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Inorganic Chemistry Communications 8 (2005) 610–613

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Synthesis and reactivity of an 2-azabutadiene-based π-conjugated dithioether: Formation of a *N,S*-ligated molybdenum chelate complex and *C,N,S*-pincer complexes of palladium and platinum

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Received 9 March 2005; accepted 22 March 2005
Available online 23 May 2005

Abstract

Nucleophilic attack of sodium isopropylthiolate on 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene [$Cl_2C{=}C(H){-}N{=}CPh_2$}] (**1**) affords the 2-azabutadiene derivative [$(i\text{-PrS})_2C{=}C(H){-}N{=}CPh_2$] (**2**). Upon irradiation of $Mo(CO)_6$ in THF in the presence of **2**, the chelate complex *cis*-[$(OC)_4Mo\{(i\text{-PrS})_2C{=}C(H){-}N{=}CPh_2\}$] (**3**) is obtained. Coordination on Mo occurs through the imine nitrogen and a thioether group. Polydentate dithioether **2** acts as *N,C,S*-pincer ligand after orthometallation reaction with Pd(II) or Pt(II). The molecular structures of **2** and (*C,N,S*)-[$(i\text{-PrS})_2C{=}C(H){-}N{=}C(Ph)C_6H_4)PtCl$] (**4b**) have been determined by X-ray diffraction studies.

Keywords: 2-Azabutadiene; Dithioether; Chelate complex; Cyclometallation; Platinum; Palladium; Molybdenum

In a precedent paper, we have exploited the presence of two reactive vinyl-chlorine bonds of [$Cl_2C{=}C(H){-}N{=}CPh_2$}] (**1**) [1] for oxidative addition reactions across low-valent metal centers to synthesize σ-alkenyl complexes *trans*-[$MCl\{(C(Cl){=}C(H){-}N{=}CPh_2)\}(PPh_3)_2$] (M = Pd, Pt) and the μ-vinylidene compound [$(PPh_3)ClPd\{\mu\text{-}(C{=}C(H){-}N{=}CPh_2)\}PdCl(PPh_3)_2$], ligated by a π-conjugated organic array [2]. In the context of our research on dithioether coordination chemistry [3–5], we were interested in functionalisation of **1** by thioether groups to assemble a polydentate ligand system possessing both sulphur and nitrogen donor sites [6].

With this goal in mind, we reacted **1** with an excess of thiolate in dry DMF. This led under mild conditions exclusively to the dithioether derivative [$(i\text{-PrS})_2C{=}C(H){-}N{=}CPh_2$] (**2**), consistent with formal substitution of the two chloro-substituents by SR^- on the vinylic C(3) atom. After workup, **2** was isolated as stable yellow crystalline solid with 55% yield.[1] Note that the regioselectivity of the nucleophilic attack of $i\text{-PrS}^-$ on C(3) contrasts with our finding that attack by sodium alkoxydes

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[1] Selected data for **2**: IR(KBr): *v*(C=C) 1555, *v*(C=N) 1523 cm^{-1}. ^1H NMR (acetone-d_6): δ 1.18 (d, 6H, ^3J = 6,7 Hz, $CH(CH_3)_2$), 1.31 (d, 6H, ^3J = 6.7 Hz, $CH(CH_3)_2$), 3.30 (sept, 1H, ^3J = 6.7 Hz, $CH(CH_3)_2$), 3.91 (sept, 1H, *J* = 6.8 Hz, $CH(CH_3)_2$), 7.11 (s, 1H, H_{vinyl}), 7.15–7.80 (m, 10H, phenyl). Anal. Calcd. for $C_{21}H_{25}NS_2$: C, 70.94; H, 7.09; N, 3.94. Found: C, 70.71; H, 7.15; N, 3.70%.

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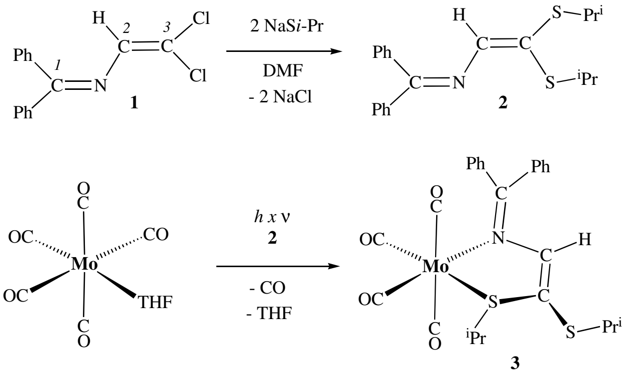
doi:10.1016/j.inoche.2005.03.016



Scheme 1.

occurs at the more electrophilic C(2) atom [7] (see Scheme 1).

As evidenced by an X-ray diffraction study, the *transoid* conformation of the 2-azabutadiene chain of precursor **1** is also found in the solid-state structure of **2** (see Fig. 1). Compared with the C=C bond distance found for **1**, that of **2** is slightly elongated [1.319(3) vs. 1.337(5) Å], while the imine bond distances are almost the same (1.293(3) vs. 1.288(5) Å) in both compounds.[2] One of the phenyl groups attached on C(1) is roughly coplanar with the diene unit. However, the dihedral angle between the C10–C15 ring in **2** with the C1–N–C2–C3 chain is equal to 27.9(2)°, making so in doubt the existence of a strong π-conjugation.

Upon irradiation of $Mo(CO)_6$ in THF, first the adduct $[Mo(CO)_5THF]$ was prepared in situ, then the irradiation was continued in the presence of **2** until complete disappearance of the ν(CO) vibrations due to $[Mo(CO)_5THF]$. After work-up, a red solid was isolated, whose elemental analysis and IR data were consistent with formation of a chelate complex *cis*-$[(OC)_4Mo\{(i\text{-}PrS)_2C{=}C(H){-}N{=}CPh_2\}]$ **3**.[3] Our suggestion of a less strained five-membered *S,N*-chelation instead of a strained *S,S*-chelation is furthermore corroborated by the observation of three very distinct carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectrum at δ 209.1, 216.2 and 223.2. Since one resonance corresponds to two equivalent axial carbonyls, the quite diverging chemical shifts of the two remaining equatorial carbonyls is indicative for a dissymmetric *S,N*-chelation [8].

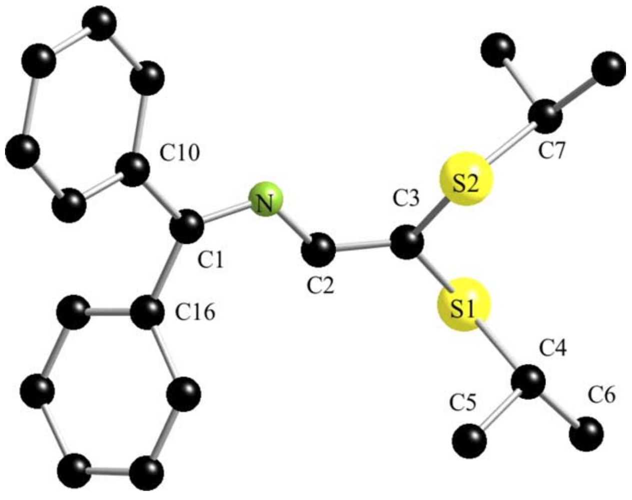
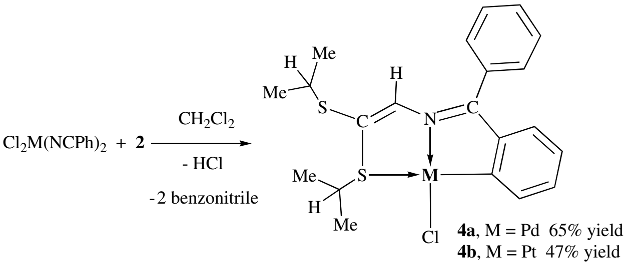


Fig. 1. View of the crystal structure of **2**. Selected bond lengths [Å] and angles [°]: C(7)–S(2) 1.817(4), C(4)–S(1) 1.823(4), C(3)–S(1) 1.766(4), C(3)–S(2) 1.752(4), C(3)–C(2) 1.337(5), N–C(2) 1.397(4), N–C(1) 1.288(4) and S(1)–C(3)–S(2) 119.9(3), C(2)–C(3)–S(1) 117.9(3), C(2)–C(3)–S(2) 122.1(3), N–C(2)–C(3) 122.7(4), C(1)–N–C(2) 119.5(4), N–C(1)–C(16) 124.6(4), N–C(1)–C(10) 117.9(4), C(16)–C(1)–C(10) 117.5(4).



Scheme 2.

The air-stable cyclometallated complexes *C,N,S*-$[(i\text{-}PrS)_2C{=}C(H){-}N{=}C(Ph)C_6H_4)MCl]$ (**4a**, M = Pd; **4b**, M = Pt) were formed after stirring under reflux a dichloromethane solution of $[MCl_2(NCPh)_2]$ overnight in the presence of 1.1 equiv. of **2** according to Scheme 2.[4]

In addition to a dative S (*thioether*) and N (*imine*) bond, a covalent σ–M–carbon bond has been formed between the metal center and a phenyl group. This orthometallation reaction with concomitant elimination of HCl leads to a *C,N,S*-pincer coordination of the

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[2] Crystal data for **2**: (293(2) K) $C_{21}H_{25}NS_2$: $M_r = 355.54$, monoclinic, $P2_1/n$, $a = 11.192(3)$, $b = 9.003(2)$, $c = 20.434(4)$ Å, $\beta = 93.75(2)°$, $V = 2054.5(8)$ Å^3, $\mu = 0.261$ mm^{-1}, $Z = 4$; Mo K α = 0.71073 Å, Enraf–Nonius CAD4; structure refined by full-matrix least-squares on observed F^2 to give final indices $R_1 = 0.0489$ and $wR_2 = 0.1060$; GOF = 1.112.

[3] Selected data for **3**: IR(CCl_4): ν(CO) 2017 m, 1896 s, 1861 s cm^{-1}. ^1H NMR (acetone-d_6): δ 1.29 (d, 6H, $^3J = 6.7$ Hz, $CH(CH_3)_2$), 1.39 (d, 6H, $^3J = 6.6$ Hz, $CH(CH_3)_2$), 3.51 (sept, 1H, $^3J = 6.7$ Hz, $CH(CH_3)_2$), 3.91 (sept, 1H, $J = 6.6$ Hz, $CH(CH_3)_2$), 7.20–7.65 (m, 11H, phenyl + H_{vinyl}). Anal. Calcd. for $C_{25}H_{29}MoNS_2$: C, 50.23; H, 4.43; N, 2.48. Found: C, 53.18; H, 4.36; N, 2.52%.

[4] Selected data for **4a**: ^1H NMR ($CDCl_3$): δ 1.39 (d, 6H, $^3J = 6.7$ Hz, $CH(CH_3)_2$), 1.65 (d, 6H, $^3J = 6.8$ Hz, $CH(CH_3)_2$), 3.69 (sept, 1H, $^3J = 6.7$ Hz, $CH(CH_3)_2$), 3.93 (sept, 1H, $J = 6.8$ Hz, $CH(CH_3)_2$), 6.84–8.32 (m, 10H, phenyl + H_{vinyl}). Anal. Calcd. for $C_{21}H_{24}$ ClNPdS$_2$: C, 50.81; H, 4.87; N, 2.82. Found: C, 50.42; H, 4.46; N, 2.53%. Selected data for **4b**: ^1H NMR ($CDCl_3$): δ 1.28 (d, 6H, $^3J = 6.2$ Hz, $CH(CH_3)_2$), 1.61 (d, 6H, $^3J = 5.9$ Hz, $CH(CH_3)_2$), 3.40 (m, 1H, $CH(CH_3)_2$), 4.05 (m, 1 H, $CH(CH_3)_2$), 6.81–7.97 (m, 10H, phenyl + H_{vinyl}). Anal. Calcd for $C_{21}H_{24}ClNPtS_2$: C, 50.81; H, 4.87; N, 2.82. Found: C, 50.42; H, 4.46; N, 2.53%.

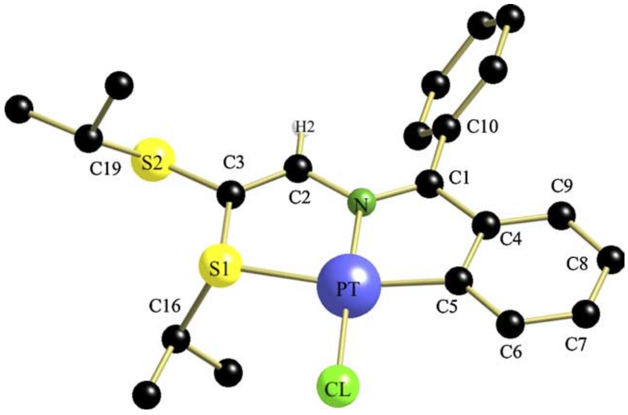

Fig. 2. View of the crystal structure of **4b**. One of the two independent molecules present in asymmetric unit is shown. Selected bond lengths [Å] and angles [°]: Pt–Cl 2.3067(9), Pt–S(1) 2.3642(9), Pt–C(5) 2.002(3), Pt–N 1.990(3), C(3)–S(1) 1.779(4), C(3)–S(2) 1.757(4), C(3)–C(2) 1.343(5), N–C(2) 1.400(4), N–C(1) 1.315(5) and N–Pt–Cl 177.03(9), N–Pt–S(1) 85.77(9), S(1)–Pt–C(5) 166.6(1), N–Pt–C(5) 81.0(1), Cl–Pt–S(1) 96.08(3), C(5)–Pt–Cl 97.2(1), N–C(2)–C(3) 120.7(3), C(1)–N–C(2) 124.3(3), S(2)–C(3)–S(1) 120.3(2).

2-azabutadiene ligand [9–11]. This terdentate bonding mode of **2** was furthermore evidenced by an X-ray diffraction study performed on a single crystal of *C,N,S*-[$(i\text{-PrS})_2C{=}C(H){-}N{=}C(Ph)C_6H_4)PtCl$] **4b**.[5] The quasi-square planar geometry around Pt (slight deformation of D_{2d} type symmetry) consists of two 5-membered platinacycles, which are annelated by a common Pt–N edge [Pt–N 1.990(3) Å], and a chloro ligand in *trans*-position relative to the imine-N atom [N–Pt–Cl = 177.03(9)°]. The root mean square deviation from the plane fitted through N–S(1)–Cl–Pt–C(5) amounts to 0.04 Å (mean of two independent molecules). Due to the formation of a Pt–carbon σ-bond between Pt and C(5), the aromatic ring C(4)–C(9) is almost coplanar with the π-conjugated C(3)–C(2)–N–C(1) array, the dihedral angle being close to 2° (mean for two molecules) (see Fig. 2).

In conclusion, the easy preparation of **2** allows a promising development in organometallic chemistry. As shown in the case of the molybdenum complex **3**, this ligand system is prone to ligate to metal centers both via the soft thioether function or the harder imine nitrogen. The potential of this polydentate ligands to act as *C,N,S*-pincer ligand after orthometallation reaction with Pd(II) and Pt(II) has also been demonstrated. In a forthcoming paper we will report on the reactivity of these pincer complexes towards insertion reactions of unsaturated organic molecules [12,13], their electronic structures and their photophysical properties [14–22].

Appendix A. Supplementary data

Crystallographic data for the structural analyses of compounds **2** and **4b** have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 265265 and 265266, respectively). Copies of this information may be obtained free of charge from: The director, CCDC, Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). The UV-vis spectra of **1** and **2** can be found in the online version at doi:10.1016/j.inoche.2005.03.016.

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[5] Crystal data for **4b** (at 110(1) K) $C_{21}H_{24}ClNPtS_2$: $M_r = 585.07$, triclinic, $P\bar{1}$, $a = 9.4840(2)$, $b = 11.9340(3)$, $c = 19.5280(6)$ Å, $\alpha = 96.695(1)°$, $\beta = 95.568(1)°$, $\gamma = 99.445(1)°$, $V = 2150.1(1)$ Å^3, $Z = 4$; Nonius Kappa CCD, Mo Kα = 0.71073 Å, $\mu = 6.850$ mm^{-1}; structure refined by full-matrix least-squares on observed F^2 to give final indices $R_1 = 0.0273$ and $wR_2 = 0.0669$, GOF = 1.005. There are two independent molecules in the asymmetric unit without significant geometrical differences.

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