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Preliminary communication

Synthesis, structure, and stability of cyclopentadienyl(triphenylphosphine)(α-benzenesulfonylalkyl)nickel complexes

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Abstract

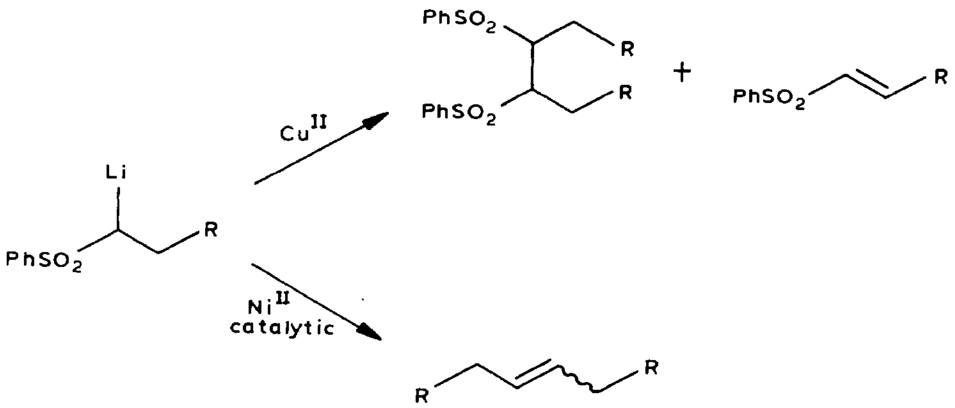
The title complexes have been prepared in moderate yields by reaction of α-sulfonyl carbanions with $Cp(PPh_3)NiCl$; the crystal structure of two of these complexes shows that the nickel atom is linked to the α-carbon of the sulfonyl group and there is no interaction between the metal and the SO_2 moiety. When their solution in benzene are warmed to 90 °C, these complexes very cleanly yield the corresponding α,β-unsaturated sulfone (E isomer). An efficient method of dehydrogenating secondary alkyl sulfones is reported.

α-Benzenesulfonyl carbanions are oxidized by stoichiometric amounts of copper(II) [1] or iron(III) [2] salts to give either the disulfones via dimerization or the corresponding α,β-unsaturated sulfones via dehydrogenation. On the other hand, the same carbanions, when treated with catalytic amounts of nickel(II) salts in refluxing THF yield the symmetric dimeric olefins [3] (eq. 1).

In order to get a better understanding of this versatile reactivity, we decided to prepare and study α-benzenesulfonylalkylnickel complexes; complexes of these type have not been reported before. The cyclopentadienyl(triphenylphosphine)nickel system, which yields easily prepared and fairly stable alkyl derivatives [4], was chosen.

Preparation of the complexes

Reaction of α-lithiated sulfones with cyclopentadienyl(triphenylphosphine)nickel



(1)

chloride [5] in THF gave greenish complexes, which can be isolated and purified by chromatography or crystallisation (eq. 2).

$$\mathrm{CpNi(PPh_3)Cl + PhSO_2CH(Li)R \rightarrow CpNi(PPh_3)CH(R)SO_2Ph}$$

$$\begin{array}{l}(\mathrm{Ia{:}\ R = H, 45\%;} \\ \mathrm{Ib{:}\ R = C_2H_5, 35\%;} \\ \mathrm{Ic{:}\ R = n\text{-}C_6H_{13}, 41\%;} \\ \mathrm{Id{:}\ R = n\text{-}C_{11}H_{23}, 60\%} \\ \mathrm{Ie{:}\ R = CH{=}C(CH_3)_2, 57\%)}\end{array}$$

A competitive reaction, assumed to be oxidation of the carbanion by the nickel(II) complex, together with decomposition of the reduced cyclopentadienyl(triphenylphosphine)nickel moiety, seems to be responsible of the limitation of the yields. Attempts to increase the yield of the complexes by replacing triphenylphosphine by the more electron-releasing tributylphosphine were successful: a 70% yield was obtained in the preparation of $\mathrm{CpNi(PBu_3)CH_2SO_2Ph}$, and 62% for $\mathrm{CpNi(PBu_3)CH(n\text{-}C_{11}H_{23})SO_2Ph}$. Unfortunately, up to now, these tributylphosphinenickel complexes have been obtained only as waxy solids.

Structure of the complexes

Crystallisation of the nickel derivatives of phenyl methyl sulfone, Ia (from toluene/hexane) and phenyl prenyl sulfone, Ie, (from THF/hexane) gave crystals suitable for the X-ray structure determinations.

Ia (see Fig. 1) is monoclinic, $P2_1/c$, a 9.211(3), b 28.011(6), c 20.465(15) Å, β 93.92(2); $Z = 8$.

Ie (see Fig. 2) is orthorhombic, $P2_12_12_1$, a 10.734(4), b 14.535(5), c 23.111(9) Å, $Z = 4$.

7121 independent reflections, collected with a Philips PW 1100 for Ia, 3560 measured with a Nonius CAD 4 for Ie, Mo-K_α radiation. Least square refinements in six blocks converged at R 3.81%, R_w 5.14%, using 5144 reflections with $F \geqslant 3\sigma(F)$, for Ia. For **Ie**, R 3.77%, R_w 4.12% using 2079 reflections. All atoms, except hydrogen were given anisotropic thermal parameters. For Ie, the correctness of the enantiomeric description was checked. Calculations were carried out with CRYSTALS [6]. Structure analysis revealed the presence of a toluene molecule in Ie.

Tables of atomic coordinates and bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.

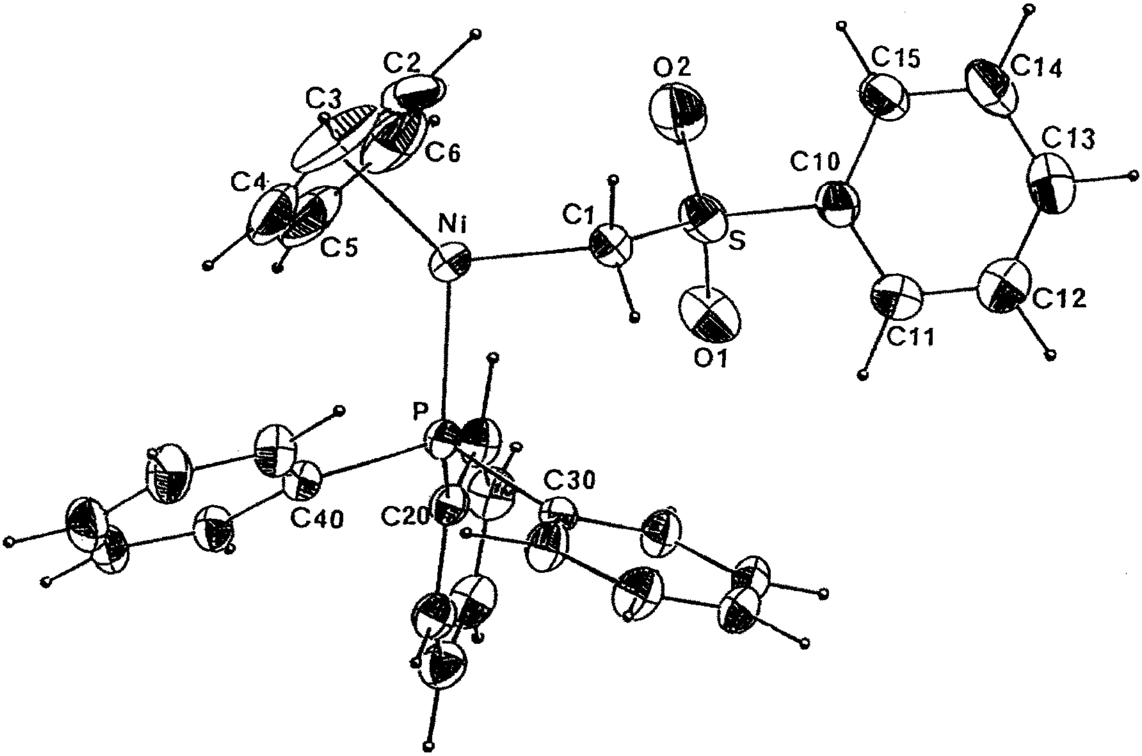


Fig. 1. A perspective view of one molecule of Ia. Selected bond lengths (Å) are:

Ni–C(1)	1.956(4)	Ni′–C′(1)	1.959(4)
Ni–C(Cp, average)	2.058(5)–2.126(5)	Ni′–C′(CP, average)	2.056(5)–2.115(6)
Ni–P	2.150(1)	Ni′–P′	2.150(1)
S–O(1)	1.442(3)	S′–O′(1)	1.445(3)
S–O(2)	1.443(3)	S′–O′(2)	1.444(4)
S–C(1)	1.748(4)	S′–C′(1)	1.739(4)
S–C(10)	1.777(4)	S′–C′(10)	1.783(4)

Atoms of the second independent molecule of the asymmetric unit are indicated by ′.

In the solid state the nickel atom is linked to the carbon and is quite far away from the oxygens of the sulfonyl group. The same situation was previously described [7] for a palladium derivative of phenyl methyl sulfone. The C–Ni bond length is 1.956 Å in **Ia**, and 1.981 Å in **Ie**, and can be compared with the C–Pd bond (2.042 Å) in the cyclooctadiene(benzenesulfonylmethyl)palladium chloride [6], or the C–Ni bond (1.972 Å) in the related $[CpNi(PPh_3)CH_2]_2S^+CH_3$ described by Barefield [8].

The situation is quite different for lithiated α-sulfonyl carbanions, for which it has been shown by Boche [9] and Gais [10] that there is no lithium–carbon bond, and that the metal is linked to one of the oxygen atoms. So it thus appears that the transmetalation corresponding to the formation of the nickel complex involves an important change in the geometry of the sulfonyl neighbourhood; for instance, the C–S bond length in lithiated phenyl methyl sulfone is 1.608 Å [10a], considerably shorter than in the nickel (1.748 Å) or palladium (1.756 Å) [7] analogues.

Thermal stability of these complexes

When a benzene solution of the σ-allylic complex Ie is warmed at 90 °C in an

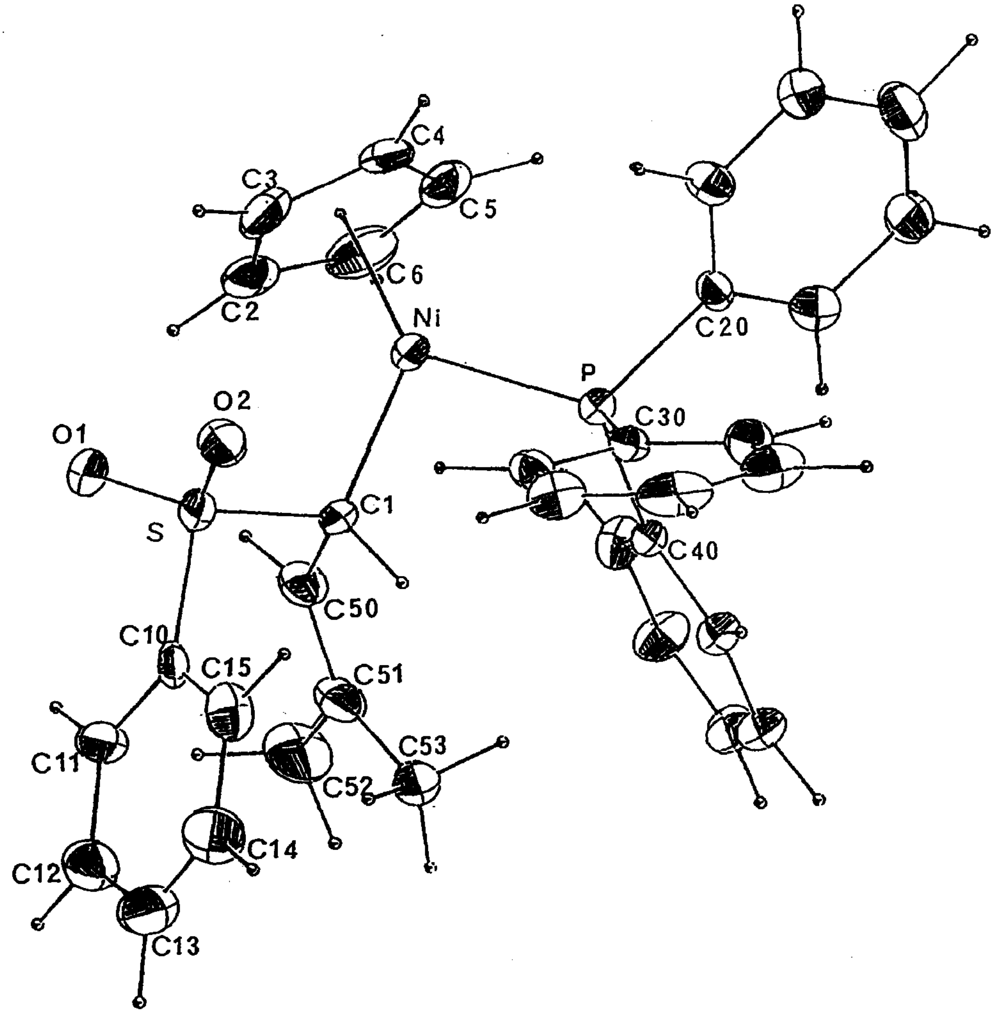
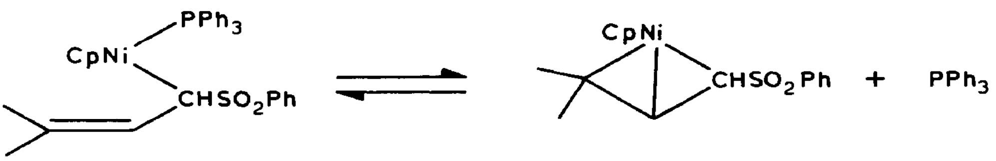


Fig. 2. A perspective view of one molecule of Ie. Selected bond lengths (Å) are:

Ni–C(1)	1.981(6)	Ni–P	2.147(2)
Ni–C(Cp, average)	2.094(8)–2.162(9)	C(1)–S	1.786(7)
C(1)–C(50)	1.49(1)	C(50)–C(51)	1.35(1)
C(51)–C(52)	1.50(1)	C(51)–C(53)	1.47(1)
S–O(1)	1.444(6)	S–O(2)	1.443(6)
S–C(10)	1.761(9)		

NMR tube, formation of the π-allylic complex If is observed, together with decoordination of the phosphine ligand. This new solution is stable at 90 °C for a few hours, but decomposes slowly during several ten hours; neither dehydrogenation nor dimerization of the prenylsulfonyl moiety were observed, but when the NMR tube was cooled reformation of complex **Ie** was observed. The equilibrium between the two allylic complexes and coordinated or free phosphine is very temperature dependent.

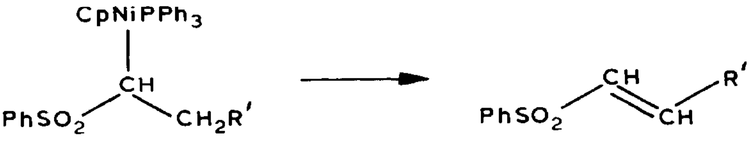
This good thermal stability of complexes Ie, If contrasts with the reactivity of lithiated phenyl prenyl sulfone, which is readily dimerized by transition metal salts



Ie	Equilibrium	If
70%	20°C	30%
20%	90°C	80%

even at low temperatures [1,2], and reacts with nickel acetylacetonate (2%) in refluxing THF to give 2,7-dimethyl-2,4,6-octatriene [3].

As expected, benzene or toluene solutions of complexes Ib–Id are less thermally stable; complete decomposition is observed after two days at 90 °C. The vinylic sulfone can be isolated in a 85% yield with pure *E* stereochemistry.

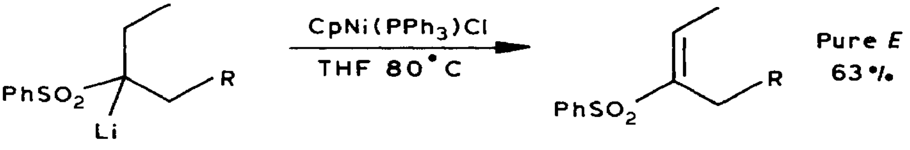


pure *E* 85%

This well-known *β*-elimination of alkylnickel complexes provides a very efficient preparation of *α*,*β*-unsaturated sulfones, which have been shown to be most valuable reagents in many organic transformations [11]. This reaction constitutes an alternative to the copper acetate promoted dehydrogenation [1b,c] of *α*-sulfonyl carbanions to vinylic sulfones.

This dehydrogenation reaction via the nickel complexes can be performed without isolation of the intermediate complex. Thus, reaction of *α*-lithiated phenyl heptyl sulfone with Cp(PPh$_3$)NiCl in boiling THF gave, after four days, the *α*,*β*-ethylenic sulfone in 55% yield, together with 45% of starting saturated sulfone. Increasing the amount of nickel complex from one to two equivalents led to a 66/34 mixture. In view of the greater availability of cupric acetate than of the nickel complex, and the difference in yield, dehydrogenation of primary alkyl phenyl sulfones with copper(II) carboxylate [1b,c] will generally be preferred.

This is no longer true for secondary alkyl sulfones, for which cupric acetate has been shown to be a very poor reagent. Reaction of the lithiated anion of 3-benzenesulfonylpentane with one equivalent of cyclopentadienyl(triphenylphosphine)nickel chloride in refluxing THF gave a 63/37 mixture of pure *E* *α*-*β* unsaturated sulfone and starting material:



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11 See, in ref. [1c], ref. 16 to 19.