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DIBENZOYL- AND DIACETYLHYDRAZIDO(2–) COMPLEXES OF PLATINUM

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SUMMARY

1,2-Dibenzoyl- and 1,2-diacetylhydrazines react with *cis*-dichlorobis(tertiary phosphine)platinum(II) in refluxing ethanol in presence of a base to give [1,2-dibenzoyl- and diacetylhydrazido(2–)-*N*,*O*]bis(tertiary phosphine)platinum(II). The dibenzoylhydrazido derivative reacts with hydrogen chloride or acetic acid to give back dibenzoylhydrazine; whereas with bromine, dibenzoyldiimine is formed in quantitative yield.

INTRODUCTION

Following work[1] on the degradation of rhenium(V) benzoylhydrazido complexes to stable rhenium(I) dinitrogen complexes, it was thought that the employment of disubstituted benzoylhydrazines might lead to the eventual preparation of dibenzoylhydrazine or dinitrogen complexes of platinum.

Benzoylhydrazine functions either as a neutral or as an anionic ligand with elements of the first transition series. The cationic complexes, $[M(H_2NNHCOPh)_2]^{2+}$ (M = Co, Cu, Mn, Ni, Zn)[2], are deprotonated by bases to give neutral derivatives, $[M(H_2NNCOPh)_2]$. 1,2-Dibenzoylhydrazine reacts with common divalent transition metal ions to form polymeric complexes of general formula $[\{M(PhCONNHCOPh)_2\}_n]$ (M = Fe, Co, Ni, Cu), of uncertain structures[3]; however with heavy transition metals its complexes are well characterised. Thus it reacts with $[ReOCl_3(PPh_3)_2]$ in ethanol in presence of hydrochloric acid and triphenylphosphine to give[1] the chelated monobenzoylhydrazido(3–) complex $[Re(N_2COPh)Cl_2(PPh_3)_2]$, one benzoyl group having been displaced as ethyl benzoate; 1-aryl-2-aroylhydrazines $Ar^1CONHNAr^2$ (Ar^1 = Ph, Ar^2 = Ph, p-$MeOC_6H_4$, p-MeC_6H_4 etc.) react[4] with $[MoOCl_2(PMe_2Ph)_3]$ to give the complexes $[MoCl_2(NAr^2)(Ar^1CON_2Ar^2)(PMe_2Ph)]$. Some platinum derivatives of azobenzene (diphenyldiimine) originally formulated as containing coordinated azobenzene were subsequently

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shown[5] to be salts, $[PhN_2HPh]_2[PtCl_6]$. Azobenzene was shown to react with potassium tetrachloroplatinate(II) in dioxane/water to give a derivative containing azobenzene coordinated via a nitrogen atom and an *ortho*-carbon bond to one phenyl ring[6]. Recently Otsuka and co-workers reported the formation of an azobenzene complex of Ni^0, Ni(PhN=NPh) [t-BuC≡CBu-t], which has been shown by Ibers and co-workers[7] to have a π-type azo-to-transition metal linkage. Simultaneously, Klein and Nixon reported[8] the preparation of the rather similar complex $[Ni(PhN{=}NPh)(PPh_3)_2]$. Both linear and cyclic platinum azo complexes have been prepared from diazonium and substituted diazonium salts[9,10] and a platinum complex containing bridging diimine ligands has been prepared by the reaction of hydrazine with $[PtCl_2(PPh_3)_2]$ at low temperature[11].

Stone and co-workers[12] reacted diethyl azodicarboxylate with *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) and tetrakis(triphenylphosphine)platinum(0) to form respectively $[(Ph_3P)_2Ir(CO)Cl(EtO_2CN_2CO_2Et)]$ and $[(Ph_3P)_2Pt(EtO_2CN_2CO_2Et)]$. In both cases he postulated a structure in which both nitrogen atoms are symmetrically bonded to the same metal giving a three-membered ring. Also $[MoO(R_2NCS_2)_2]$ reacts with diethyl azodicarboxylate to give $[MoO(R_2NCS_2)_2(EtO_2CN_2CO_2Et)]$ of unknown structure[13]. We now report the preparation of a series of dibenzoyl- and diacetylhydrazido(2–) complexes of platinum of the general formula, $[(Me_{3-x}Ph_xP)_2Pt(RCON_2COR)]$, where $x = 1$, 2 or 3 and R = Ph or CH_3.

RESULTS AND DISCUSSION

These complexes were prepared by reaction of 1,2-dibenzoyl- and 1,2-diacetylhydrazines with *cis*-dichlorobis(tertiary phosphine)platinum(II) in refluxing

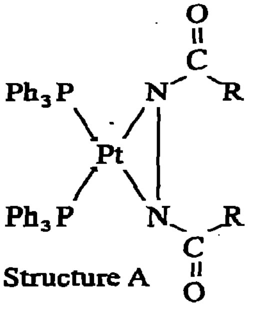
TABLE 1

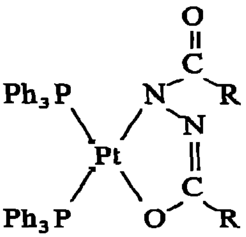
PHYSICAL AND ANALYTICAL DATA

Compound		*M.p. (°C)*	*IR*[a]	*Analyses. found (calcd.) (%)*			
				C	*H*	*N*	*Mol. wt.*[b]
(I)	$[Pt(PMe_2Ph)_2(PhCON_2COPh)]$	204	1565 1585	50.5 (50.8)	4.6 (4.6)	4.0 (3.9)	714 (709)
(II)	$[Pt(PMe_2Ph)_2(MeCON_2COMe)]$	197	1585[c]	41.4 (41.0)	5.0 (4.8)	5.0 (4.8)	596 (585)
(III)	$[Pt(PMePh_2)_2(PhCON_2COPh)$	246	1565, 1585	56.8 (57.6)	4.5 (4.4)	3.2 (3.4)	820 (833)
(IV)	$[Pt(PMePh_2)_2(MeCON_2COMe)]$	229	1585[c]	50.3 (50.8)	4.6 (4.6)	4.0 (3.9)	720 (709)
(V)	$[Pt(PPh_3)_2(PhCON_2COPh)]$	270	1570, 1585	62.6 (62.7)	4.1 (4.2)	2.9 (2.9)	960 (957)
(VI)	$[Pt(PPh_3)_2(MeCON_2COMe)]$	265	1585[c]	58.4 (57.6)	4.4 (4.4)	3.3 (3.4)	829 (833)

[a] In $CHCl_3$; ν(C=O) region, in cm^{-1}. [b] Determined osmometrically in dichloroethylene. [c] Broad unresolved band.

ethanol in presence of sodium bicarbonate. They are stable to air and to moisture and their colours range from pale yellow to orange. Alternatively the dibenzoyl complexes may be prepared by the reaction of the diimine derivative, PhCON=NCOPh, with the platinum(0) complexes $[Pt(PPh_3)_4]$ or $[Pt(PMePh_2)_4]$.


Structure A


Structure B

These complexes could have either structure (A) or (B). Structure (A) would involve a three-membered ring, as postulated by Stone[12] for the related diethyl azodicarboxylate complex which is prepared by an analogous method. In structure (B), the disubstituted ligands are coordinated to the metal in the enolised form as found in several complexes prepared by Chatt and Dilworth[1,4]. The X-ray crystal structures of both the dibenzoyl- and diacetylhydrazido(2–) complexes[14,15] indicate that the ligands are coordinated in the enolised form according to structure (B). In chloroform solution the IR spectra of the dibenzoyl-substituted complexes (see Table 1) show two bands in the region 1550–1600 cm^{-1} whereas the diacetyl complexes show only one broad unresolved peak. These could be assigned to $\nu(C{=}O)$ and $\nu(C{=}N)$ which occur in this region; the $\nu(C{-}O)$ which usually occurs at ca 1350 cm^{-1} could not be observed[16]. The ^1H NMR spectrum of the complex $[(Ph_3P)_2Pt(CH_3CON_2COCH_3)]$ has two peaks at τ 8.09 and 8.21 ppm assigned to the methyl protons, suggesting that the methyl groups are inequivalent, as expected from structure (B).

REACTIONS

As might be expected, the complex $[(Ph_3P)_2Pt(PhCON_2COPh)]$ behaves as a dibenzoylhydrazido(2–) complex towards notionally anionic displacements. Thus it reacts with 2 moles of hydrogen chloride gas to give *cis*-dichlorobis(triphenylphosphine)platinum and dibenzoylhydrazine according to reaction (1).

$$[(Ph_3P)_2Pt(PhCON_2COPh)] + 2\,HCl \longrightarrow (Ph_3P)_2PtCl_2 + PhCONHNHCOPh \qquad (1)$$

Addition of only one mole of hydrogen chloride failed to give the complex $[(Ph_3P)_2PtCl(PhCONHNCOPh)]$ and half the complex remained while the remainder reacted according to reaction (1). This is in contrast to complexes of the type $[(Ph_3P)_2Pt(PhC{\equiv}CPh)]$ where the intermediate platinum vinyl complex $[(Ph_3P)_2PtCl(PhC{=}CHPh)]$ may be isolated.

Similarly two moles of acetic acid react with it according to the following equation:

$$[(Ph_3P)_2Pt(PhCON_2COPh)] + 2CH_3COOH \rightarrow (Ph_3P)_2Pt(COOCH_3)_2 + PhCONHNHCOPh$$

Addition of two equivalents of bromine results in an almost quantitative yield of PhCON=NCOPh and dibromobis(triphenylphosphine)platinum. The enol form of the dibenzoylhydrazido(2–) anion is first formed which then tautomerises into the stable keto form of dibenzoyldiimine.

Palladium forms similar complexes with dibenzoylhydrazine; unlike the platinum analogues they are extremely unstable to air and moisture and are formed in low yield. They react with hydrogen chloride to give the dichloropalladium(II) complexes and dibenzoylhydrazine.

EXPERIMENTAL

Infrared spectra were recorded in chloroform solution on a Unicam SP200 spectrophotometer. Molecular weights were determined osmometrically and elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. Reagent-grade solvents were employed without purification except where stated. All manipulations involving tertiary phosphines were carried out under dinitrogen.

Preparations

(I), [1,2-Dibenzoylhydrazido(2–)-N,O]bis(dimethylphenylphosphine)platinum(II). *cis*-Dichlorobis(dimethylphenylphosphine)platinum(II) (1.6 g), 1,2-dibenzoylhydrazine[17] (0.9 g, 1.3 mol) and sodium bicarbonate (0.5 g) were heated under reflux in absolute ethanol (150 ml) for 4 h. The yellow solution was cooled, filtered and the filtrate evaporated to dryness under reduced pressure. The residue was crystallised as yellow needles (80% yield) from benzene/pentane at 0°.

(II), [1,2-Diacetylhydrazido(2–)-N,O]bis(dimethylphenylphosphine)platinum(II). Prepared in the same manner as complex (I) using 1,2-diacetylhydrazine[18]. Recrystallised as pale yellow needles from benzene/pentane in 85% yield.

(III), [1,2-Dibenzoylhydrazido(2–)-N,O]bis(methyldiphenylphosphine)platinum(II). Prepared as complex (I) using *cis*-dichlorobis(methyldiphenylphosphine)-platinum(II) (1.1 g) and 1,2-dibenzoylhydrazine (0.47 g, 1.2 mol). The complex was recrystallized as bright yellow crystals from absolute alcohol in 80% yield.

The same complex was also prepared by stirring tetrakis(methyldiphenylphosphine)platinum(0)[19] (0.49 g) with dibenzoyldiimine[18] (0.12 g, 1 mol) in dry benzene (30 ml) under nitrogen for 1 h at room temperature.

(IV), [1,2-Diacetylhydrazido(2–)-N,O]bis(methyldiphenylphosphine)platinum(II). Prepared as complex (III), using 1,2-diacetylhydrazine. The complex was recrystallized as yellow needles from benzene/hexane in 75% yield.

(V), [1,2-Dibenzoylhydrazido(2–)-N,O]bis(triphenylphosphine)platinum(II). Prepared as complex (I) using dichlorobis(triphenylphosphine)platinum(II) (1.61 g) and 1,2-dibenzoylhydrazine (0.5 g, 1.1 mol). The complex was recrystallised from benzene/hexane as orange needles in 72% yield.

The same complex was also obtained by stirring tetrakis(triphenylphosphine)-platinum(0) (1.0 g) with dibenzoyldiimine[20] (0.80 g, 4 mol) in dry benzene (50 ml) under nitrogen at room temperature for 1 h.

(VI), [1,2-Diacetylhydrazido(2–)-N,O]bis(triphenylphosphine)platinum(II). Prepared as complex (V) using 1,2-diacetylhydrazine. The complex was recrystallized from benzene/hexane as pale yellow needles in 73 % yield.

Reactions

Reactions with hydrogen chloride. Complex (I) (0.70 g) was dissolved in ethanol (20 ml) and 2 equivalents of an ethanolic solution of hydrogen chloride added slowly. 1,2-Dibenzoylhydrazine (0.20 g, 82 % of theoretical) was immediately precipitated. On cooling the filtrate deposited *cis*[$PtCl_2(PPhMe_2)_2$] (0.52 g, quantitative).

Reaction with acetic acid. Complex (V) (0.96 g) was dissolved in dichloromethane (30 ml) and acetic acid (0.18 g, 3 mol) was added slowly. 1,2-Dibenzoylhydrazine (0.27 g, 80 % of theoretical) was immediately precipitated. The filtrate was evaporated to dryness and the residue recrystallised from benzene/cyclohexane (1/1) (30 ml) to give pale yellow crystals of $(Ph_3P)_2Pt(COOCH_3)_2$[21] in 86 % yield.

Reaction with bromine. Complex (V) (0.9 g) was suspended in carbon tetrachloride (20 ml), and a solution of bromine (0.15 g) in carbon tetrachloride (5 ml) added slowly with shaking. The reaction mixture was maintained at 50° for 1 h and the solution filtered hot. The filtrate was cooled to −80° yielding dibenzoyldiimine (0.20 g, 90 % of theoretical).

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