Synthesis of sydnone complexes with C–Pd and C–Pt σ-bonds. Application of palladium salts for the preparation of 4-alkenylsydnones

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Abstract

4-Bromo-3-phenylsydnone (SydnBr) reacts with complexes $[Pd(PPh_3)_4]$ and $[Pt(PPh_3)_4]$ at room temperature to give $[MBr(Sydn)(PPh_3)_2]$ (M = Pd, Pt). Reaction of 4-chloromercurio-3-phenylsydnone (SydnHgCl) with electron-deficient olefins yields *trans*-isomers of 4-alkenylsydnones, (E)-SydnCH=CHX (X = COMe, CO_2Me, Ph, CN, carboranyl).

Introduction

One of the methods to prepare heterocyclic compounds containing a carbon–transition metal (Ni, Pd, Pt) σ-bond is the oxidative addition of heteryl halides to phosphine complexes of M^0. The nickel compounds $[NiX(R)(PR'_3)_2]_n$ ($n = 1$, X = Cl, R = C_9H_6N-C^8; $n = 2$, X = Cl, Br, R = μ-C_5H_4N-C^2) containing quinoline and pyridine derivatives as ligands [1,2], the platinum compound $[PtCl(C_5H_4N$-$C^2)(PPh_3)_2]$ with 2-pyridyl ligand [3], the palladium and the platinum compounds $[MCl(C_5H_3N$-$(6$-$Cl)$-$C^2)(PR_3)_2]$ (M = Pd, Pt; PR_3 = PPh_3, $PMePh_2$, dppe) with the 6-chloropyridyl ligand [4], and the palladium complex with phenothiazinone [5] have been described.

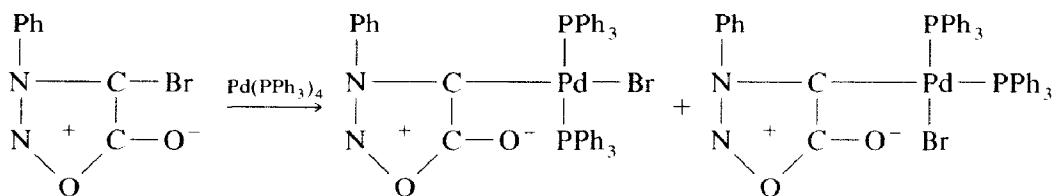We recently obtained the complex $[NiX(Sydn)(PR_3)_2]$ (X = Cl, R = Et; X = Br, R = Et, Ph), which is the first example of nickel coordination compounds containing a mesoionic group as a ligand [6]. Compounds containing a C–Pd bond are formed by cross-coupling reaction of 4-cuprio-3-phenylsydnone with aryl and vinyl halides in the presence of $[Pd(PPh_3)_4]$ [7].

Results and discussion

Synthesis of [MBr(Sydn)(PPh$_3$)$_2$] (M = Pd, Pt)

We have found that 4-bromo-3-phenylsydnone reacts smoothly with $[Pd(PPh_3)_4]$ to give the oxidative-addition product $[PdBr(Sydn)(PPh_3)_2]$. The reaction proceeds
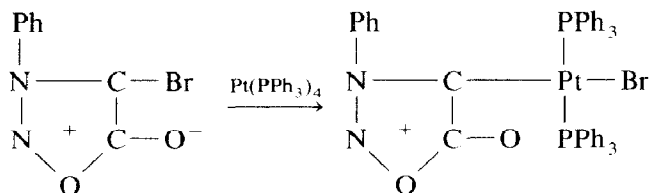
at room temperature during 20 min. The compounds obtained are yellow crystals that are poorly soluble in organic solvents.

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Ph                    Ph      PPh3        Ph      PPh3
|                     |       |           |       |
N————C——Br  Pd(PPh3)4  N————C————Pd—Br   N————C————Pd—PPh3
|    |       ———————>   |    |   |      +  |    |   |
N  + C—O⁻              N  + C—O⁻ PPh3      N  + C—O⁻ Br
 \  /                   \  /                \  /
  O                      O                   O
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The reaction was carried out in THF or benzene, and a mixture of *cis-* and *trans-*isomers is obtained. The ^{31}P NMR spectra in $CDCl_3$ show doublets of an AB-system at 19.20 and 29.39 ppm with J_{AB} 21.5 Hz, and a singlet at 21.50 ppm that corresponds to the *cis-* and *trans-*configuration. The proportion of each isomer in the reaction mixture can be determined from the ratio of integral intensities of signals in the ^{31}P NMR spectra and is dependent on the solvent: 6.7 : 1.0 in THF and 1.0 : 1.6 in benzene (*cis* : *trans*, respectively). The presence of two isomers is also reflected in the IR spectral data; Pd–Br stretching bands are found at 244 and 216 cm^{-1} for the mixture.

Up to now only *trans-*products were obtained from the oxidative addition of heteryl halides to M^0 complexes (M = Ni, Pd, Pt) [1–5].

In contrast to the palladium complex the reaction of 4-bromo-3-phenylsydnone with $[Pt(PPh_3)_4]$ is slow in THF or in benzene and yields only the *trans-*complex.

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Ph                    Ph      PPh3
|                     |       |
N————C——Br  Pt(PPh3)4  N————C————Pt—Br
|    |       ———————>   |    |   |
N  + C—O⁻              N  + C—O  PPh3
 \  /                   \  /
  O                      O
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In the ^{31}P NMR spectrum in $CDCl_3$ a singlet observed at 11.60 ppm is accompanied by satellites of the ^{195}Pt–^{31}P coupling (J_{Pt-P} = 3573 Hz) which indicates the equivalence of the two phosphorus nuclei. The IR spectra show Pt–Br stretching bands at 209 cm^{-1}.

The ^{1}H NMR data of the complexes obtained are less informative and in both cases the protons of phenyl groups of sydnone and phosphines appear in spectra as overlapping multiplets at 7–8 ppm.

Synthesis of (E)-SydnCH=CHX (X = COMe, CO_2Me, Ph, CN, carboranyl)

Arylmercury halides react with activated olefins in the presence of palladium salts to give substituted styrenes [8]. 4-Chloromercurio-3-phenylsydnone is one of the most available sydnone derivatives, however its reactivity has scarcely been investigated [9].

We have found [10] that SydnHgCl reacts with electron-deficient terminal olefins in the presence of $LiPdCl_3$ to give the vinyl substitution products of 1-(4-sydnonyl)-2-substituted ethylenes (Table 1). Methyl vinyl ketone, methyl acrylate, styrene, acrylonitrile and vinyl carboranes were used as the olefin component.

Table I

Analytical, HNMR, and mass-spectral data, melting points, and of the products

Compound	Anal. (Found (calc.) (%))			M.p. (°C)	Yield (%)	^{1}H NMR (in CDCl$_3$) (mmp)^a	Mass spectrum m/z
	C	H	N				
SydnCH=CHCOMe	62.72 (62.61)	4.30 (4.35)	12.26 (12.17)	124.5–126	50	2.28(c, 3H), 7.09(d, J 15.5 Hz, 1H), 7.31(d, J 15.5 Hz, 1H), 7.5–7.8(m, 5H)	230 [M]$^+$, 172 [M–NOCO]$^+$, 105 [PhN$_2$]$^+$, 77[Ph]$^+$
SydnCH=CHCO$_2$Me	58.45 (58.54)	4.09 (4.06)	11.45 (11.38)	113–114.5	52	3.70(c, 3H), 6.90(d, J 15.6 Hz, 1H), 7.18(d, J 15.6 Hz, 1H), 7.5–7.7(m, 5H)	246 [M]$^+$, 215 [M–OMe]$^+$, 188 [M–NOCO]$^+$, 77 [Ph]$^+$
SydnCH=CHPh				178–181 ^{b}	87	6.59(d, J 16.2 Hz, 1H), 7.3–7.4(m, 5H), 7.5–7.8(m, 5H), 7.75(d, J 16.2 Hz, 1H)	264 [M]$^+$, 206 [M–NOCO]$^+$, 77 [Ph]$^+$
SydnCH=CHCN				134–135	7	6.44(d, J 15.7 Hz, 1H), 6.90(d, J 15.7 Hz, 1H), 7.5–7.9(m, 5H)	213 [M]$^+$, 155 [M–NOCO]$^+$, 105 [PhN$_2$]$^+$, 77 [Ph]$^+$
SydnCH=CH–CH / B$_{10}$H$_{10}$ / CH–CH				125–126	21	6.35(d, J 16.2 Hz, 1H), 6.81(d, J 16.2 Hz, 1H), 7.3–7.8(m, 5H)	328–331 [M]$^+$, 268–274 [M–NOCO]$^+$, 105 [PhN$_2$]$^+$, 77 [Ph]$^+$
SydnCH=CHB$_{10}$H$_9$ / CH–CH	43.36 (43.62)	5.64 (5.49)	8.13 (8.48)	163–165	51	6.67(d, J 17.9 Hz, 1H), 6.84(d, J 17.9 Hz, 1H), 7.5–7.8(m, 5H)	328–331 [M]$^+$, 268–274 [M–NOCO]$^+$, 105 [PhN$_2$]$^+$, 77[Ph]$^+$
SydnCH=CHB$_{10}$H$_9$C$_2$H$_2$-m	43.81 (43.62)	4.69 (5.49)	8.67 (8.48)	176–177.5	40	6.54(d, J 17.9 Hz, 1H), 6.99(d, J 17.9 Hz, 1H), 7.5–7.8(m, 5H)	328–332 [M]$^+$, 269–274 [M–NOCO]$^+$, 105 [PhN$_2$]$^+$, 77[Ph]$^+$

^{a} The carboranyl substituent protons appear as a broad signal centered at $\delta \approx 2.2$ ppm ($\Delta\nu \approx 590$ Hz). The proton directly bonded with the carbon atom appears as a wide singlet at $\delta \approx 3.57$ ppm for 1-vinyl-o-carborane, at 3.66 ppm for 3-vinyl-o-carborane, and 2.98 ppm for 2-vinyl-m-carborane ($\Delta\nu \approx 30$ Hz). ^{b} Lit. [7], m.p. 178–181°C.

$$X = COMe, CO_2Me, Ph, CN, C_2B_{10}H_{11}$$
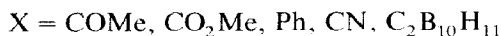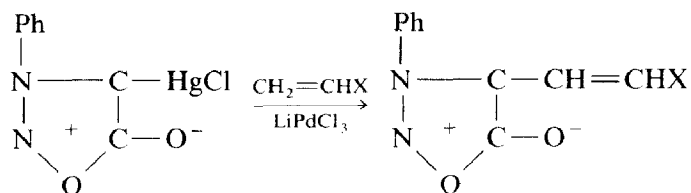
The best results were obtained when acetonitrile was used as solvent. The vinyl sydnones were obtained in good yields when methyl vinyl ketone, methyl acrylate, styrene and 3-vinyl-*o*-carborane were used. 2-Vinyl-*m*-carborane and 1-vinyl-*o*-carborane also were used.

All the olefins synthesized are the *trans*-isomers. It follows from ^{1}H NMR spectral data in which the olefin proton signals are an AB system with J_{AB} 15.5–17.9 Hz and depending on the X-substituents they appear at 6–8 ppm (Table 1). In the mass spectra the signals from the molecular ions and the fragmentation products characteristic for the sydnone structure were found.

Elaboration of the common method for the preparation of 4-alkenylsydnones greatly increases the synthetic potential of sydnones.

Experimental

NMR spectra were recorded on a Bruker WP-200SY spectrometer in $CDCl_3$. IR spectra were recorded on a Bruker IFS113v spectrometer in Nujol, molecular weights were determined on a Kratos MS 890 mass spectrometer. [Pd(PPh$_3$)$_4$] [11], [Pt(PPh$_3$)$_4$] [12], 4-bromo-3-phenylsydnone [13], 4-chloromercurio-3-phenylsydnone [14], were synthesized by procedures previously described. The reactions were carried out in absolute solvents under argon.

Synthesis of [MBr(Sydn)(PPh$_3$)$_2$] (M = Pd, Pt)

To a solution of 4-bromo-3-phenylsydnone (0.5 g, 2.1 mmol) in 50 ml THF or benzene was added [Pd(PPh$_3$)$_4$] (2.39 g, 2.1 mmol) at room temperature. After stirring for 20 min the precipitate that had found was filtered off, washed with 40 ml THF or benzene, and dried in vacuo to give a mixture of *cis*- and *trans*-PdBr(Sydn)(PPh$_3$)$_2$ (87%). Anal. Found: C, 60.83; H, 4.06; N, 3.07; Br, 9.13. $C_{44}H_{35}N_2O_2P_2BrPd$ calc.: C, 60.62; H, 4.18; N, 3.21; Br, 9.18%.

Similarly, [PtBr(Sydn)(PPh$_3$)$_2$] was isolated in 76% yield from THF or benzene, after 30 min, as white crystals, m.p. 281–283°C. Anal. Found: C, 55.05; H, 3.89; P, 6.51. $C_{44}H_{35}N_2O_2P_2BrPt$ calc.: C, 55.00; H, 3.65; P, 6.46%.

Synthesis of (E)-SydnCH=CHX (X = COMe, CO$_2$Me, Ph, CN, carboranyl)

To a suspension of PdCl$_2$ (0.26 g, 1.5 mmol) in 30 ml of CH$_3$CN at room temperature was added LiCl (0.06 g, 1.5 mmol). The mixture was stirred until it became a homogeneous solution (30 min). 4-Chloromercurio-3-phenylsydnone (0.59 g, 1.5 mmol) and methyl vinyl ketone (0.11 g, 1.5 mmol) were added. After 36 h stirring the solvent was removed in vacuo and the products were separated by thin layer chromatography on SiO$_2$ (CHCl$_3$).

Reactions were also carried out with methyl acrylate, styrene, acrylonitrile, 1-vinyl-*o*-carborane, 3-vinyl-*o*-carborane, 2-vinyl-*m*-carborane to give (*E*)-1-(3-phenylsydnon-4-yl)-2-(acetyl)ethylene, (*E*)-1-(3-phenylsydnon-4-yl)-2-(carbmethoxy)ethylene, (*E*)-1-(3-phenylsydnon-4-yl)-2-(phenyl)ethylene, (*E*)-1-(3-phenylsydnon-4-yl)-2-(nitrile)ethylene, (*E*)-1-(3-phenylsydnon-4-yl)-2-(*o*-carboran-1-yl)ethylene, (*E*)-1-(3-phenylsydnon-4-yl)-2-(*o*-carboran-3-yl)ethylene, (*E*)-1-(3-phenylsydnon-4-yl)-2-(*m*-carboran-2-yl)ethylene. The analytical, NMR and mass-spectral data, together with the yields and the melting points of the products are listed in Table 1.

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