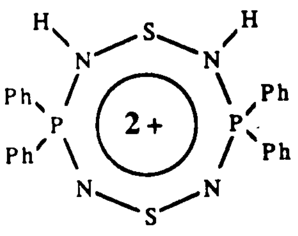
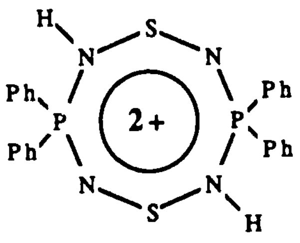


FIGURE 4. ORTEP plot for $1,5\text{-}Ph_4P_2N_4S_2Me^+CF_3SO_3^-$

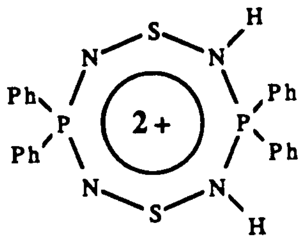
The ^{31}P NMR spectra of the diprotonated and dimethylated derivatives indicate that these adducts are a mixture of the isomers 6a or 6b and 6c. A singlet at 42-43 ppm is assigned to one of the symmetrically substituted isomers 6a or, more likely, 6b. A pair of doublets ($^4J_{PP}$ = 3-5 Hz) at 35-41 ppm and 42-50 ppm is attributed to the asymmetrically substituted isomer 6c.



6a



6b



6c

Ab initio HFS-SCF calculations of the interaction of the model system 1,5-$H_4P_2N_4S_2$ with two protons to give either 6b or 6c reveal little difference in the interaction energies consistent with the lack of regiospecificity observed in diadduct formation.

Platinum Complexes of the 1,5-$P^V_2N_4S_2$ Ring and Related Ligands

The reaction of $Pt(C_2H_4)(PPh_3)_2$ with 3 or 1,5-$(Me_2NC)_2N_4S_2$ [19] in toluene at 23°C produces yellow precipitates of 1:1 complexes (ca. 80% yield) in which ethylene has been displaced by the heterocyclic ligand.

$$Pt(C_2H_4)(PPh_3)_2 + E_2N_4S_2 \xrightarrow{-C_2H_4} \underset{(7a,\ E=Ph_2P;\ 7b\ E=Me_2NC)}{Pt(E_2N_4S_2)(PPh_3)_2} \qquad (5)$$

The ^{31}P NMR spectra for 7a and 7b show singlets at +15.3 ($^1J_{Pt-P}$=2850 Hz) and +19.9 ppm ($^1J_{Pt-P}$=3225 Hz), respectively, for the Ph_3P groups indicating that the heterocyclic ligands are bonded symmetrically to platinum. A singlet is also observed at +39.0 ppm (J_{Pt-P}=580 Hz) for the Ph_2P groups in 7a.

An X-ray structural determination of 7b has established the η^2-S,S' bonding mode for this complex.[12] The coordination around platinum is approximately square planar with <P-Pt-P = 102° and <S-Pt-S=79°. The S-S separation is elongated from 2.43Å in the free ligand[19] to 3.0Å in the complex.

Density functional calculations for the model compound Pt[1,5-$(H_2NC)_2N_4S_2$]$(PH_3)_2$ indicate that the bonding between platinum and the heterocyclic ligand is indeed analogous to that found in complexes of platinum with olefins.[20] The Pt-L bond energy for the model compound lies between those calculated for Pt[$C_2(CN)_4$]-$(PH_3)_2$ and Pt$(C_2H_4)(PH_3)_2$. The major component of this bonding involves back donation from metal d orbitals to the LUMO σ*(S-S) of the ligand.

ACKNOWLEDGEMENT

We thank Drs. A. Meetsma, J.C. van de Grampel and J.L. de Boer (University of Groningen) for the X-ray structures of **4a** and **4b** and Dr. J.F Richardson for the X-ray structure of 1,5-$Ph_4P_2N_4S_2Me^+$ $CF_3SO_3^-$. The financial support of NSERC (Canada) is also gratefully acknowledged.

REFERENCES

1. O.J. Scherer and R. Wies, Ang. Chem., Int. Ed. Engl., 10, 812 (1971).
2. J. Kuyper, J.J. Mayerle and G.B. Street, Inorg. Chem., 18, 2237 (1979).
3. A. Gieren, H. Betz, T. Hübner, V. Lamm, M. Herberhold and G. Guldner, Z. Anorg. Allg. Chem., 513, 160 (1984).
4. M. Herberhold and K. Schamel, J. Organometal. Chem., 346, 13 (1988).
5. F. Edelmann, C. Spang, M. Noltemeyer, G.M. Sheldrick, N. Keweloh and H.W. Roesky, Z. Naturforsch., 42b, 1107 (1987).
6. A. Gieren, T. Hübner, M. Herberhold, K. Guldner and G. Süss-Fink, Z. Anorg. Allg. Chem., 544, 137 (1987).
7. T. Chivers, C. Lensink and J.F. Richardson, Phosphorus and Sulphur, 30, 189 (1987).

8. T. Chivers, C. Lensink and J.F. Richardson, Organometallics, 6, 1904 (1987).
9. T. Chivers, C. Lensink, A. Meetsma, J.C. van de Grampel and J.L. de Boer, J. Chem. Soc., Chem. Commun., 335 (1988).
10. B. Wrackmeyer, K. Schamel, K. Guldner and M. Herberhold, Z. Naturforsch., 42b, 703 (1987).
11. T. Chivers, K.S. Dhathathreyan, S.W. Liblong and T. Parks, Inorg. Chem., 27, 1305 (1988).
12. J. Fait, personal communication.
13. N. Burford, T. Chivers, P.W. Codding and R.T. Oakley, Inorg. Chem., 21, 982 (1982).
14. N. Burford, T. Chivers and J.F. Richardson, Inorg. Chem., 22, 1482 (1983).
15. T. Chivers, S.W. Liblong, J.F. Richardson and T. Ziegler, Inorg. Chem., 27, 860 (1988).
16. T. Chivers, S.W. Liblong, J.F. Richardson and T. Ziegler, Inorg. Chem. in press.
17. R.T. Boeré, A.W. Cordes, S.L. Craig, R.T. Oakley and R.W. Reed, J. Am. Chem. Soc., 109, 868 (1987).
18. (a) M.J.S. Dewar, Bull. Soc. Chim. France, 18, C79 (1953).
    (b) J. Chatt and L.A. Duncanson, J. Chem. Soc., 103, 1540 (1981).
19. I. Ernest, W. Holick, G. Rihs, D. Schomburg, D. Wenkert and R.B. Woodward, J. Am. Chem. Soc., 103, 1540 (1981).
20. T. Ziegler, personal communication.