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HYDRAZIDO COMPLEXES OF THE TRANSITION METALS

III *. THIOBENZOYLHYDRAZIDE COMPLEXES OF PALLADIUM(II), PLATINUM(II) AND MANGANESE(I)

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Summary

Thiobenzoylhydrazides of the type PhCSNHNHR (R = H, Ph or Me) react with $(Ph_3P)_2MCl_2$ (M = Pd or Pt) and $Mn(CO)_5Cl$ at room temperature.

Introduction

Reactions of hydrazides of the type RCONHNHPh (R = alkyl or aryl) with transition metals give various products depending on the metal. With $ReOCl_3(PPh_3)_2$ the N—N bond in the hydrazides is cleaved to give the phenylimido complex $ReCl_3(NPh)(PPh_3)_2$ [1], whereas the diazene derivative $OsCl_2(RCON_2Ph)(PPh_3)_2$ is obtained by reaction with $OsOCl_3(PPh_3)_2$ [2]. $MoOCl_2(PMe_2Ph)_3$ combines with 1-benzoyl-2-phenylhydrazine to form a molybdenum complex having both diazene and phenylimido groups $MoCl_2(NPh)(PhCON_2Ph)$ [3].

Recently we investigated the reactions of dibenzoyl- and diacetyl-hydrazides with *cis*-dichlorobis(tertiary phosphines)platinum(II) [4]. In these compounds the ligands are coordinated via the O and the terminal N atoms of the hydrazides. We found that the ligands PhCONH—NHR (R = H, Me or Ph) do not give the corresponding hydrazido (2—) derivatives with the platinum(II) chloride complexes.

In view of the better donor properties of sulphur than of oxygen, one would expect that the sulphur analogues of the benzoylhydrazide ligands, namely PhCSNHNHR (R = H, Ph and Me), would readily form complexes with class B metals such as palladium(II) and platinum(II). These thiobenzoylhydrazides which are structurally related to thiosemicarbazide can exist in the tautomeric forms I and II.

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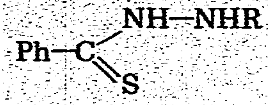
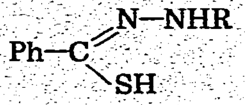
* For Part II see ref. 9.



(I)



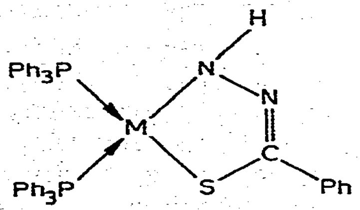
(II)

I can act either as an uncharged monodentate ligand via the sulphur atom or as an unchanged bidentate ligand through the sulphur and the terminal nitrogen atoms. II can act as a singly charged bidentate ligand by loss of a proton from the sulphur atom or as a doubly charged bidentate ligand by loss of protons from the sulphur and nitrogen atoms. Metal complexes of the thiosemicarbazide in both the uncharged and singly charged forms have been studied extensively and the ligand chelates through the sulphur atom and the terminal nitrogen atom [5]. Thiobenzoylhydrazide, $PhCSNH{-}NH_2$, forms 2 : 1 adducts with nickel(II) salts in neutral solution [6]; the hydrazide is acting as a neutral bidentate ligand. In alkaline media however, the sulphur is bonded as a thiolo group to the metal giving inner type complexes.

Recently Dilworth [7] reported the reactions of thiobenzoylhydrazide of the type PhCSNHNHR (R = Ph or H) with $MoO_2(acac)_2$ (acac = acetylacetonato) to form $Mo(PhCSN_2R)_3$; in contrast, however, with monobenzoylhydrazide, the acac and oxo groups are partially substituted by the hydrazido (2—) moiety. Herein we report the reactions of *cis*-dichlorobis(triphenylphosphine)platinum(II) and palladium(II) and chloropentacarbonylmanganese(I) with thiobenzoylhydrazide ligands of the type PhCSNHNHR (R = H, Ph or Me). The reactions were carried out in ethanolic solution in presence of a base at room temperature and proceed readily compared to those of the oxygen analogues.

Results and discussion

The ligand $PhCSNHNH_2$ acts as a doubly charged bidentate ligand displacing the two chloro groups of the metal complexes $(Ph_3P)_2MCl_2$ (M = Pd or Pt) to form $(Ph_3P)_2$ M(PhCSNNH) having the possible structure given below.



The reaction of the hydrazide (R = Ph) with *cis*-$(Ph_3P)_2PtCl_2$ proceeds similarly and leads to the formation of $(Ph_3P)_2Pt(PhCSNNPh)$, possibly of similar structure. With the palladium derivative however, the hydrazide acts as a singly charged bidentate ligand by displacing a triphenylphosphine ligand and a chloride ion.

The same type of product is formed with the hydrazide (R = Me) and $(Ph_3P)_2MCl_2$. The hydrazide ligand is coordinated to the metal via the sulphur as a thiolo group and the terminal protonated nitrogen atom containing the methyl group. The increased dative σ character of the terminal nitrogen atom due to the presence of the methyl group could account for the displacement of

TABLE 1

ANALYTICAL DATA, MELTING POINTS AND IR SPECTRAL DATA OF COMPOUNDS I--III

Complex	Analyses: found (calcd.) (%)				M.P. (°C) [a]	ν(N—H) (cm^{-1})	ν(C=N) (cm^{-1})	Far IR stretching (cm^{-1})
	C	H	N	S				
$PtNH—N=C(S)Ph(PPh_3)_2$ (I)	59.6 (59.4)	4.2 (4.1)	3.1 (4.2)	3.6 (3.6)	267	3380	1435	390
$PtNPh—N=C(S)Ph(PPh_3)_2 \cdot 2C_6H_6$ (II)	66.3 (66.4)	4.9 (4.7)	2.4 (2.5)	2.8 (2.9)	[c]		1440	390
$PtClNHCH_3—N=C(S)Ph(PPh_3)$ (III)	47.6 (47.5)	3.4 (3.5)	4.0 (4.2)	4.9 (4.8)	175	3280	1440	390
$PdNH—N=C(S)Ph(PPh_3)_2 \cdot 2C_2H_5OH$ (IV)	64.9 (64.6)	5.3 (5.5)	3.3 (3.2)	3.6 (3.6)	125	3350	1435	395
$PdClNHPh—N=C(S)Ph(PPh_3)$ (V)	58.6 (58.9)	4.2 (4.1)	4.4 (4.4)	5.1 (5.0)	200	3290	1450	395
$PdClNHCH_3—N=C(S)Ph(PPh_3)$ (VI)	54.6 (54.0)	4.1 (4.2)	4.9 (4.9)	5.4 (5.6)	260	3270	1460	395
$Mn(CO)_4NHCH_3—N=C(S)Ph$ [b] (VII)	43.4 (43.3)	3.0 (2.7)	8.6 (8.4)	9.6 (9.6)	130	3285	1445	380, 396

[a] With decomposition. [b] IR in chloroform solution in CO region 2063(m) 2004(sh) and 2012(s). [c] At 110°C compound II changes into an amorphous mass which decomposes over 270°C.

TABLE 2

^1H NMR SPECTRA OF THE LIGAND PhSCNH—NHMe AND ITS COMPLEXES IN $CDCl_3$ SOLUTION

Compound	Chemical shift (τ) and coupling constants	Assignment
PhCSNH—NHMe	6.74 [a]	Methyl protons
	4.04 br s	H of NH
	2.69 s	Phenyl protons
III	6.61 d ^4J(HCNPtP) 2.1 Hz	Methyl protons
	2.43—2.75 complex m	Protons of phenyl and phosphine phenyl groups and H of NH
VI	6.53 d ^4J(HCNPdP) 1.8 Hz	Methyl protons
	2.33—2.77 complex m	Protons of phenyl and phosphine phenyl groups and H of NH
VII	6.08 s	Methyl protons
	2.78 s	H of NH
	2.60 s	Phenyl protons

[a] s, singlet; d, doublet; m, multiplet, br, broad.

the triphenylphosphine ligand in the above reactions and also the substitution of one CO group in the reaction between $Mn(CO)_5Cl$ and PhCSNHNHMe to give $Mn(CO)_4NHMe—N=C(S)Ph$. The reactions of $Mn(CO)_5Cl$ with the other thiobenzoylhydrazides lead to decomposition products.

These complexes are stable to air and moisture, monomeric in benzene and the assigned bands of their IR spectra together with other properties are given in Table 1. The ^1H NMR signals of the ligand (R = Me) are assigned as shown in Table 2. The broadening of the singlet resonance at τ4.04 is due to the lability of the N—H bond, which makes the protons on both N atoms equivalent on NMR time scale. The methyl protons are however split into a doublet in both the platinum and palladium complexes by the phosphorous atom of the triphenylphosphine; spin-decoupling by irradiation with ^{31}P resonance collapses the doublet into a singlet. As expected the methyl protons of the manganese carbonyl derivative appear as a singlet.

Experimental

Infrared spectra were obtained from nujol mulls or KBr discs on a Beckman IR 5 spectrophotometer. Varian A 60 and HA 100 instruments were used to obtain ^1H NMR spectra of solutions in $CDCl_3$ with tetramethylsilane as internal standard. Molecular weights were determined osmometrically and elemental analyses were performed by the Microanalytical laboratory of the Chemistry Department of the University of Illinois, Urbana. IL 61801, U.S.A. The ligands were prepared as reported in the literature [8,9]. Reagent grade solvents were used without purification.

Thiobenzoylhydrazido(2—)-S,N'-bis(triphenylphosphine)platinum(II)(I). cis-Dichlorobis(triphenylphosphine)platinum(II) (1.6 g), thiobenzoylhydrazide (0.3 g, 1.0 mol and sodium bicarbonate (0.5 g) were stirred in absolute ethanol (150 ml) at room temperature for 6 h. The yellow slurry was filtered, the residue was crystallised as dark yellow needles (80% yield) from benzene/pentane at 0°C.

N'-Phenyl-thiobenzoylhydrazido(2—)-S,N'-bis(triphenylphosphine)platinum-(II) (II). Prepared in the same manner as complex I using *N'*-phenylthiobenzoylhydrazide. When recrystallised from benzene/pentane mixture, complex appeared as purple leaflets (50% yield) with two molecules of chloroform as solvate.

N'-Methyl-thiobenzoylhydrazido(1—)-S,N'-chloro(triphenylphosphine)platinum-(II) (III). Prepared in the same manner as complex I using *N'*-methylthiobenzoyl hydrazide. However the yellow slurry was washed several times with boiling ether prior to recrystallisation with benzene/pentane to give yellow needles (80% yield).

Thiobenzoylhydrazido(2—)-S,N'-bis(triphenylphosphine)palladium(II) (IV). Prepared as complex I using *cis*-dichlorobis(triphenylphosphine)palladium(II) (1.4 g) and thiobenzoylhydrazide (0.3 g, 1.0 mol). The pink slurry was filtered, filtrate was kept at 0°C overnight to give dark purple needles (80% yield) with two molecules of ethanol as solvate.

N'-Phenyl-thiobenzoylhydrazido(1—)-S,N'-chlorotriphenylphosphinepalladium(II) (V). Prepared as complex II using *cis*-dichlorobis(triphenylphosphine)-palladium(II). The complex was recrystallised from the brown slurry as brown needles from benzene/pentane in 70% yield.

N'-Methyl-thiobenzoylhydrazido(1—)-S,N'-chlorotriphenylphosphinepalladium-(II) (VI). Prepared as complex III using *cis*-dichlorobis(triphenylphosphine)-palladium(II). The complex was recrystallised from benzene/pentane as red needles (75% yield).

N'-Methyl-thiobenzoylhydrazido(1—)-S,N'-tetracarbonylmanganese(I) (VII). Chloropentacarbonylmanganese(I) (0.8 g) and *N'*-methylthiobenzoylhydrazide (0.75 g, 1 mol) were stirred in THF (75 ml) in presence of sodium carbonate (0.5 g) for 12 h. The orange solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was crystallized as orange needles (90% yield) from benzene/pentane at 0°C.

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