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HYDRAZIDO COMPLEXES OF THE TRANSITION METALS

II *. SYNTHESIS AND REACTIONS OF DIBENZOYL- AND DIACETYL-HYDRAZIDO (2—) (*N,N′, O,O′*)-BIS(CARBONYLTRIPHENYLPHOSPHINE)-RHODIUM(I) AND -IRIDIUM(I)

AHMED S. KASENALLY *
School of Agriculture, University of Mauritius, Réduit (Mauritius)
and (in part) FAROUK M. HUSSEIN
Department of Chemistry, University of Khartoum, P.O. Box 321, Khartoum (Sudan)
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Summary

Interaction of 1,2-dibenzoyl- and diacetyl-hydrazides with *trans*-M(CO)-Cl$(PPh_3)_2$ in refluxing ethanol in the presence of sodium bicarbonate gives the bridged species $[M(CO)(PPh_3)]_2R \cdot CO \cdot N_2 \cdot CO \cdot R$ (M = Rh or Ir, R = C_6H_5 or CH_3) for which a structure is suggested. Chlorination and bromination yield the oxidised dimer and carbonylation gives a substituted dimer.

Introduction

Hydrazine derivatives are of special interest because of their reactions leading to compounds which can be considered as model intermediates in biological nitrogen fixation [2].

Dibenzoyl- and diacetyl-hydrazides form a series of hydrazido complexes with transition metals. 1,2-Dibenzoylhydrazide reacts with $ReOCl_3(PPh_3)_2$ in ethanol in the presence of hydrochloric acid and triphenylphosphine to give a monobenzoylhydrazido (3—) complex $[Re(N_2COPh)Cl_2(PPh_3)_2]$, one benzoyl group having been displaced as ethyl benzoate [3]. Dibenzoyl- and diacetyl-hydrazides react with *cis*-$PtCl_2(PPh_3)_2$ in ethanol in presence of a base to form [Pt-$(RCON_2COR)(PPh_3)_2$] with R = Ph or CH_3; the hydrazido ligands are unsymmetrically bound to the metal via a nitrogen atom and the oxygen atom of the opposite benzoyl or acetyl group [1,4]. The two hydrazido ligands may act as bridging tetradentate ligands in two ways. The first involves only the two nitro-

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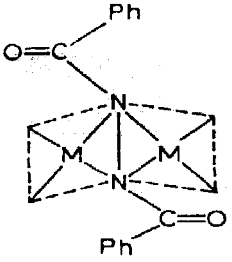
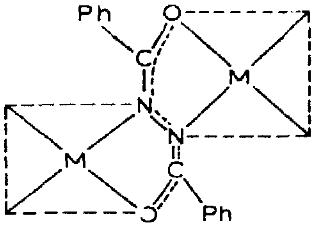
* For part 1 see ref. 1.

gen atoms as bridging sites, the two carbonyl groups not participating in the bonding (type A). In the second, one metal is bound to one nitrogen atom and the oxygen atom of the opposite benzoyl group or acetyl groups and the other metal is bound to the remaining nitrogen and oxygen atoms (type B); such a bridging arrangement is unusual in that each metal atom is coordinated to different nitrogen and oxygen atoms in the same ligand.



(A)



(B)

Results and discussion

Extension of the reactions involving 1,2-dibenzoyl- and diacetyl-hydrazides with *trans*-$M(CO)Cl(PPh_3)_2$ in ethanolic solution in presence of a base gives rise to the bridged species $[M(CO)PPh_3]_2RCON_2COR$ (where M = Rh or Ir, R = C_6H_5 or CH_3). These reactions most probably involve initial elimination of two molecules of HCl from two molecules of $M(CO)Cl(PPh_3)_2$ and one molecule of the hydrazine, followed by displacement of a triphenylphosphine on each metal by the carbonyl oxygen atoms present in the bridging ligand. The complexes are stable to air and moisture, dimeric in benzene in cases in which the solubility allows measurements, diamagnetic, and non-electrolytes in nitromethane. In a preliminary note [5] a structure of type A was postulated for the bridged complexes. Since both the diacetyl- and dibenzoyl-hydrazido ligands coordinate via the N and O atoms in the platinum complexes, it is probable that these dimers would have type B structures. The metal is still in formal oxidation state I with square planar coordination. The bridging chelate ring would show fractional bond orders and general delocalization of electron density. In view of the separation between the two metal centres it is unlikely that the two planes incorporating the metal and its chromophores would be bent to allow for metal—metal interaction as in $[Rh(CO)_2Cl]_2$ [6]. The IR spectra show a strong and a weak band in the metal carbonyl stretching region (1925—2000 cm^{-1}) and another strong band in the region (1500—1550 cm^{-1}) which can be assigned to $\nu(C{=}N)$ (see Table 1). The absorption band 1520 cm^{-1} in compound II is shifted to 1495 cm^{-1} in the ^{15}N-labelled derivative which supports its being associated with $\nu(C{=}N)$. The Raman spectrum of compound II shows a strong band at 1540 cm^{-1} which is also shifted to 1520 cm^{-1} in the ^{15}N-labelled analogue and is therefore associated with the vibration involving the N—N bond. ^1H NMR studies would not provide additional structural information in the benzoyl derivatives while the complexes with acetyl substituents were not sufficiently soluble for NMR measurements.

TABLE 1

PHYSICAL AND ANALYTICAL DATA

Compound	Molecular formula	M.p. (°C)	IR [a]	Analyses found (calcd.) (%)			
				C	H	N	Mol. wt. [b]
I	$C_{38}H_{32}N_2O_4P_2Rh_2$	224	1976vs, 1926vw 1530vs	49.1 (49.5)	4.2 (4.2)	3.6 (3.6)	765 (776)
II	$C_{52}H_{40}N_2O_4P_2Rh_2$	260	1974vs 1531vs	60.8 (60.9)	4.1 (3.9)	2.6 (2.7)	
III	$C_{42}H_{36}N_2O_4P_2Rh_2$	279	1976vs, 1920vw 1520vs, 1308w	55.9 (56.0)	4.0 (4.0)	3.1 (3.1)	[c]
IV	$C_{52}H_{40}Ir_2N_2O_4P_2$	199	1978vs, 1923vw 1530vs, 1312w	52.0 (51.9)	3.4 (3.3)	2.3 (2.3)	1186 (1202)
V	$C_{42}H_{36}Ir_2N_2O_4P_2$	156—160	1967vs, 1910vw 1521vs, 1308w	46.9 (46.7)	3.2 (3.3)	2.5 (2.6)	[c]
VI	$C_{52}H_{40}Br_4N_2O_4P_2Rh_2$ [d]	258—260	2064vs, 1997vw 1547vs	46.6 (46.4)	3.1 (2.9)	1.9 (2.0)	[c]
VII	$C_{52}H_{40}Br_4Ir_2N_2O_4P_2$ [e]	301	2057vs, 2010vw 1540vs	41.2 (41.0)	2.7 (2.6)	1.8 (1.8)	[c]
VIII	$C_{52}H_{40}Cl_4N_2O_2P_2Rh_2$	293	2078vs, 2015vw 1549vs	53.6 (53.5)	3.5 (3.4)	2.4 (2.4)	[c]
IX	$C_{18}H_{10}O_6N_2Rh_2$	210	2070vs, 2010vs 1530vs	38.7 (38.8)	1.9 (1.8)	5.0 (5.0)	[c]

[a] In Nujol mulls. [b] Determined osmometrically in benzene. [c] Compound not soluble enough. [d] Br: found 23.5%, calcd. 23.8%. [e] Br: found 20.7%, calcd. 21.0%.

Unlike the corresponding platinum complexes, compounds II and IV do not react with bromine or chlorine to give dibenzoyldiazene. Instead the hydrazido bridging ligand remains intact and each metal in the dimer picks up one molecule of halogen to give an octahedrally coordinated rhodium(III) or iridium(III). The metal carbonyl stretching frequencies of the oxidised products are shifted to higher frequencies. Reactions with hydrogen chloride gas yield 1,2-dibenzoyl- and diacetyl-hydrazides and uncharacterisable products. The triphenylphosphine ligands in compound II can be replaced by CO under high pressure to give $[Rh(CO)_2]_2PhCON_2COPh$. One would expect the structure of the substituted product to be similar to that of the original compound. IR measurements in chloroform solution show two strong bands (2010 and 2070 cm^{-1}) in the metal carbonyl stretching region which confirms a planar structure for the whole dimer and coupling of the CO vibrations in the two halves of the molecule. The mass spectrum of the compound shows the molecular ion as the highest mass fragment and ions corresponding to the stepwise loss of the four terminal CO molecules; this is followed by the progressive loss of 2 CO molecules (from the benzoyl groups) and N_2, to give the metastable ion $Rh_2Ph_2^+$, which then successively loses one phenyl group and one rhodium atom.

Experimental

Infrared spectra were obtained from Nujol mulls, KBr discs, or in solution on a Beckman IR5 spectrophotometer. Mass spectra were recorded at 70 eV on

AEI MS 902 spectrometer using the direct-probe insertion method. Molecular weights were determined osmometrically and elemental analyses were performed by Scandinavian Microanalytical Laboratory, Harlev, Denmark and the Microanalytical Laboratory of the Chemistry Department of the University of Illinois, Urbana, Ill. Reagent-grade solvent were employed without further purification.

Preparations

$[Rh(CO)(PMe_2Ph)]_2Ph \cdot CO \cdot N_2 \cdot CO \cdot Ph$ (I). *Mer*-$RhCl_3(PMe_2Ph)_3$ (0.6 g), 1,2-dibenzoylhydrazine (0.24 g, 10 mol) and sodium bicarbonate (0.5 g) were heated under reflux in absolute ethanol (50 ml) for 4 h. The yellow solution was filtered hot and the filtrate was concentrated under reduced pressure. Yellow needles (54% yield) were deposited when the solution was set aside overnight at 0° C.

The same compound was also prepared by heating *trans*-$Rh(CO)Cl(PMe_2Ph)_2$ (0.28 g), 1,2-dibenzoylhydrazine (0.09 g, 0.5 mol) and sodium bicarbonate (0.5 g) under reflux in absolute ethanol (25 ml) for 2 h.

$[Rh(CO)PPh_3]_2Ph \cdot CO \cdot N_2 \cdot CO \cdot Ph$ (II). *Trans*-$Rh(CO)Cl(PPh_3)_2$ (0.36 g), 1,2-dibenzoylhydrazine (0.06 g, 0.5 mol) and sodium bicarbonate (0.5 g) were heated under reflux in absolute ethanol (50 ml) for 4 h. The mixture was filtered hot and the residue washed with boiling ethanol. Crystallization from benzene/petroleum ether (30—40° C) gave yellow needles (60% yield).

$[Rh(CO)(PPh_3)]_2CH_3 \cdot CO \cdot N_2 \cdot CO \cdot CH_3$ (III). This was prepared by the above method from *trans*-$Rh(CO)Cl(PPh_3)_2$ (0.28 g) and diacetylhydrazine (0.02 g, 0.5 mol). The product was recrystallised as yellow needles (65% yield) from benzene.

$[Ir(CO)PPh_3)]_2Ph \cdot CO \cdot N_2 \cdot CO \cdot Ph$ (IV). This was prepared in the same way as compound II from *trans*-$Ir(CO)Cl(PPh_3)_2$ (0.58 g) and dibenzoylhydrazine (0.09 g, 0.5 mol). The solution was refluxed for 5 h, the residue was dissolved in benzene, and n-pentane added to the filtrate. The mixture was set aside at 0°C overnight to give yellow needles (85% yield).

$[Ir(CO)(PPh_3)]_2CH_3 \cdot CO \cdot N_2 \cdot CO \cdot CH_3$ (V). This was prepared by the same method from *trans*-$Ir(CO)Cl(PPh_3)_2$ (0.78 g) and diacetylhydrazine (0.06 g, 0.5 mol). The residue crystallized from benzene as yellow needles (70% yield).

$[Rh(CO)Br_2(PPh_3)]_2Ph \cdot CO \cdot N_2 \cdot CO \cdot Ph$ (VI). A suspension of compound II (0.51 g) in CCl_4 (15 ml) was treated with Br_2 in the same solvent (0.16 g, 1 mol). The mixture was shaken vigorously, kept at 50°C for 1 h, then filtered. The filtrate was concentrated under reduced pressure and cooled in an ice-bath. The precipitate was crystallised as orange needles (80% yield) from benzene/ethanol.

$[Ir(CO)Br_2(PPh_3)]_2Ph \cdot CO \cdot N_2 \cdot CO \cdot Ph$ (VII). This was made in the same way as compound VI but from compound IV. It crystallised as dark orange needles (80% yield) from benzene/ethanol.

$[Rh(CO)Cl_2(PPh_3)]_2Ph \cdot CO \cdot N_2 \cdot CO \cdot Ph$ (VIII). A solution of compound II (0.25 g) in chloroform (10 ml) was treated with a slow stream of chlorine gas for 2 min, during which it darkened in colour. The solution was evaporated to dryness under reduced pressure. The residue recrystallised to give orange needles (70% yield) from benzene/pentane.

$[Rh(CO)_2]_2Ph \cdot CO \cdot N_2 \cdot CO \cdot Ph$ (IX). 1 g of compound II was dissolved in

benzene (50 ml) and the solution was kept for 12 h at 120°C in a high pressure bomb under CO (800 psi). The product crystallised as dark orange needles (80% yield) from benzene.

References

1 J.R. Dilworth, A.S. Kasenally and F.M. Hussein, J. Organometal. Chem., 60 (1973) 203.
2 J. Chatt and G.J. Leigh, Chem. Soc. Rev., (1972) 121 and references therein.
3 J. Chatt, J.R. Dilworth, G.J. Leigh and V.D. Gupta, J. Chem. Soc. A, (1971) 2631.
4 J.A. Ibers and S.D. Ittel, J. Chem. Soc. A, (1973) 2290.
5 F.M. Hussein and A.S. Kasenally, J. Chem. Soc. Chem. Commun., (1972) 3.
6 L.F. Dahl, C. Martell and D.L. Wampler, J. Amer. Chem. Soc., 83 (1961) 1761.