Journal of Organometallic Chemistry 695 (2010) 2377–2380

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Communication

Synthesis of a new camphor derived P,S(O) ligand. The importance of C—H···O bonding in the ligand exchange reactions with $Co_2(\mu$-alkyne$)(CO)_6$ complexes

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ARTICLE INFO

Article history:
Received 15 June 2010
Received in revised form
9 July 2010
Accepted 15 July 2010
Available online 23 July 2010

Keywords:
P,S ligands
Pauson–Khand reaction
Sulfoxides
Weak hydrogen bonds

ABSTRACT

Herein we describe the synthesis and structure of a new chiral bidentate P,S(O) ligand containing a stereogenic sulfur atom. We also report on its coordination properties to acetylene dicobalt hexacarbonyl complexes, providing X-ray structures of the ligand alone and of a ligand–cobalt complex. Solid state structure of complex **4** shows the formation of a weak C—H···O bond between a polarised methine group in the ligand and a sulfone group on the alkyne that helps to stabilize the bridged coordination mode.

1. Introduction

Bidentate ligands are paramount in modern organometallic chemistry and are widely used in synthesis and catalysis. Numerous structures based on P,N, P,P and P,S coordination are available for metal coordination [1].

While studying the intermolecular asymmetric Pauson–Khand (PK) reactions [2,3] we reported several useful bidentate P,S ligands that provide diastereoselective bridged coordination with the dicobaltcarbonyl–alkyne complexes [4,5]. Reaction of diastereomerically pure complexes with a reactive olefin (e.g. norbornadiene) under thermal or NMO-promoted conditions yields the PK adducts with high enantiomeric excess (Scheme 1). This highly stereoselective cycloaddition process is probably due to the hemilabile nature of the ligand, which directs coordination of the olefin to a single cobalt atom.

The first generation of chiral ligands [4] was derived from natural products (PuPHOS and CamPHOS; Fig. 1). These ligands, react with acetylene cobalt complexes to yield only moderate selectivities on ligand exchange reactions with cobalt–alkyne complexes. Interestingly, we were able to improve selectivity in the ligand exchange process by exploiting a non-classic C—H···O hydrogen bonding interaction between a hydrogen bond acceptor placed in the alkyne complex and a polarised methine group in the auxiliary (Fig. 1) [6].

We recently described a second generation of chiral bidentate P,S ligands: *N*-phosphinosulfinamides (PNSO ligands) [5a–c] and sulfinylmethylphosphines (PCSO ligands) [5d] which relied on a stereogenic sulfur atom (Fig. 1). These new classes of ligands behave in front acetylene dicobaltcarbonyl complexes as a P,S bridging ligands and provide high levels of selectivity. The chiral centre directly coordinated to the metal atom may be crucial for the outcome. All these reported methodologies have proven invaluable in the preparation of enantiopure biologically active cyclopentanic compounds [7].

Assessing these results, we reasoned that it would be interesting to study the combination of a chiral carbon backbone with sulfur chirality. Herein we describe the synthesis and coordination properties of a new hybrid ligand that combines a camphor skeleton with a stereogenic sulfur atom.

2. Results

We envisioned that diastereoselective oxidation of the sulfur atom in CamPHOS would afford a straightforward route to a new chiral sulfoxide that could be used as a ligand. In addition, CamPHOS has been shown to provide effective C—H···O hydrogen bonding interactions when a hydrogen bond acceptor is in place [6]. We attempted to oxidise the sulfur atom in CamPHOS using *m*-CPBA, which has been used successfully in related oxidations [8]. We thought that the chiral structure of the auxiliary could direct

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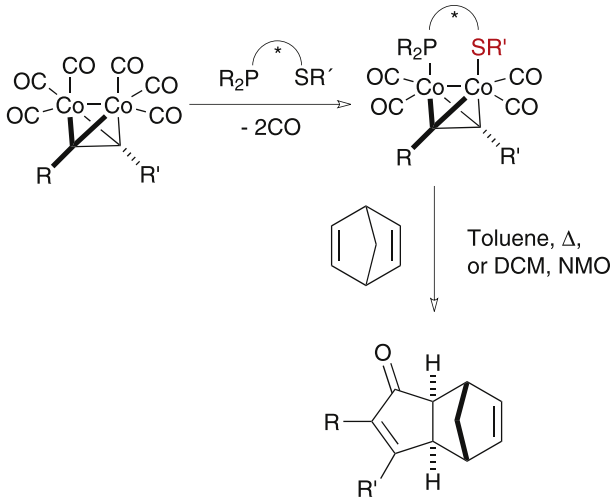
doi:10.1016/j.jorganchem.2010.07.021



Scheme 1. Use of bidentate P,S ligands in the asymmetric Pauson–Khand reaction.

sulfur oxidation to yield one of the two possible isomers and that protection of the phosphorus atom with borane would prevent its oxidation.[9] As expected, reaction of CamPHOS-BH_3 (**1**) with *m*-CPBA in dichloromethane furnished sulfoxide **2** as a single diastereomer (as revealed by ^{1}H NMR analysis of the crude) in 78% yield after purification (Scheme 2).

X-ray diffraction analysis of ligand **2** enabled us to establish its structure: we observed that the oxygen atom of the sulfoxide is in the equatorial position (S_R-configuration). Steric shielding of the gem-dimethyl group in the camphor structure prevents oxidation of the axial *S*-lone pair (Fig. 2).

We then studied the reactivity of ligand **2** with acetylene dicobalt complexes. Thermal reaction of **2** with terminal alkyne complexes (Phenylacetylene and TMS-acetylene) in the presence of DABCO provided complex reaction mixtures of bridged and unbridged complexes (only P-coordination) as shown by IR analysis. Despite our efforts we were unable to shift the equilibrium towards the bridged species. CO removal by purging with vacuum and argon refilling did not affect the reaction, while extended heating led to product decomposition.

We hypothesised that the steric hindrance from the camphor scaffold was preventing complete coordination to yield the bridged P,S complex. Unlike the CamPHOS and PuPHOS, the sulfur atom in ligand **2** cannot coordinate to the metal cluster through its equatorial lone pair which is oxidized. Whilst coordination through the oxygen of the sulfoxide to yield a P,O bridge has been described in other cobalt clusters with different oxidation states [10], based on our experience, this was unlikely for cobalt(0)-alkyne complexes [11].

At this point we thought that an extra bonding interaction could enhance coordination for ligand **2** in a bridging fashion. The methine

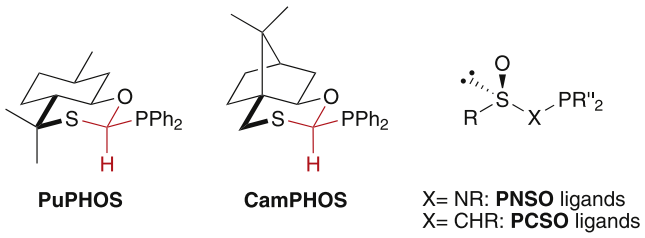
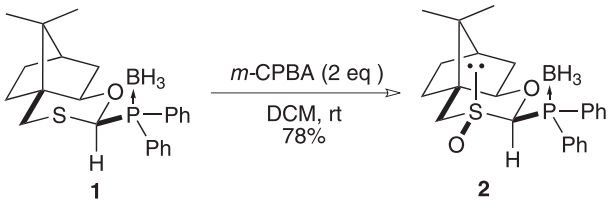


Fig. 1. Bidentate chiral ligands used in the Pauson–Khand reaction. The polarised methine groups responsible for C–H···O hydrogen bonding are shown in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Scheme 2. Synthesis of ligand **2**.

group contained in **2** should be even more acidic than in the parent CamPHOS ligand due to the presence of the sulfoxide, and thus, their H-bond donor abilities should be enhanced. With this purpose, we then proceeded to react ligand **2** with the dicobalt hexacarbonyl complex of bis-*tert*-butylsulphonylethyne, **3** [12]. This alkyne complex contains two sulfone units that can act as H-bond acceptor groups. Moreover, the intrinsic symmetry of **3** should provide a single isomer upon complexation of **2**, simplifying the analysis of the reactions mixture. We were pleased to find that after 5 h of heating a mixture of complex **3**, ligand **2** and DABCO in toluene (70 °C), a single red cobalt complex was formed in 85% yield (Scheme 3). IR and ^{1}H NMR data were consistent with the formation of a tetracarbonyl complex (**4**). Moreover, we were able to grow single crystals (ethyl acetate/pentane mixtures) suitable for X-ray analysis (Fig. 3).

The unit cell contains two independent molecules (a and b) with slightly different conformations of the ligand. Additionally the elementary cell contains one disordered molecule of n-pentane. Fig. 3 shows only one of the two different molecules in the cell (molecule a; see SI for a plot of both structures and all structural parameters). As expected, the ligand is coordinated to the metal cluster through the P and S atoms forming a five-membered ring in a half-chair conformation. In both structures the distance S–Co is 2.20 Å, similar to those previously reported, and the distance P–Co is 2.23 Å. As coordination of the sulfur atom through an equatorial position in a chair conformation is no longer possible, the oxathiane ring in the ligand moiety adopts a highly strained boat-twisted conformation to allow coordination, displacing the oxygen to an axial position.

As intended a non-classical hydrogen bond interaction between the methane and oxygen in a sulfone group is present and contributes

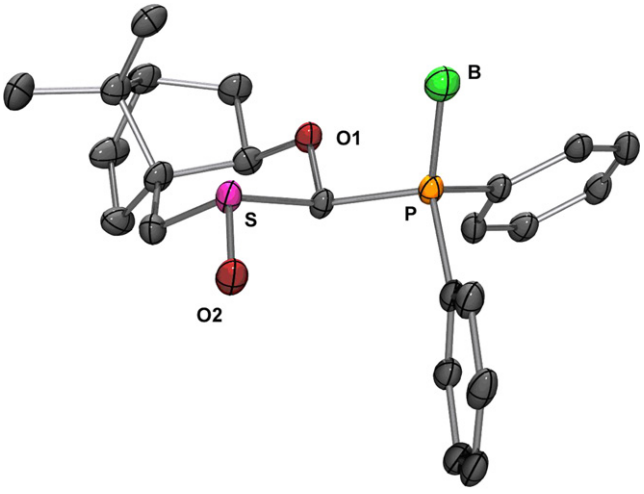
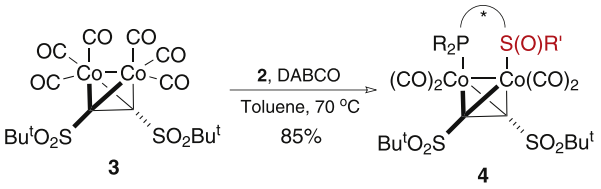


Fig. 2. ORTEP plot of the crystal structure of ligand **2**. Thermal ellipsoids are shown at 50% probability. B green, P orange, S violet, O red, C gray. Hydrogen atoms have been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Scheme 3. Reaction of ligand **2** with bis-*tert*-butylsulphonylethyne dicobaltcarbonyl complex. DABCO = 1,4-diazabicyclo[2.2.2]octane.

to the stability of the bridged complex. In molecule A the distance O(9a)-H is 2.54(1) Å and the angles θ (C–H···O) and ϕ (H···O–S) are 134.4(5)° and 126.3(5)°. In molecule B the distance O(2a)–H is 2.49(1) Å and the angles θ (C–H···O) and ϕ (H···O–S) are 132.3(5)° and 129.2(5)°. All these values are consistent with a hydrogen bond interaction according to literature. This attractive interaction may be a key factor for the formation of complex **4** since it might compensate energetically the penalty paid for the strained conformation that the ligand has to adopt for sulfur coordination [13].

In conclusion we have synthesised a new bidentate P,S(O) ligand, that combines a stereogenic sulfur atom and the chiral camphor scaffold. We have shown that the presence of hydrogen bond within the structure allowed the ligand to coordinate dicobalt–alkyne complexes in a bridged fashion, even when this coordination mode confers a great strain to the ligand structure. These results highlight the importance to anticipate weak interactions in ligand design in order to stabilize a particular coordination mode.

3. Experimental

3.1. General

All reactions were conducted under nitrogen or argon atmosphere. ^{1}H NMR spectra were referenced relative to TMS or solvent residual peak in the case of benzene. ^{13}C NMR spectra were referenced relative to residual solvent peaks. ^{31}P spectra were referenced with an external H_3PO_4 sample. The carbon signals corresponding to the cluster carbons in cobalt complexes do not show up in the ^{13}C spectra and have been omitted. Carbon multiplicities have been assigned by gradient heteronuclear single quantum correlation experiments (gHSQC). Melting points have been determined by differential scanning calorimetry (DSC) using a Mettler Toledo DSC or on a Büchi melting point B-540 instrument. Toluene was distilled from molten sodium, and methylene chloride was distilled from CaH_2. Silica gel used for filtration and flash chromatography of cobalt complexes was previously washed through with Et_2O. CamPHOS–borane complex and dicobalt hexacarbonyl complexes were obtained according to known procedures [4b,6a].

3.2. (−)-(1S,3R,4S,6R,8R)-4-diphenylphosphino-11,11-dimethyl-5-oxa-3-thiotricyclo[6.2.1.0^{1,6}] undecane S-oxide P-borane complex (**2**)

CamPHOS-BH_3 complex (400 mg, 1.00 mmol) were dissolved in 20 mL of dichloromethane. The solution was cooled to 0 °C and 70% *m*-CPBA (490 mg, 2.0 mmol) in dichloromethane (25 mL) were added drop wise. The mixture was allowed to reach room temperature and stirred overnight. The mixture was then transferred to a separatory funnel and washed with $NaHCO_3$ sat (2 × 25 mL) and brine (25 mL). The organic extracts were washed over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting white foam was purified by flash column chromatography (SiO_2/Ethyl acetate: hexanes, 1:1) to yield **2** (335 mg, 78%) as a white foam. Mp: 188–189 °C. $[\alpha]_D = -87.9$ (c 1.0, $CHCl_3$). IR (KBr): ν_{max} 2956, 2388, 1653, 1559, 1436 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80–1.40 (br. m, 3H, BH_3) 0.88 (s, 3H), 1.01 (s, 3H), 1.05–1.15 (m, 1H), 1.45–1.55 (m, 1H), 1.57–1.93 (m, 5H), 2.95 (dd J = 14.0 and 0.5 Hz, 1H), 3.06 (d, J = 14.0 Hz, 1H), 3.96 (dd, J = 1.0 and 8.0 Hz, 1H), 5.16 (d, J = 5.0 Hz, 1H), 7.10–7.60 (m, 6H), 7.70–7.85 (m, 4H) ppm. ^{13}C NMR (100 MHz,

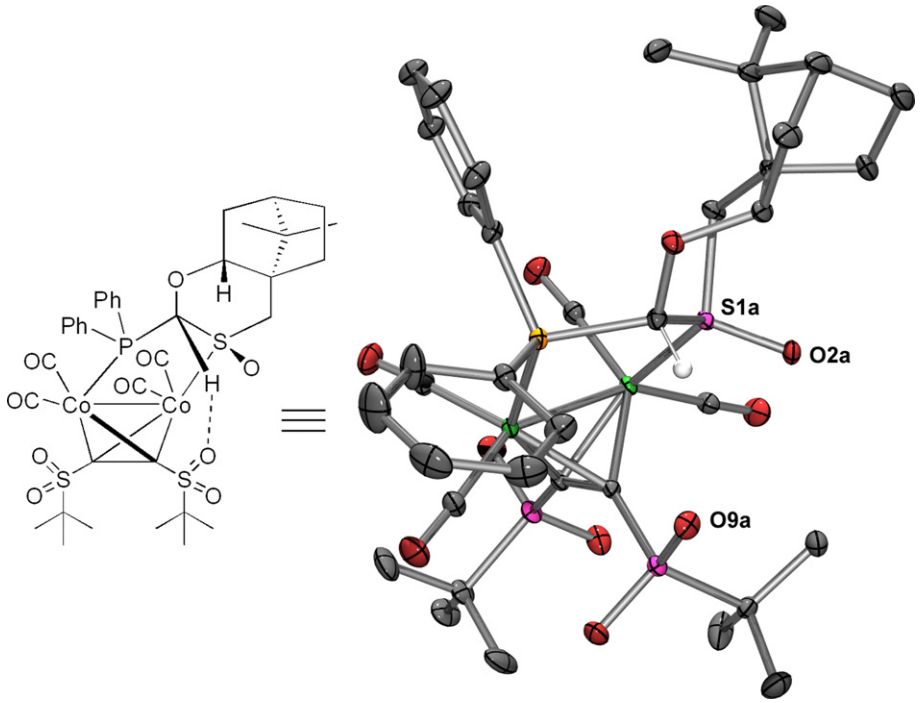


Fig. 3. ORTEP plot of crystal structure of **4**. Thermal ellipsoids are shown at 50% probability; Co green P orange, S violet, O red, C gray. Only the hydrogen responsible for the C–H···O interaction is depicted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

$CDCl_3$) δ 20.1 (CH_3), 21.3 (CH_3), 27.5 (CH_2), 33.0 (CH_2), 37.6 (CH_2), 44.0 (CH), 46.4 (C), 48.6 (CH_2), 48.7 (C), 86.6 (d, $J_P = 7.0$ Hz, CH), 97.0 (d, $J_P = 42.0$ Hz, CH), 125.3 (d, $J_P = 54.5$ Hz, C), 125.9 (d, $J_P = 54.5$ Hz, C), 128.9 (d, $J_P = 10.$ Hz, CH), 129.2 (d, $J_P = 10.0$ Hz, CH), 132.0 (d, $J_P = 3.5$ Hz, CH), 132.4 (d, $J_P = 3.5$ Hz, CH), 133.4 (d, $J_P = 9.0$ Hz, CH), 133.5 (d, $J_P = 9.0$ Hz, CH) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 20.0 (m) ppm. MS (CI, CH_4) $m/e = 413$ ($[M + H]^+$, 52%), 412 ($[M]^+$, 37%), 411 ($[M - H]^+$, 100%), 399 ($[M - BH_3]^+$, 95%), 383 ($[M - BH_3 - CH_3]^+$, 100%). EA: Calc. for $C_{23}H_{30}BO_2PS$: C 67.00, H 7.33, S 7.78; found C 67.23, H 7.43, S 7.40.

3.3. $Co_2(\mu$-t-BuSO$_2$-C$_2$SO$_2$t-Bu)(CO)$_4(\mu$-C$_{23}$H$_{27}$O$_2$PS) (**4**)

Dicobalt hexacarbonyl complex of bis-*tert*-butylsulfonylethyne **3** (80 mg, 0.14 mmol), compound **2** (62 mg, 0.14 mmol) and DABCO (25 mg, 0.21 mmol) were placed in a Schlenk flask under argon atmosphere. Dry toluene (4 mL) was then added and the mixture was heated to 70 °C. CO was eliminated from the reaction media by periodic vacuum/argon refill cycles. After 5 h solvent was eliminated by distillation under reduced pressure and the residue purified by flash column chromatography (SiO_2/Ethyl acetate: hexanes, 20:80) to obtain **4** (107 mg, 85%) as a red solid. IR (KBr): ν_{max} 2930, 2065, 2945, 2019,1437, 1287, 1107 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ −0.30 (s, 3H), 0.36 (s, 3H), 0.72 (m, 1H), 0.87–0.93 (m, 1H), 1.20–1.45 (m, 4H), 1.58 (s, 9H), 1.76 (s, 9H), 1.76 (m, 1H), 2.24 (d, $J = 14.0$ Hz, 1H), 3.08 (d, $J = 14.0$ Hz, 1H), 4.07 (m, 1H), 6.91–6.96 (m, 4H), 7.05 (m, 2H), 7.16 (s, 1H), 7.46–7.60 (m, 4H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ 14.2 (C), 18.2 (CH_3), 19.9 (CH_3), 22.7 (CH), 24.9 (3×CH_3), 25.5 (3×CH_3), 27.0 (CH_2), 32.3 (CH_2), 37.2 (CH_2), 43.6 (CH), 71.1 (C), 48.2 (C), 55.7 (CH_2), 60.1 (C), 62.1 (C), 62.9 (C), 82.7 (CH), 105.7 (d, $J_P = 20.0$ Hz, CH), 128.9 (d, $J_P = 10.5$ Hz, CH), 130.4 (CH), 130.6 (C), 130.9 (C), 131.4 (CH), 132.0 (d, $J_P = 10$ Hz, CH), 136.0 (d, $J_P = 10$ Hz, CH). ^{31}P NMR (121 MHz, C_6D_6): δ −42.1 ppm. MS (FAB$^+$–NBA) $m/e = 810$ ($[M - 3CO]^+$, 7%), 710 ($[M + H - 4CO]^+$, 100%) EA: Calc. for $C_{37}H_{45}Co_2O_{10}PS_3$ C 49.67, H 5.07, S 10.75; found C 49.61, H 5.25, S 10.42.

Acknowledgments

We thank Ministerio de Ciencia e Innovación (MICINN, CTQ2008-00763) and Generalitat de Catalunya (AGAUR, SGR2009-901) for financial support.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.jorganchem.2010.07.021.

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[13] Unfortunately Pauson–Khand reaction of complex **4** with norbornadiene did not provided the expected cyclopentenone. Internal alkynes are much less reactive than the terminal ones (see Ref. [5c]). The presence of bulky *tert*-butylsulfony groups attached to the alkyne prevents olefin insertion in compound **4**.