Preparation and X-Ray Structures of Tridentate (N,N,S) Complexes of the Diazene *trans*-[PhSNC(4-MeC$_6$H$_4$)N=NC(4-MeC$_6$H$_4$)NSPh] with Platinum and Palladium

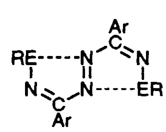
Tristram Chivers,* Katherine McGregor and Masood Parvez

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

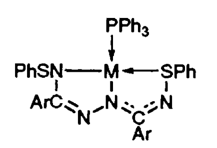
The reaction of *trans*-[PhSNC(MeC$_6$H$_4$)N=NC(MeC$_6$H$_4$)NSPh] with (C$_2$H$_4$)Pt(PPh$_3$)$_2$ or Pd(PPh$_3$)$_4$ in toluene produces the complexes M{PhSNC(MeC$_6$H$_4$)N–NC(MeC$_6$H$_4$)NSPh}(PPh$_3$) (M = Pt, Pd) in which the ligand is bonded to the metal in a tridentate (N,N,S) fashion and the diazine is formally reduced to an azine.

The chalcogen-substituted diazenes **1** are easily prepared by the reaction of ArCN$_2$(SiMe$_3$)$_3$ with RSeCl$_3$ (R = Me, Ph) or PhECl (E = S, Se).[1] These diazenes are expected to possess a rich coordination chemistry, owing to the chelating potential of nitrogen and chalcogen atoms. In general 1,2 diazenes form η^1 or bridged complexes *via* the lone pairs on nitrogen.[2] Metallacycle formation *via* orthometallation is also common for aromatic azo complexes. In some instances olefin-like η^2 bonding has been observed, notably in {(4-MeC$_6$H$_4$)$_3$P}$_3$-Ni(η^2-Ph$_2$N$_2$).[3] Therefore, it was of interest to initially explore the coordination chemistry of **1** with some zero-valent d^{10} systems such as Pt^0 and Pd^0. This communication describes the preparation and X-ray structures of the first metal complexes **2** of this unusual class of compounds.

A toluene solution (20 cm^3) of **1** (Ar = 4-MeC$_6$H$_4$; E = S) was added dropwise to an equimolar amount of (C$_2$H$_4$)Pt(PPh$_3$)$_2$, also in toluene solution (20 cm^3), at −78 °C. The solution was allowed to attain ambient temperature and stirred under argon for several hours. After such time the



1



2a; M = Pt, Ar = 4-MeC$_6$H$_4$
b; M = Pd, Ar = 4-MeC$_6$H$_4$

intense purple colour of the diazene had been replaced by a bright-yellow solution. The volume of this yellow solution was reduced to *ca.* 15 cm^3 and a yellow precipitate **2a** was isolated after 24 h at −18 °C in 65% yield. The $^{31}P\{^1H\}$ NMR spectrum† of **2a** in THF (tetrahydrofuran) solution shows a singlet at δ 19.51, with $^1J_{^{195}Pt^{31}P}$ 3612 Hz [*cf.* $(C_2H_4)Pt(PPh_3)_2$ in toluene: δ 35.6, $^1J_{^{195}Pt^{31}P}$ 3750 Hz)], whilst a ^1H NMR spectrum demonstrates the presence of two inequivalent *p*-tolyl groups in the ligand. Bright-yellow rectangular crystals of **2a** were obtained from a THF–hexanes solution at 23 °C, and were identified as the azine metallacycle Pt{PhSNC-(MeC_6H_4)N–NC(MeC_6H_4)NSPh}$(PPh_3)\cdot0.5$THF by X-ray crystallography.†

It is apparent from the structural determination (see Fig. 1) that the diazene ligand **1** has undergone a significant transformation upon coordination to platinum. The structure is comprised of discrete monomeric Pt{PhSNC(MeC_6H_4)N–NC(MeC_6H_4)NSPh}(PPh_3) molecules in which the ligand is attached to platinum *via* N(1), N(3) and S(1) in a tridentate fashion forming two planar five-membered rings. The consequent loss of the intramolecular S···N interactions found in derivatives of type **1** (E = S,Se) accounts for the dramatic difference in colour between **1** (R = 4-MeC_6H_4, E = S) and **2a**. The geometry of the formally Pt^{II} centre is square planar with small distortions due to constraints imposed by the bite angle of the ligand. The platinum atom deviates from the plane formed by N(1), N(3), S(1) and P(1) by 0.0914 Å, whilst the Pt–P, Pt–S and Pt–N distances fall within the expected ranges.[4] For comparison, *p*-tolyl-*o*-(2-sulfoxybenzyl)azobenzene undergoes a classic orthometallation with K_2PtCl_4 to give a metallaacycle in which the ligand is bonded to Pt^{II} in a tridentate (C,N,S) fashion and the –N=N double bond is retained.[4c]

Within the ligand there are a number of noteworthy changes. In addition to the conformational alteration imposed by the tridentate mode of coordination, the most striking feature is the N(2)–N(3) bond distance of 1.41(1) Å [*cf.* N=N of 1.263(4) Å in *trans*-[MeSeNC(Ph)N=NC(Ph)NSeMe] **1** (R = Me, E = Se)[5]], a value characteristic of an N–N single bond.[6,7] Furthermore, the C(7)–N(2) bond distance of 1.26(1) Å in **2a** signifies the presence of a C=N double bond [*cf.* the corresponding C–N distance of 1.433(5) Å in **1** (R = Me, E = Se)].[5] The N(3)–C(15) and C(15)–N(4) bond distances of 1.34(1) and 1.31(1) Å, respectively, indicate significant delocalization in the NCN segment of the second five-membered ring. Overall, the structural changes that occur on coordination of **1** (R = 4-MeC_6H_4, E = S) to platinum imply the formal reduction of the ligand and concomitant oxidation to Pt^{II}, *i.e.* an internal redox process.

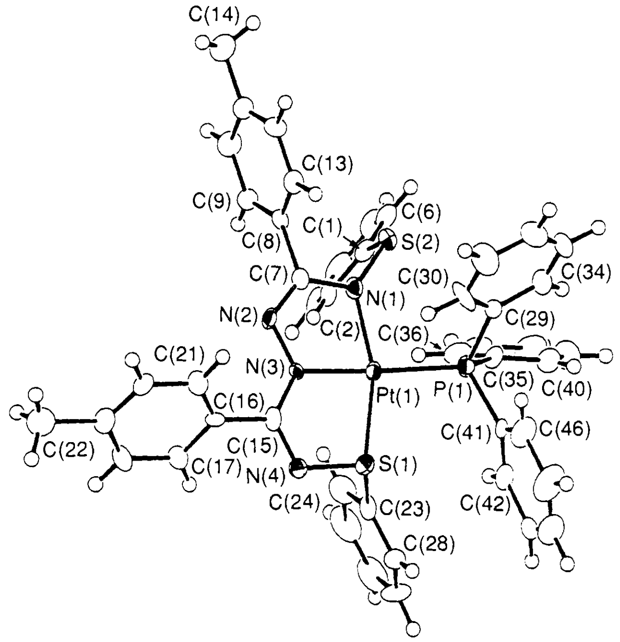


Fig. 1 ORTEP diagram for Pt{PhSNC(MeC_6H_4)N–NC-(MeC_6H_4)NSPh}(PPh_3), (**2a**, THF omitted); selected bond lengths (Å) and bond angles (°). Pt(1)–S(1) 2.266(3), Pt(1)–P(1) 2.279(3), Pt(1)–N(1) 2.031(8), Pt(1)–N(3) 1.987(7), S(1)–N(4) 1.725(8), S(2)–N(1) 1.682(8), N(1)–C(7) 1.41(1), N(2)–N(3) 1.41(1), N(2)–C(7) 1.26(1), N(3)–C(15) 1.34(1), N(4)–C(15) 1.31(1), S(1)–Pt(1)–P(1) 99.69(9), S(1)–Pt(1)–N(1) 160.0(2), S(1)–Pt(1)–N(3) 81.6(2), P(1)–Pt(1)–N(1) 99.9(2), P(1)–Pt(1)–N(3) 172.5(2), N(1)–Pt(1)–N(3) 78.5(3), Pt(1)–S(1)–N(4) 101.3(3), Pt(1)–N(1)–S(2) 128.4(4), Pt(1)–N(1)–C(7) 110.0(6), S(2)–N(1)–C(7) 119.0(7), N(3)–N(2)–C(7) 111.6(8), Pt(1)–N(3)–N(2) 117.0(5), Pt(1)–N(3)–C(15) 119.8(6), N(2)–N(3)–C(15) 122.9(7), S(1)–N(4)–C(15) 114.1(7), N(1)–C(7)–N(2) 122.8(9), N(3)–C(15)–N(4) 122.9(9).

The reaction of equimolar amounts of **1** (R = 4-MeC_6H_4, E = S) with $Pd(PPh_3)_4$ in toluene at −78 °C results in the isolation of red crystals of **2b** in 85% yield, which were identified as Pd{PhSNC(MeC_6H_4)N–NC(MeC_6H_4)NSPh}-$(PPh_3)\cdot1.5$ THF by spectroscopic‡ and X-ray crystallographic studies‡ An ORTEP plot of **2b** is shown in Fig. 2, illustrating the important features of **2b** together with selected bond distances and bond angles. It is apparent that a palladium(II) azine metallacycle analogous to **2a** has been formed, thus demonstrating the generality of the reaction for zerovalent platinum and palladium. There are no significant differences in either geometry or configuration between **2a** and **2b**. All bond distances and bond angles involving palladium lie within the expected ranges.[4b,8]

Compounds **2a** and **2b** both undergo reversible one-electron oxidations in acetonitrile at +0.66 and +0.62 V *vs.* SCE, respectively. The oxidations are believed to be ligand-based in

† *Crystal data* for $C_{48}H_{43}O_{0.5}N_4S_2PPt$: M = 974.08, monoclinic, space group $P2_1/c$, a = 14.234(5), b = 18.922(3), c = 16.032(3) Å, β = 105.19(2)°, V = 4167(1) $Å^3$, D_c = 1.553 g cm^{-3}, Z = 4, μ(Mo-Kα) = 3.533 mm^{-1}, F(000) = 1952. Data were collected on a Rigaku AFC6S diffractometer operating in the ω-2θ mode at −103.0 °C. Of the 7586 unique reflections collected (Mo-Kα radiation, λ = 0.71069 Å, graphite monochromator), 4117 were judged to be observed using the criterion $I > 3\sigma(I)$. Crystal dimensions 0.13 × 0.20 × 0.40 mm. The structure was solved by direct methods and was refined by full-matrix least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms to R = 3.8%, R_w = 3.1%. An absorption correction and allowance for anomalous dispersion were made. The data were corrected for Lorentz and polarization effects.

Crystal data for $C_{52}H_{51}O_{1.5}N_4S_2PPd$: M = 957.49, triclinic space group $P\bar{1}$, a = 13.334(6), b = 14.682(7), c = 12.861(6) Å, α = 111.32(3), β = 99.31(2), γ = 94.27(3)°, V = 2290(2) $Å^3$, D_c = 1.388 g cm^{-3}, Z = 2, μ(Mo-Kα) = 0.576 mm^{-1}, F(000) = 992. Data were collected on a Rigaku AFC6S diffractometer at −123.0 °C. Of the 6196 unique reflections collected (Mo-Kα radiation, λ = 0.71069 Å, graphite monochromator), 3323 were judged to be observed using the criterion $I > 3\sigma(I)$. Crystal dimensions 0.40 × 0.30 × 0.10 mm. The structure was solved by direct methods and was refined by full-matrix least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms to R = 5.0%, R_w = 4.9%. An absorption correction (DIFABS) and allowance for anomalous dispersion were made. The data were corrected for Lorentz and polarization effects.

Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *Selected spectroscopic data* for **2a**: ^{31}P NMR (THF): δ 19.51 (s), $^1J_{^{195}Pt^{31}P}$ 3612 Hz ^1H NMR ($CDCl_3$): δ 8.04–6.39 (m), C_6H_5 and $CH_3C_6H_4$, 33H; δ 3.76 (m), C_4H_8O; δ 2.35 (s), $CH_3C_6H_4$, 3H; δ 2.27 (s), $CH_3C_6H_4$, 3H; δ 1.86 (m), C_4H_8O. **2b**: ^{31}P NMR (THF): δ 25.69 (s), ^1H NMR ($CDCl_3$): δ 8.00–6.47 (m), C_6H_5 and $CH_3C_6H_4$, 33H; δ 2.36 (s), $CH_3C_6H_4$, 3H; δ 3.76 (m), C_4H_8O; δ 2.26 (s), $CH_3C_6H_4$, 3H; δ 1.86 (m), C_4H_8O. Satisfactory C,H,N analyses obtained for **2a** and **b**.

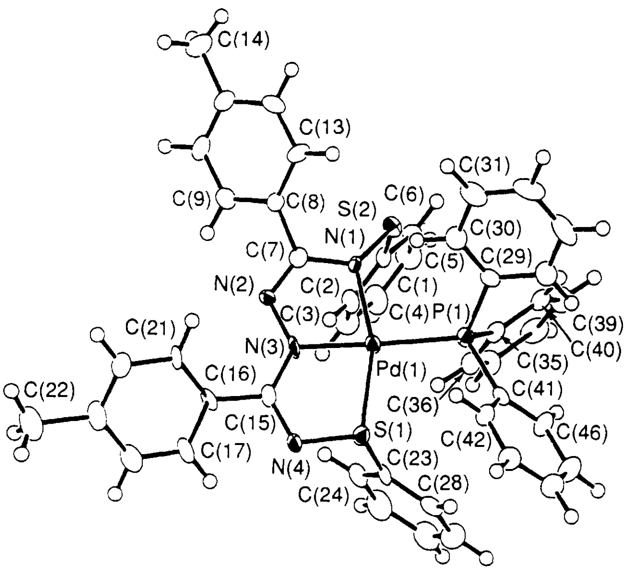


Fig. 2 ORTEP diagram for Pd{PhSNC(MeC_6H_4)N-NC(MeC_6H_4)NSPh}(PPh_3) (**2b**, THF omitted); selected bond lengths (Å) and bond angles (°). Pd(1)–S(1) 2.277(3), Pd(1)–P(1) 2.308(3), Pd(1)–N(1) 2.031(7), Pd(1)–N(3) 1.975(7), S(1)–N(4) 1.684(8), S(2)–N(1) 1.680(7), N(1)–C(7) 1.42(1), N(2)–N(3) 1.39(1), N(2)–C(7) 1.28(1), N(3)–C(15) 1.36(1), N(4)–C(15) 1.33(1), S(1)–Pd(1)–P(1) 101.53(10), S(1)–Pd(1)–N(1) 159.7(2), S(1)–Pd(1)–N(3) 81.1(2), P(1)–Pd(1)–N(1) 98.7(2), P(1)–Pd(1)–N(3) 177.4(3), N(1)–Pd(1)–N(3) 78.7(3), Pd(1)–S(1)–N(4) 101.8(3), Pd(1)–N(1)–S(2) 123.3(4), Pd(1)–N(1)–C(7) 109.6(6), S(2)–N(1)–C(7) 119.5(6), N(3)–N(2)–C(7) 111.3(8), Pd(1)–N(3)–N(2) 118.0(6), Pd(1)–N(3)–C(15) 120.6(6), N(2)–N(3)–C(15) 121.1(8), S(1)–N(4)–C(15) 115.2(6), N(1)–C(7)–N(2) 122.0(8), N(3)–C(15)–N(4) 120.7(8).

origin and the identification of the oxidised species produced is currently under investigation.

In conclusion, we have the demonstrated the potential of the unusual diazenes **1** as ligands, which combine both hard and soft donor atoms, by the preparation and structural characterization of the first metal complexes. The formation of the metallacycles **2a** and **2b** occurs *via* an internal redox reaction, resulting in the reduction of the diazene N=N double bond and subsequent formation of a metal azine species. This type of behaviour is rare for metal complexes of 1,2 diazenes[7,9] and the first example observed for complexes of platinum and palladium. Further studies of the coordination chemistry of **1** (R = 4-MeC_6H_4, E = S) and its selenium analogue with a wide range of transition metals are in progress.

We thank the NSERC (Canada) for financial support in the form of an operating grant (T. C.) and an International Fellowship (K. McG.). We also thank Professor A. S. Hinman and P. Wiebe for assistance with the electrochemical measurements.

Received, 5th February 1993; Com. 3/00729D

References

1 V. Chandrasekhar, T. Chivers, S. S. Kumaravel, M. Parvez and M. N. S. Rao, *Inorg. Chem.*, 1991, **30**, 4125.
2 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley Interscience, New York, 5th edn., 1987, p. 378.
3 S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, 1973, **57**, 389.
4 (*a*) T. Chivers, M. Edwards, P. N. Kapoor, A. Meetsma, J. C. van de Grampel and A. van der Lee, *Inorg. Chem.*, 1990, **29**, 3068; (*b*) R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1988, 803; (*c*) S. Chattopadhyay, C. Sinha, P. Basu and A. Chakravorty, *J. Organomet. Chem.*, 1991, **414**, 429.
5 V. Chandrasekhar, T. Chivers, J. F. Fait and S. S. Kumaravel, *J. Am. Chem. Soc.*, 1990, **112**, 5373.
6 F. W. B. Einstein, D. Sutton and K. G. Tyers, *Inorg. Chem.*, 1987, **26**, 111.
7 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 1469.
8 C. Kumar Pal, S. Chattopadhyay, C. Sinha and A. Chakravorty, *J. Organomet. Chem.*, 1992, **439**, 389; A. G. Orpen, L. Braummer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
9 H. Kisch, P. Reisser and F. Knoch, *Chem. Ber.*, 1991, **124**, 1143; H. Kisch, C. Kruger, H. E. Marcolin and A. X. Trautwein, *Z. Naturforsch. Teil B*, 1987, **42**, 1435; G. Avar, W. Russler and H. Kisch, *Z. Naturforsch. Teil B*, 1987, **42**, 1441.