Reactions of Bis[tricarbonyl(triphenylphosphine)iridium] with Triphenyl Phosphite, Triphenylphosphine, and Sulphur Dioxide

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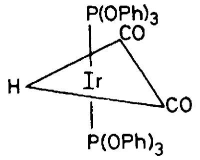
The compound $[\{Ir(CO)_3(PPh_3)\}_2]$ (1) reacts with $P(OPh)_3$ to give $[\{Ir(CO)_2[P(OPh)_3]_2\}_2]$ from which $[\{Ir(CO)_3[P(OPh)_3]\}_2]$ may be obtained. Compound (1) also gives $[Ir_2(CO)_5(PPh_3)_3]$ with PPh_3, $[Ir_2(CO)_5\{PPh_2(C_6H_4Me\text{-}p)\}_2(PPh_3)]$ with $PPh_2(C_6H_4Me\text{-}p)$, and $[\{Ir(CO)_2(PPh_3)(SO_2)\}_2]$, having two bridging sulphur dioxide molecules, with SO_2. Reaction of the last compound with hydrogen gives $[\{Ir(CO)_2H(PPh_3)\}_2SO_2]$ and reaction with iodine gives $[\{Ir(CO)_2(PPh_3)I_2\}_2SO_2]$, having two bridging and two terminal iodine atoms and one bridging sulphur dioxide molecule, but no metal–metal bond. The compounds $[\{Ir(CO)_2[P(OPh)_3]_2\}_2]$ and $[\{Ir(CO)_3[P(OPh)_3]\}_2]$ and sulphur dioxide gives $[\{Ir(CO)[P(OPh)_3]_2(SO_2)\}_2]$ and $[\{Ir(CO)_2[P(OPh)_3](SO_2)\}_2]$ respectively in each of which a metal–metal bond is postulated.

As a continuation of our work on the reactions of the title compound $[\{Ir(CO)_3(PPh_3)\}_2]$ (1),[1,2] we report the results obtained from the reactions of this compound with aryl phosphites and phosphines and with sulphur dioxide.

RESULTS AND DISCUSSION

Reactions with Triphenyl Phosphite.—Reaction of (1) with triphenyl phosphite at 90 °C occurs with substitution of the triphenylphosphine and one of the carbonyl groups by the phosphite to give $[\{Ir(CO)_2[P(OPh)_3]_2\}_2]$ (2) as a yellow microcrystalline powder. This compound rapidly decomposes in solution to form $[\{Ir(CO)_3[P(OPh)_3]\}_2]$ (3), which could be isolated, and probably $[Ir(CO)H\{P(OPh)_3\}_3]$, which could not. This reaction thus appears to be a disproportionation with partial extraction of hydrogen from the solvent. The molecular weight of (2) could not be measured directly. However, a dimeric formulation seems probable since the compound is diamagnetic, shows an i.r. spectrum having four CO stretching bands, and reacts with CO in benzene to form the diamagnetic compound (3). An *X*-ray study has shown that compound (3) has a dimeric structure with a metal–metal bond.† Compound (2) gives a very intense i.r. band at 1 975 cm^{-1} having two shoulders. This band is at higher wavenumber than the corresponding band (1 940 cm^{-1}) of the derivative (1), in agreement with the greater π-acceptor character of the phosphite.

The reaction of (2) with dihydrogen is similar to that of (1).[1] The metal–metal bond is cleaved to give the monomeric $[Ir(CO)_2H\{P(OPh)_3\}_2]$ (4). Compound (4) shows two very close ν(Ir–H) stretching bands in the i.r. at 2 120 and 2 100 cm^{-1}, but only a single band in solution at 2 100 cm^{-1}. The CO stretching bands are of equal intensity and lie at 1 980—2 020 cm^{-1} (in Nujol mull), *i.e.* at considerably higher wavenumber than those for the analogous $[Ir(CO)_2H(PPh_3)_2]$.[3] The n.m.r. spectrum of (4) shows a triplet at τ 22.16 with *J*(P–H) 20 Hz, which is characteristic of a hydrogen atom coupled to two equivalent phosphorus atoms. The most obvious explanation of these results is that the structural isomer (A) exists in solution. This would satisfy the



(A)

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† Work in progress.

[1] L. Malatesta, M. Angoletta, and F. Conti, *J. Organometallic Chem.*, 1971, **33**, C43—C44.

[2] L. Malatesta, M. Angoletta, and G. Caglio, *J. Organometallic Chem.*, 1974, **73**, 265.

[3] G. Yagupsky and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 725.

condition that the phosphite molecules are in equivalent positions with respect to the hydrogen atom and that the carbonyl groups are *cis* to one another.

The hydride (4) is readily protonated; addition of perchloric acid gives the perchlorate salt $[Ir(CO)_2H_2\{P(OPh)_3\}_2][ClO_4]$ (5), isolated as a crystalline compound. Compound (5) shows two bands in the i.r. at 2 180 and 2 160 cm^{-1}, attributable to ν(Ir–H) modes of two *cis*-hydrogen atoms, and two strong bands at 2 100 and 2 080 cm^{-1} attributed to ν(CO) modes of two carbonyl groups, again *cis* to one another. The n.m.r. spectrum gives a triplet at τ 21.8 with J(P–H) 14.5 Hz, characteristic of two equivalent hydrogen atoms in *cis* positions with respect to two phosphorus atoms. Cation (5) thus appears to have the structure (B).

TABLE 1

Compound	Colour	Analysis (%) * C	H	Others		
(2) $[\{Ir(CO)_2[P(OPh)_3]_2\}_2]$	Yellow	52.9 (52.5)	3.50 (3.55)	O 14.7 (14.7)		
(3) $[\{Ir(CO)_3[P(OPh)_3]\}_2]$	Pale yellow	43.15 (43.0)	2.50 (2.55)	O 16.9 (16.35)	P 5.40 (5.30)	
(4) $[Ir(CO)_2H\{P(OPh)_3\}_2]$	White	52.0 (52.5)	3.30 (3.60)			
(5) $[Ir(CO)_2H_2\{P(OPh)_3\}_2][ClO_4]$	White	47.5 (47.0)	3.10 (3.30)	O 20.5 (19.8)		
(6) $[Ir_2(CO)_5(PPh_3)_3]$	Yellow	54.5 (54.2)	3.20 (3.35)	O 5.90 (6.1)	P 7.40 (7.15)	Ir 29.0 (29.5)
(7) $[Ir_2(CO)_5\{PPh_2(C_6H_4Me\text{-}p)\}_2(PPh_3)]$	Yellow	55.0 (54.7)	3.75 (3.65)			
(8) $[\{Ir(CO)_2(PPh_3)(SO_2)\}_2]$	Yellow	41.9 (41.8)	2.20 (2.60)	O 11.0 (11.15)	S 5.40 (5.55)	
(9) $[\{Ir(CO)_2H(PPh_3)\}_2SO_2]$	White	44.0 (44.2)	2.90 (2.95)	O 8.90 (8.85)	S 2.95 (2.95)	Ir 33.7 (35.4)
(10) $[\{Ir(CO)_2D(PPh_3)\}_2SO_2]$	White	43.8 (44.2)	2.75 (2.95)			
(11a) $[\{Ir(CO)(PPh_3)I_2\}_2SO_2]\cdot 0.5C_6H_6$	Red	32.8 (32.7)	2.20 (2.25)	I 31.0 (31.5)		
(11b) $[\{Ir(CO)(PPh_3)I_2\}_2SO_2]\cdot 0.5CH_2Cl_2$	Red	30.25 (29.8)	1.95 (1.90)			
(12) $[\{Ir(CO)[P(OPh)_3]_2(SO_2)\}_2]$	White	49.2 (49.1)	3.20 (3.30)	O 15.85 (15.9)	S 3.50 (3.55)	
(13) $[\{Ir(CO)_2[P(OPh)_3](SO_2)\}_2]$	Pale yellow	38.65 (38.6)	2.50 (2.50)	S 4.95 (5.15)		

* Calculated values are given in parentheses.

TABLE 2

Compound	I.r. data (Nujol) (cm^{-1}) ν(CO)	Other absorptions	N.m.r. data (τ) * Solvent	Ir–H	CH_3	J(PH)/Hz
(2)	2 020m, 1 980s, 1 950vs, 1 920s					
(3)	2 000 (sh), 1 975vs, 1 920 (sh)					
(4)	2 020s, 1 980s	ν(Ir–H) 2 100m, 2 120m ν(Ir–H) (C_6H_6) 2 100m	C_6D_6	22.16 (t)		20
(5)	2 100s, 2 080vs	ν(Ir–H) 2 180s, 2 160vs	$CDCl_3$	21.86 (t)		14.5
(6)	1 975s, 1 960s, 1 920s					
(7)	1 950s, 1 920s		CD_2Cl_2		7.64 (s), 7.72 (s)	
(8)	2 118s, 2 080m, 2 043s	ν_{asym}(SO) 1 230s, 1 210m ν_{sym}(SO) 1 060m, 1 050vs ν_{sym}(SO) 1 190 (sh), 1 117m ν_{sym}(SO) 1 046m, 1 037s				
(9)	2 055s, 2 029m, 2 003s	ν(Ir-H) 2 127s, δ(Ir-H) 815m, 840s, ν_{asym}(SO) 1 190 (sh), 1 117m ν_{sym}(SO) 1 047m, 1 037s	$CDCl_3$	21.31 (d)		
(10)	2 076s, 2 055s, 2 023s, 2 012 (sh)	ν(Ir–D) (KBr) 1 500m				
(11a)	2 050vs	ν_{sym}(SO) 1 215 ν_{sym}(SO) 1 060				
(11b)	2 050vs	ν_{asym}(SO) 1 215 ν_{sym}(SO) 1 060				
(12)	2 030s, 2 070 (sh)	ν_{sym}(SO) 1 055ms, 1 070 (sh)				
(13)	2 090ms, 2 070s, 2 055ms, 2 040ms	ν_{sym}(SO) 1 075s				

* t = Triplet, s = singlet, and d = doublet,

*Reactions with Triphenylphosphine and Diphenyl(*p*-tolyl)phosphine.*—A suspension of (1) in benzene reacts with an excess of triphenylphosphine at 30 °C to give substitution of only one of the carbonyls and formation of $[Ir_2(CO)_5(PPh_3)_3]$ (6). All attempts to prepare the disubstituted compound, corresponding to the phosphite derivative (3), were unsuccessful; increases in reaction time and temperature lead to hydrogen abstraction from the solvent to give the known compound $[Ir(CO)H(PPh_3)_3]$.[4] The instability of the disubstituted phosphine compound may be attributed to

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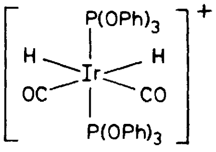
[4] M. Angoletta and G. Caglio, *Ist. Lombardo Scienze e Lettere*, 1963, **97**, 823.

both steric and electronic factors. It is well known that phosphite is less bulky than phosphine and more readily substitutes a CO group than does a phosphine because of its higher π-acceptor strength.

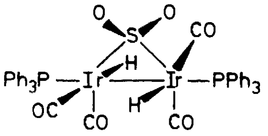


(B)

On treating (1) with diphenyl(*p*-tolyl)phosphine, the compound $[Ir_2(CO)_5\{PPh_2(C_6H_4Me\text{-}p)\}_2(PPh_3)]$ (7) is obtained. We assume that the bonded phosphines exchange with the free phosphines to yield the least-soluble compound. The presence of two molecules of $PPh_2(C_6H_4Me\text{-}p)$ and one of PPh_3 is confirmed by the n.m.r. spectrum (integrated intensity ratios of the methyl groups and the hydrogens of the aromatic rings).

Reaction with Sulphur Dioxide.—The action of sulphur dioxide on (1) leads to substitution of two carbonyls by two sulphur dioxide molecules to form $[\{Ir(CO)_2(PPh_3)(\mu\text{-}SO_2)\}_2]$ (8). It is well known that sulphur dioxide may co-ordinate either as a Lewis base (in which case the MSO_2 moiety is planar) or as a Lewis acid (giving a pyramidal MSO_2 group) or, thirdly, as a bridging ligand (to give a structure having tetrahedral sulphur atoms). Some indication as to the bonding of the SO_2 is obtainable from the ν(SO) stretching frequencies. In compounds in which SO_2 behaves as an acid these frequencies are higher than in those in which SO_2 behaves as a base, *e.g.* compare $[IrCl(CO)(PPh)_2(SO_2)]$ (SO_2 acting as an acid)[5] with $[RuCl(NH_3)_4(SO_2)]$ (SO_2 acting as a base).[6] The frequencies of bridging SO_2, of which only few examples are known,[7-10] are close to those of SO_2 bonding as an acid, as expected, since in both cases the sulphur has a tetrahedral geometry. The ν(SO) stretching frequencies in (8) are compatible with either acid or bridging SO_2. The latter alternative is preferred as the compound is not oxidised by oxygen, whereas acid SO_2 derivatives are readily oxidised by oxygen to form sulphato-compounds.[11-13] The possibility that the SO_2 is co-ordinated through oxygen, suggested by the referees, can be ruled out, in our opinion, for in that case the bands attributable to ν(CO) would fall at *ca.* 1 440 and 950 cm^{-1}.[14] In addition, compound (8) reacts with hydrogen to form $[\{Ir(CO)_2H(PPh_3)\}_2SO_2]$ (9), in which an SO_2 molecule has been substituted by two hydrogen atoms. The same compound is obtained by first transforming (1) into $[Ir(CO)_3(PPh_3)H]$[1] known only in solution, and then treating this with SO_2.

The structure of (9) has been confirmed by *X*-ray analysis[15] to be as in (C). Compound (9) shows an Ir–H stretching band at 2 127 cm^{-1} [which shifts to 1 550 cm^{-1} in the deuteride (10)], C–O stretching bands at 2 055, 2 029, and 2 003 cm^{-1}, asymmetric S–O at 1 177 and 1 190 cm^{-1}, and symmetric S–O at 1 046 and 1 037 cm^{-1}. The SO_2 molecule in compound (9) may formally be considered to act as a diradical, sharing two electrons with the iridium to form two covalent bonds. An alternative is to consider it as accepting two electrons from the metal to form the anion $[SO_2]^{2-}$ [dioxosulphate(2−)] which then bridges as a bidentate ligand. In either case the sulphur would be sp^3 hybridised and the iridium would have a formal oxidation state of II. The fact that the ν(CO) stretching bands in (8) appear at slightly higher wavenumbers than those in the hydride (9) leads to the conclusion that in (8) the iridium is again in formal oxidation state II, *i.e.* the SO_2 bonds as in (9).



(C)

The n.m.r. spectrum of compound (9) should be interpreted as the AA′ part of the system AA′XX′: the two equivalent hydrogen atoms couple with both ^{31}P nuclei, but non-equivalently. The spectrum consists of two narrow lines separated by *ca.* 17 Hz between which there are some other overlapped lines. The analysis of the AA′XX′ theoretical spectrum[16] suggests that the separation of the two highest peaks should be equal to the sum $|J(HP^1) + J(HP^2)|$.

Compound (9) is very stable in solution, both in air and under carbon monoxide. In contrast, reaction with CO causes compound (8) to re-form the starting compound (1), *i.e.* the reaction of (1) with SO_2 is reversible. It is also observed that the derivative with only one molecule of SO_2 is not obtained and this agrees with the suggestion that SO_2 bridges as $[SO_2]^{2-}$. In fact in order that the metal–metal-bonded iridium atoms, in this type of bonding, remain without unpaired electrons, either two or no molecules of SO_2 are required. The stability of the hydride (9) to reaction with CO, which contrasts with the reactivity of (8), may thus be attributed as above, since eventual substitution of two CO molecules by an SO_2 group, bonding as an $[SO_2]^{2-}$

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[5] L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, 1966, **88**, 1333.

[6] L. H. Vogt, jun., J. L. Katz, and S. E. Witerley, *Inorg. Chem.*, 1965, **4**, 1157.

[7] E. H. Braye and W. Hübel, *Angew. Chem. Internat. Edn.*, 1963, **2**, 217.

[8] A. A. Vlček and F. Basolo, *Inorg. Chem.*, 1965, **5**, 156.

[9] S. Otsuka, Y. Tatsuno, M. Miki, T. Aoki, M. Matsumoto, H. Yoshioka, and K. Nakatsu, *J.C.S. Chem. Comm.*, 1973, 445.

[10] M. R. Churchill, B. G. DeBoer, and K. L. Kalba, *Inorg. Chem.*, 1973, **12**, 1646.

[11] J. Valentine, D. Valentine, and J. Collman, *Inorg. Chem.*, 1971, **10**, 219.

[12] J. J. Levison and S. D. Robinson, *J.C.S. Dalton*, 1972, 2014.

[13] M. H. B. Stiddard and R. E. Townsend, *J. Chem. Soc.* (*A*), 1970, 2719.

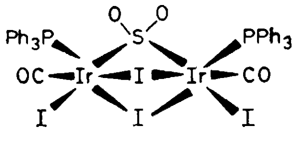
[14] D. C. Moody and R. R. Ryan, *J.C.S. Chem. Comm.*, 1976, 503.

[15] M. Angoletta, P. L. Bellon, M. Manassero, and M. Sansoni, *J. Organometallic Chem.*, 1974, **81**, C40—C42.

[16] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, p. 396.

bridge, would be accompanied by considerable electron redistribution with, probably, scission of the metal–metal bond. In addition, it may be recalled that other hydrides not containing bridging SO_2 have been found to be very unstable.[12]

Compound (8) reacts with dichlorine and dibromine to give the known dimeric derivative $[\{Ir(CO)(PPh_3)X_3\}_2]$, having a halogen bridge.[2] With iodine, rather like dihydrogen, only one of the SO_2 molecules is substituted. However, in contrast to dihydrogen, iodine also causes scission of the metal–metal bond before coordinating to the iridium. The resulting compound is $[Ir_2(CO)_2(PPh_3)_2(SO_2)I_4]$ (11), the structure of which has been confirmed by *X*-ray crystallography.[17] In compound (11) the two metal atoms are at the centres of two octahedra sharing a face, defined by the bridging SO_2 and by two bridging iodine atoms. The distance Ir–Ir (3.43 Å) indicates a non-bonding interaction.



(D)

The reaction between the phosphite-containing compounds (2) and (3) and sulphur dioxide is analogous to that for (1). The compounds formed, $[\{Ir(CO)[P(OPh)_3]_2(SO_2)\}_2]$ (12) and $[\{Ir(CO)_2[P(OPh)_3](SO_2)\}_2]$ (13), probably contain two bridging SO_2 molecules and a metal–metal bond.

EXPERIMENTAL

Bis[dicarbonylbis(triphenyl phosphite)iridium](Ir–Ir) (2).—The compound $[\{Ir(CO)_3(PPh_3)\}_2]$ (1) (0.274 g) and triphenyl phosphite (15 cm^3) were heated at 90—100 °C and the orange solution was poured into hexane (150 cm^3) with stirring. The yellow microcrystalline powder was recrystallised from benzene–hexane, yield 0.346 g (78%), m.p. 101 °C.

Bis[tricarbonyl(triphenyl phosphite)iridium](Ir–Ir) (3).—Compound (2) (0.17 g) in benzene (15 cm^3) was stirred under CO for 30 min at room temperature. Degassed ethanol (*ca.* 30 cm^3) was added while CO was bubbled through the solution. After 48 h (with a continuous flow of CO) a pale yellow crystalline precipitate was obtained (0.045 g, 38%), m.p. 185 °C.

Dicarbonylhydridobis(triphenyl phosphite)iridium (4).—Compound (2) (0.1 g) was suspended in benzene (15 cm^3) and treated with H_2 at room temperature, with stirring, until a clear colourless solution was obtained. This was evaporated almost to dryness and light petroleum was added. A white microcrystalline compound separated (0.075 g, 75%), *M* (benzene) 865 (calc.: 867).

Dicarbonyldihydridobis(triphenyl phosphite)iridium Perchlorate (5).—Compound (4) (0.15 g) in ethanol (10 cm^3) was added to $HClO_4$ (70%, 0.3 cm^3) and the mixture was warmed to 40—50 °C and filtered. Cooling the solution gave white crystals (0.143 g, 85%), m.p. 120 °C (decomp.).

Pentacarbonyltris(triphenylphosphine)di-iridium(Ir–Ir) (6).—Compound (1) (0.120 g) dissolved in benzene (30 cm^3) was heated under reflux with PPh_3 (0.120 g, mol ratio 1 : 4) in a stream of CO for 15 min. The limpid yellow-orange solution was cooled in a current of dinitrogen, ethanol (*ca.* 30 cm^3) was added, and the mixture concentrated *in vacuo*. The yellow precipitate obtained was recrystallised from benzene–ethanol, yield 0.056 g (40%), m.p. 180—182 °C, *M* (benzene) 1 350 (calc.: 1 310).

Pentacarbonylbis[diphenyl(p-*tolyl)phosphine](triphenylphosphine)di-iridium*(Ir–Ir) (7).—Compound (1) (0.160 g) and diphenyl(*p*-tolyl)phosphine (0.165 g), dissolved in benzene (20 cm^3), were heated under reflux under CO for 20 min. The yellow solution obtained was cooled and ethanol (*ca.* 30 cm^3) was added. The yellow crystals which precipitated were recrystallised from benzene–ethanol, yield 0.052 g (26%), m.p. 130 °C.

Di-μ-(sulphur dioxide)-bis[dicarbonyl(triphenylphosphine)-iridium] (8).—Compound (1) (0.180 g) dissolved in benzene (25 cm^3) was stirred under SO_2 at room temperature until a limpid yellow solution was obtained. Concentration of this solution gave a yellow microcrystalline solid. This was recrystallised from chloroform–light petroleum, yield 0.123 g (64%), m.p. 205 °C, *M* ($CHCl_3$) 1 100 (calc.: 1 148).

μ-(Sulphur dioxide)-bis[dicarbonylhydrido(triphenylphosphine)iridium] (Ir–Ir) (9).—A solution of (8) (0.188 g) in benzene (25 cm^3) was stirred under H_2 at *ca.* 50 °C to give, after *ca.* 20 min, a limpid pale yellow solution. On cooling this solution a white crystalline precipitate separated, which was recrystallised from $CHCl_3$, yield 0.141 g (79%), m.p. 205 °C, *M* ($CHCl_3$) 1 050 (calc.: 1 080).

μ-(Sulphur dioxide)-bis[dicarbonyldeuterio(triphenylphosphine)iridium] (Ir–Ir) (10) was prepared as for (9) using D_2 instead of H_2.

Di-μ-iodo-μ-(sulphur dioxide)-bis[carbonyliodo(triphenylphosphine)iridium]-Benzene (2/1) (11).—A solution of (8) (0.187 g) in benzene (25 cm^3) was treated with I_2 (0.068 g) in benzene (mol ratio 1 : 3) with stirring at room temperature. After a few minutes a limpid red solution was obtained. This was concentrated *in vacuo* to a third of its volume and methanol (*ca.* 30 cm^3) was added. The red crystalline precipitate obtained was recrystallised from hot benzene–methanol. The compound (11a) contains half a molecule of benzene of crystallisation and melts at 175 °C, yield 0.150 g (56%). Slow crystallisation gave a compound with two molecules of benzene of crystallisation. Recrystallisation from dichloromethane–ethanol resulted in substitution of the benzene of crystallisation in (11a) by dichloromethane to give (11b).

Di-μ-(sulphur dioxide)-bis[carbonylbis(triphenyl phosphite)-iridium](Ir–Ir) (12).—A solution of (2) (0.160 g) in benzene (20 cm^3) was stirred under SO_2 for 20 min and the pale yellow solution obtained was concentrated to *ca.* 5 cm^3 and poured into hexane (40 cm^3). The white microcrystalline compound precipitated was recrystallised by adding a benzene solution of it to stirred hexane, yield 0.132 g (78%), *M* (C_6H_6) 1 850 (calc.: 1 808).

Di-μ-(sulphur dioxide)-bis[dicarbonyl(triphenyl phosphite)-iridium](Ir–Ir) (13).—After a few minutes stirring, a solution of (3) (0.065 g) in benzene (20 cm^3) under SO_2 gave a limpid colourless solution. Concentration of the solution and addition of hexane caused precipitation of a pale yellow crystalline compound which was recrystallised from benzene–hexane, yield 0.544 g (83%), m.p. 102 °C.

[7/617 *Received, 7th April,* 1977]

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[17] P. L. Bellon, M. Manassero, and M. Sansoni, Atti II convegno Cristallografico Italo–Jugoslavo, Dubrovnik, May—June 1976.