Reactivity Studies on Tantalocene(sulfido)hydride $Cp'_2Ta(=S)H$ ($Cp' = Bu^tC_5H_4$): Cycloaddition on and Protonation of the Ta=S Ligand

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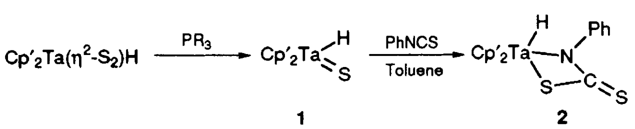
Reactions of the tantalocene(sulfido)hydride $Cp'_2Ta(=S)H$ with PhNCS and HCl exhibit a surprisingly low metal-hydride reactivity; the Ta=S bond being involved either in a [2 + 2] cycloaddition or a protonation.

Interest in the chemistry of metallocenes containing doubly bonded chalcogene ligands[1] is particularly focused on oxo compounds.[2–4] The metal–sulfur double bond of group 4 metallocene sulfides may also exhibit exceptional reactivity.[5] A peculiar property of the higher group 5 metallocene sulfides (M = Nb, Ta) is that they contain an additional hydride ligand.[6] A typical example is $Cp'_2Ta(\eta^2\text{-}S_2)H$ (Cp' = $Bu^tC_5H_4$), which readily undergoes a desulfurisation reaction in the presence of phosphine, resulting in the formation of the monosulfur complex **1**, $Cp'_2Ta(=S)H$ (Scheme 1). The combination of a nucleophilic sulfur ligand with a hydride ligand may be expected to form a difunctional metallocene. Characteristic of the M–H moiety (M = Nb, Ta) are insertion reactions with heterocumulenes,[7] elemental sulfur[8] and activated alkynes.[9] We now report the first results on the reaction

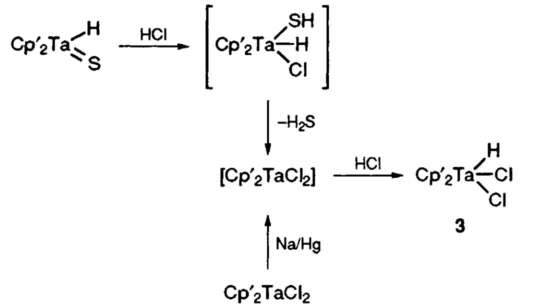


Scheme 1

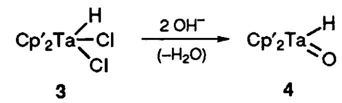
of **1** with PhNCS and HCl, showing that the Ta=S bond may also be activated.

Complex **1** reacts with phenylisothiocyanate in boiling toluene to form a cream-coloured product. After chromatography and crystallisation from chloroform colourless crystals of **2** are obtained in 45% yield (Scheme 1). The spectroscopic† data are consistent with a product resulting from a cycloaddition of the ligand to the Ta=S double bond, only one isomer being formed. In the IR spectrum, the disappearance of the Ta=S absorption was concomitant with strong absorptions at 1483 and 1379 cm^{-1}, characteristic of a conjugated N–C–S bond system. Another striking feature is the downfield shift of the TaH resonance in the ^1H NMR spectrum from δ 2.79 in $Cp'_2Ta(S_2)H$ to δ 7.91. A similar shift is observed for **1** and may be characteristic of Ta^V complexes containing electron-withdrawing ligands. There is no proof for the insertion into

† *Spectroscopic data* for **2**: ^1H NMR (400 MHz, CD_3COCD_3): δ 1.17 (s, 18H, Bu^t), 5.31 (q, 2H, C_5H_4), 5.54 (q, 2H, C_5H_4), 6.00 (q, 2H, C_5H_4), 6.40 (q, 2H, C_5H_4), 6.94–7.19 (m, 5H, C_6H_5), 7.91 (s, 1H, TaH). IR(CsI): ν/cm^{-1} = 1842 (ν_{TaH}). FDMS (*m/z*): 591.3 ($C_{25}H_{32}TaNS_2$ requires 591.62).



Scheme 2



Scheme 3

the tantalum–hydride bond as observed in the reaction of heteroallenes with monohydride-tantalum(III) complexes.[7] An X-ray analysis (Fig. 1) confirms that 2 contains a planar *N,S*-coordinated dithiocarbamate.‡ However, there is only indirect evidence for the hydride: the orientation of the chelate is such that the N atom is close to the plane defined by the two ring centres and Nb. The remarkable selectivity of the chelate formation might have been initiated by a frontal attack of the C=N bond at the metal, followed by a [2 + 2] cycloaddition. Such a mechanism has been well documented for the insertion of alkynes into the M–L bond of bent metallocenes.[10] A lateral attack would have lead to the orientation of S next to the hydride but is probably hindered by the Bu^t substituents.

Another aspect of the reactivity of 1 is illustrated by its behaviour towards HCl (Scheme 2). The ABCD pattern of the aromatic protons in the ^1H NMR spectrum§ indicates that product 3 is in agreement with an unsymmetric distribution of the hydrido and the two chloro ligands. Thus, the formation of 3 seems to occur by an electrophilic attack of H^+ at sulfur, followed by a reductive elimination of H_2S and then by an oxidative addition of HCl. The nature of 3 is supported by an independent experiment: the 16e complex Cp'_2TaCl, prepared by reduction of Cp'_2TaCl_2 with 1 equiv. of Na/Hg, also reacts with HCl to afford a compound with similar properties.

As the latter reaction provides an easy access to 3, the reactivity of this new type of Ta^V compounds was investigated by treatment of 3 with 10% aq. KOH. From this reaction the

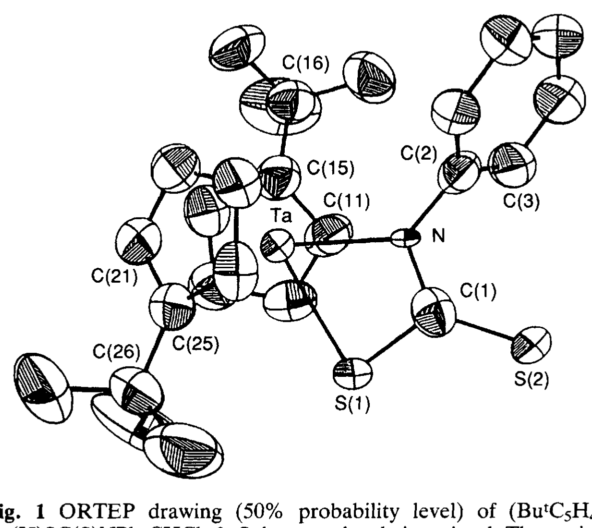


Fig. 1 ORTEP drawing (50% probability level) of $(Bu^tC_5H_4)_2Ta(H)SC(S)NPh{\cdot}CHCl_3$ 2. Solvent molecule is omitted. The position of the hydride follows from stereochemical considerations (see text). Selected bond lengths (Å) and angles (°): Ta–S(1) 2.567(3), Ta–N 2.203(8), S(1)–C(1) 1.73(1), S(2)–C(1) 1.68(1), N–C(1) 1.33(1); S(1)–Ta–N 62.4(3), Ta–S(1)–C(1) 82.3(4), Ta–N–C(1) 107.4(7), Ta–N–C(2) 131.6(6), C(1)–N–C(2) 120.4(8), S(1)–C(1)–N 107.9(7), S(1)–C(1)–S(2) 122.8(6), N–C(1)–S(2) 129.3(8).

oxo-hydrido-tantalocene 4, another representative of doubly bonded main group ligand, was obtained in good yields (Scheme 3). IR, ^1H NMR and mass spectroscopy data¶ are close to those of $(C_5Me_5)_2Ta(=O)H$, which has been characterised X-ray crystallographically.[2] Finally, it should be noted that compounds 3 and 4 as well as 1 and 2 exhibit ^1H NMR resonances that suggest a proton rather than hydride character for the TaH group. The reaction potential of this novel class of compounds is under investigation.

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References

1 J. E. Nelson, G. Parkin and J. E. Bercaw, *Organometallics*, 1992, **11**, 2181.
2 G. Parkin, A. van Asselt, D. J. Leahy, L. Whinnery, N. G. Hua, R. W. Quan, L. M. Henling, W. P. Schaeffer, B. D. Santarsiero and J. E. Bercaw, *Inorg. Chem.*, 1992, **31**, 82.
3 G. Parkin and J. E. Bercaw, *J. Am. Chem. Soc.*, 1989, **111**, 391.
4 R. S. Pilato, C. E. Housmekerides, P. Jernakoff, D. Rubin, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1990, **9**, 2333.
5 M. J. Carney, P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1992, **11**, 761; C. E. Housmekerides, D. L. Ramaga, C. M. Kretz, J. T. Shoutz, R. S. Pilato, G. L. Geoffroy, A. L. Rheingold and B. S. Haggerty, *Inorg. Chem.*, 1992, **31**, 4453.
6 H. J. Bach, H. Brunner, J. Wachter, M. M. Kubicki, J. C. Leblanc, F. Volpato, B. Nuber and M. L. Ziegler, *Organometallics*, 1992, **11**, 1403.
7 J. F. Leboeuf, J. C. Leblanc and C. Moise, *J. Organomet. Chem.*, 1987, **335**, 331.
8 H. Brunner, G. Gehart, W. Meier, J. Wachter and B. Nuber, *J. Organomet. Chem.*, in the press.
9 J. Amaudrut, J. C. Leblanc, C. Moise and J. Sala-Pala, *J. Organomet. Chem.*, 1985, **295**, 167.
10 S. Nakamura and S. Otsuka, *J. Am. Chem. Soc.*, 1972, **94**, 1886; *J. Mol. Catal.*, 1975, **1**, 285.

‡ *Spectroscopic data* for 3: ^1H NMR (400 MHz, CD_3COCD_3): δ 1.38 (s, 18H, Bu^t), 5.16 (q, 2H, C_5H_4), 5.59 (q, 2H, C_5H_4), 5.75 (q, 2H, C_5H_4), 6.25 (q, 2H, C_5H_4), 11.30 (s, 1H, TaH). IR (CsI): ν/cm^{-1} = 1631 (ν_{TaH}), 275 (ν_{TaCl}). FDMS (*m/z*): 494.2 ($C_{18}H_{27}Ta^{35}Cl_2$ requires 494.1).

§ *Crystal data* for 2: $C_{26}H_{34}NS_2Ta$, M = 712.0, monoclinic space group $P2_1/c$ (No. 14), a = 12.121(2), b = 16.288(3), c = 15.458(4) Å, β = 110.83(2)°, V = 2852.3 Å^3, Z = 4, D_c = 1.378 g cm^{-3}, μ (Mo-Kα) = 39.589 cm^{-1}. Intensity data were measured on an Enraf-Nonius CAD4 Diffractometer. The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier and full-matrix least-squares methods. 2 crystallises with one solvent molecule ($CHCl_3$) per formula unit. The hydrogen atoms (except the hydride and that of $CHCl_3$) were included in calculated positions. The final R and R_w factors are 0.046 and 0.052 for 3843 reflections with $I \geq 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ *Spectroscopic data* for 4: ^1H NMR (400 MHz, CD_3COCD_3): δ 1.31 (s, 18H, Bu^t), 5.62 (q, 4H, C_5H_4), 5.97 (q, 2H, C_5H_4), 6.10 (q, 2H, C_5H_4), 6.97 (s, 1H, TaH). IR (CsI): ν/cm^{-1} = 1819 (ν_{TaH}), 850 (ν_{TaO}). FDMS (*m/z*): 440.3 ($C_{18}H_{27}TaO$ requires 440.15).