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Photo-induced Degradation of $Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}CNPh)Cl_2$ and $Pd_2(\mu\text{-}Ph_2PCH_2Ph_2)_2Cl_2$, and the Crystal Structure of $Pd_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}CNPh)Cl_2$*

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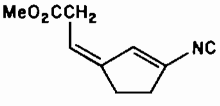
Abstract

Spectroscopic studies of $Pd_2(dppm)_2(\mu\text{-}CNPh)Cl_2$ (**1**) and $Pd_2(dppm)_2Cl_2$ show that they are light sensitive. Complete degradation of both complexes, to give a mixture of products including $Pd(dppm)Cl_2$, occurs within 0.5–1 h when *ca.* 5×10^{-5} M solutions in dichloromethane are irradiated with a 100 W tungsten lamp. Crystal structure analysis of **1** has shown that it is tetragonal (space group $P4_1$, $Z = 4$). Cell dimensions and final R-value are: $a = 21.233(2)$, $c = 14.252(3)$ Å, $R = 0.042$ for 3892 observed reflections. A most interesting feature of **1** is a continuous channel, about 10 Å in diameter, extending along the 4_1 axis. The unusually large channel can accommodate molecules of solvent such as cyclohexane or dichloromethane. In the case of **1**, uptake of solvent is readily reversible without concomitant collapse of the crystal lattice.

Introduction

A great deal of interest has been shown in the reactivity and structural properties of the bimetallic complexes of bridging ligands such as bis(diphenylphosphino)methane (dppm) because of their rich chemistry and potential catalytic activity [1–3]. The so-called 'A-frame' complexes [4] constitute an important group of compounds of this type. A survey of the crystal structures of 'A-frame' complexes shows that five of these, $Pd_2(dpam)_2(\mu\text{-}CO)Cl_2$ (**2**) (dpam = $Ph_2AsCH_2AsPh_2$) [5], $Pd_2(dppm)_2(\mu\text{-}S)Cl_2$ (**3**) [6], $Pd_2(dppm)_2(\mu\text{-}F_3CCCCF_3)Cl_2$ (**4**) [7], $Rh_2(dppm)_2(\mu\text{-}F_3CCCCF_3)Cl_2$ **5** [8] and $Rh_2(dppm)_2(\mu\text{-}CH_2)(\mu\text{-}F_3CCCCF_3)Cl_2$ (**6**) [9], belong to the tetragonal space group $P4_1$ (or $P4_3$). A remarkable feature of this structure is a continuous channel, about 10 Å in diameter, extending along the 4_1 axis. There has been some speculation concerning the stability of such an open structure, and it was surmised that loosely held solvent molecules in the channels were necessary to stabilise the crystal packing [5]. However, the more recently determined [7–9] structures of this type contain no solvent of crystallisation, and the crystals appear to be quite stable. We became interested in such complexes during a recent investigation [10] of the mixture of isomeric adducts $(Pd_2(dppm)_2(\mu\text{-}CNR)Cl_2$ (**7**), R = $C_9H_{11}O_2$) formed from the labile isocyanide methy-3-(3′-isocyanocyclopent-2′-enylidene) propanoate **8** and $Pd_2(dppm)_2Cl_2$ (**9**). On recrystallisation, **7** gave crystals isostructural to those of complexes **2**–**6**. The crystals from **7** contained no solvent of crystallisation, and were unstable, a 30% decrease of intensity of a standard reflection being observed during data collection. However, since these crystals darkened when exposed to light, it seemed likely that degradation was due to photodecomposition rather than collapse of crystal lattice as a result of the absence of solvent of crystallisation. In order to develop a better understanding of the factors responsible for the relative stabilities of these complexes, and to obtain accurate parameters for the briding isocyanide moiety, it was decided to investigate an 'A-frame' complex derived from a more stable isocyanide ligand. We report herein the results of a crystal structure study of $Pd_2(dppm)_2(\mu\text{-}CNPh)Cl_2$ (**1**), and the observation that both this complex and its precursor, $Pd_2(dppm)_2Cl_2$ (**9**), are light sensitive.



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Experimental

The preparation of **1** and spectroscopic measurements were carried out in air using commercially available dichloromethane as solvent. Infrared and electronic spectra were recorded on Perkin Elmer

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283B and Cary 14 spectrophotometers respectively. Analytical t.l.c. was carried out on silica gel (Merck Kieselgel $60F_{254}$) plates with dichloromethane-methanol (1:19) as eluant. An authentic sample of the complex Pd(dppm)Cl_2, prepared [11] for t.l.c. comparison, showed λ_{max} 352 nm (ϵ = 7010 dm^3 mol^{-1} cm^{-1}).

Preparation of $Pd_2(dppm)_2(\mu$-CNPh)Cl_2 (1) (cf. refs. 12, 13)

A solution (1 cm^3) of phenylisocyanide (7 mg) was added to a solution (5 cm^3) of $Pd_2(dppm)_2Cl_2$ (70 mg). On standing overnight at ambient temperature, **1** was deposited as orange needles. After washing with dichloromethane-diethyl ether (1:2, 3 X 2 cm^3), and then ether (2 cm^3), and drying in air, these (71 mg) had m.p. 204–205 °C (lit. [12], 195–196 °C); λ_{max} 446, 390 sh and 284 nm (ϵ = 14,100, 6,450 and 25,600 dm^3 mol^{-1} cm^{-1} respectively); ν_{max} (nujol) 1624 and 1574 cm^{-1}.

Irradiation of 1 and of $Pd_2(dppm)_2Cl_2$ (9)

Solutions of **1** and of **9**, and a finely ground sample of **1**, were irradiated (through Pyrex or borosilicate glass containers) at *ca.* 25 °C with a tungsten lamp (100 W) placed *ca.* 20 cm from the sample. Progress of the photolyses is illustrated in Figs. 1 and 2.

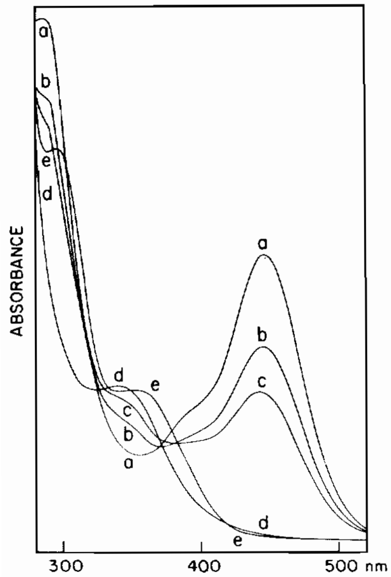

Fig. 1. Photolysis of $Pd_2(\mu$-CNPh)$(dppm)_2Cl_2$ (**1**); electronic spectra in dichloromethane solution. (a) Freshly prepared (**1**), 57.84 mg dm^{-3}. (b) Sample of (**1**) which had been stored for several weeks at ambient temperature without protection from light, 54.72 mg dm^{-3}. (c) Sample (b) after grinding to a fine powder and irradiation for 48 h with a 100 W tungsten lamp before dissolution in dichloromethane, 52.80 mg dm^{-3}. (d) Sample (a) after irradiation for 1.25 h in dichloromethane solution with a 100 W tungsten lamp. (e) Irradiation as for (d) under dry nitrogen in freshly dried solvent, *ca.* 50 mg dm^{-3}.

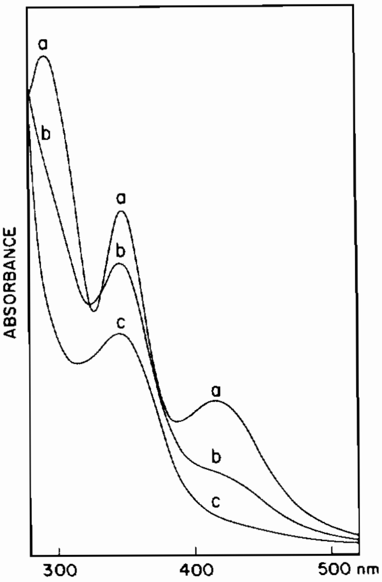

Fig. 2. Photolysis of $Pd_2(dppm)_2Cl_2$ (**9**); electronic spectra in dichloromethane solution. (a) Freshly prepared (**9**), 47.57 mg dm^{-3}. (b) Solution (a) after irradiation for 0.5 h with a 100 W tungsten lamp. (c) Solution (b) after further irradiation for 1 h.

Crystallography

Preliminary unit cell dimensions were determined from photographic data, and more accurate values from the least-squares analysis of the diffractometer settings of 24 high angle (99–104°) reflections (radiation = $CuK\alpha_1$, λ = 1.54056 Å).

Crystal Data

Orange needles (c) $C_{57}H_{49}Cl_2NP_4Pd_2$, M = 1158.6, tetragonal, T = 23 °C, a = 21.233(2), c = 14.252(2) Å, U = 6425 $Å^3$, D_m = 1.21–1.49 g cm^{-3} (in carbon tetrachloride–cyclohexane, initial density measurement gave a value of 1.21; on standing overnight a limiting value of 1.49 was obtained; after redrying in air for 2 h, the crystals did not show any deterioration and gave a value of 1.23), D = 1.195 g cm^{-3}, Z = 4, $F(000)$ = 2336, μ = 66.1 cm^{-1}, space group $P4_1$ ($P4_3$).

A crystal of dimensions 0.12 X 0.15 X 0.50 mm was mounted along the needle axis and the data were collected on a Picker 4-circle diffractometer, using Ni-filtered CuKα radiation. The $\theta-2\theta$ scan method was used, and individual reflection profiles were analysed as described by Grant and Gabe [14]. Three standard reflections, monitored after every 60 measurements, showed no significant intensity changes during data collection.

The standard deviations were evaluated from the counting statistics; reflections with $I_{net} > 2\sigma(I_{net})$ were classed as 'observed' and were used in the subsequent analysis. These numbered 3892 of a possible

TABLE I. Atomic Parameters for **1**. (e.s.d.s refer to the last digit printed).

Atom	x	y	z	B_{eq}[a]
Pd(1)	0.71908(3)	1.00942(3)	0.00000	3.42
Pd(2)	0.61351(3)	0.93530(4)	0.11453(7)	3.57
Cl(1)	0.7813(1)	1.1060(1)	−0.0076(2)	5.2
Cl(2)	0.5478(1)	0.9277(2)	0.2525(2)	5.8
P(1)	0.6359(1)	1.0588(1)	−0.0778(2)	3.7
P(2)	0.7967(1)	0.9498(1)	0.0750(2)	3.4
P(3)	0.5355(1)	0.9773(1)	0.0171(2)	3.8
P(4)	0.6946(1)	0.8809(1)	0.1891(2)	4.4
N	0.6644(4)	0.8836(4)	−0.0518(7)	4.3
C(1)	0.5654(4)	1.0094(5)	−0.0933(8)	4.1
C(2)	0.7684(4)	0.8745(4)	0.1212(8)	3.5
C(3)	0.6674(4)	0.9312(4)	0.0028(8)	3.6
C(11)	0.6536(5)	1.0849(5)	−0.1952(8)	4.4
C(12)	0.6874(6)	1.1429(6)	−0.2030(11)	7.1
C(13)	0.7059(6)	1.1618(7)	−0.2947(10)	7.2
C(14)	0.6909(6)	1.1263(7)	−0.3720(10)	7.4
C(15)	0.6581(7)	1.0709(7)	−0.3646(10)	7.8
C(16)	0.6398(6)	1.0489(6)	−0.2744(9)	6.2
C(21)	0.6054(4)	1.1292(5)	−0.0189(8)	4.3
C(22)	0.6296(6)	1.1475(6)	0.0659(10)	5.9
C(23)	0.6066(7)	1.2035(7)	0.1151(14)	8.9
C(24)	0.5541(7)	1.2338(7)	0.0707(13)	8.5
C(25)	0.5307(7)	1.2155(6)	−0.0138(14)	8.4
C(26)	0.5556(6)	1.1624(6)	−0.0608(10)	6.5
C(31)	0.8600(4)	0.9252(5)	−0.0030(9)	4.1
C(32)	0.8901(5)	0.8652(5)	0.0043(11)	6.1
C(33)	0.9357(6)	0.8500(6)	−0.0622(10)	6.6
C(34)	0.9535(5)	0.8923(6)	−0.1315(11)	6.6
C(35)	0.9252(6)	0.9497(6)	−0.1384(10)	6.8
C(36)	0.8772(5)	0.9656(5)	−0.0756(9)	5.1
C(41)	0.8360(5)	0.9870(5)	0.1739(7)	4.0
C(42)	0.8153(6)	1.0448(5)	0.2070(8)	5.0
C(43)	0.8450(7)	1.0695(6)	0.2861(11)	7.6
C(44)	0.8917(7)	1.0388(7)	0.3336(10)	7.6
C(45)	0.9129(7)	0.9810(7)	0.3000(10)	7.9
C(46)	0.8874(6)	0.9550(6)	0.2179(12)	7.9
C(51)	0.4827(5)	0.9154(5)	−0.0240(8)	4.7
C(52)	0.4481(5)	0.9198(6)	−0.1049(9)	6.0
C(53)	0.4097(6)	0.8685(7)	−0.1323(12)	7.7
C(54)	0.4066(7)	0.8157(7)	−0.0798(12)	8.5
C(55)	0.4413(7)	0.8097(7)	0.0020(14)	9.2
C(56)	0.4806(6)	0.8586(6)	0.0326(11)	6.8
C(61)	0.4828(5)	1.0381(5)	0.0655(8)	4.3
C(62)	0.4303(5)	1.0569(6)	0.0108(11)	6.4
C(63)	0.3921(6)	1.1068(6)	0.0514(11)	6.9
C(64)	0.4038(6)	1.1316(6)	0.1356(11)	7.0
C(65)	0.4554(6)	1.1095(6)	0.1886(10)	6.4
C(66)	0.4968(6)	1.0634(5)	0.1512(9)	5.3
C(71)	0.6739(5)	0.7992(6)	0.2114(13)	8.1
C(72)	0.7044(9)	0.7512(8)	0.1767(21)	15.7
C(73)	0.6861(11)	0.6858(9)	0.1849(28)	20.5
C(74)	0.6379(10)	0.6755(8)	0.2348(33)	23.4
C(75)	0.6122(13)	0.7194(10)	0.2830(38)	32.0
C(76)	0.6289(12)	0.7849(9)	0.2693(26)	21.9
C(81)	0.7204(5)	0.9134(7)	0.3018(8)	6.8
C(82)	0.6973(6)	0.9719(8)	0.3266(10)	8.2
C(83)	0.7163(7)	1.0012(11)	0.4120(13)	12.0
C(84)	0.7559(7)	0.9650(14)	0.4667(13)	15.1
C(85)	0.7801(7)	0.9098(14)	0.4459(14)	15.6
C(86)	0.7610(7)	0.8798(12)	0.3578(12)	13.8
C(91)	0.7006(5)	0.8694(5)	−0.1299(9)	4.7
C(92)	0.7013(6)	0.8049(5)	−0.1561(9)	5.8
C(93)	0.7362(7)	0.7862(7)	−0.2337(11)	7.9
C(94)	0.7699(7)	0.8290(7)	−0.2837(11)	7.8
C(95)	0.7701(7)	0.8899(8)	−0.2602(12)	9.4
C(96)	0.7345(6)	0.9124(6)	−0.1820(9)	6.3

[a] $B_{eq} = 8\pi^2 [1/3(U_{11} + U_{22} + U_{33})]$.

4707 ($2\theta_{max}$ = 116°). Lorentz, polarisation and absorption correction (Gaussian integration, transmission coeff. 0.295–0.512) were applied to the intensities.

The structure was solved by the heavy atom method and refined by block-diagonal least-squares, minimising $\Sigma w(|F_o| - |KF_c|)^2$, where $w = [\sigma^2(F_o) + 0.0005\ F_o^2]^{-1}$. Positional and anisotropic thermal parameters were refined for all the non-hydrogen atoms. Convergence was achieved with the final R-value = 0.042 for 'observed' reflections, R_w = 0.051. The space group $P4_1$ was proved to be the correct choice since the final R_w value for the space group $P4_3$ was 0.062. The final difference map had no features of any chemical significance, the largest peak being 0.3 e Å^{-3}.

The computer programs used for calculations have been described by Larson and Gabe [15]. The atomic scattering factors were taken from International Tables, Vol. IV [16]. Final atomic coordinates are listed in Table I. Figure 3 shows the atomic numbering scheme and selected bond lengths, while the bond angles are given in Table II. Tables of

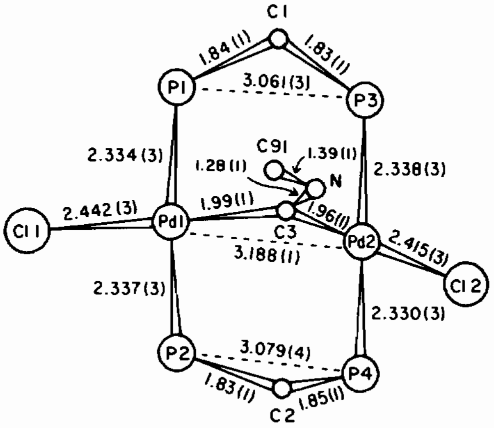

Fig. 3. Selected bond lengths (A) and atomic numbering scheme for **1**.

TABLE II. Selected Bond Angles (°).

Cl(1)–Pd(1)–P(1)	90.7(1)
Cl(1)–Pd(1)–P(2)	95.4(1)
Cl(1)–Pd(1)–C(3)	178.5(3)
P(1)–Pd(1)–P(2)	173.8(1)
P(1)–Pd(1)–C(3)	88.2(3)
P(2)–Pd(1)–C(3)	85.8(3)
Pd(1)–C(3)–N	132.5(8)
Pd(1)–C(3)–Pd(2)	107.5(5)
Cl(2)–Pd(2)–P(3)	95.7(1)
Cl(2)–Pd(2)–P(4)	91.3(1)
Cl(2)–Pd(2)–C(3)	173.6(3)
P(3)–Pd(2)–P(4)	169.6(1)
P(3)–Pd(2)–C(3)	87.1(3)
P(4)–Pd(2)–C(3)	85.2(3)
Pd(2)–C(3)–N	120.0(7)
C(3)–N–C(91)	129.3(9)

structure factors and anisotropic thermal parameters are available upon request from the authors.

Results and Discussion

X-ray analysis of **1** shows that it is isostructural to 2–7 [5–10]. The crystal structure consists of discrete molecules packing in a spiral fashion along the 4_1 axis with an unusually large channel, approximately 10 Å in diameter, in the center. Figure 4 gives the packing diagram for **1**. For the sake of clarity all the phenyl groups are omitted, except one which protrudes into the channel. No solvent molecules were found in the crystal, indicating that crystal stability is not solvent dependent. Although the results of crystal density measurement (see Experimental) show that solvent can readily gain access to the channel, when crystals which have been allowed to sit in solvent are exposed to air the solvent is readily lost without observable degradation of the crystals.

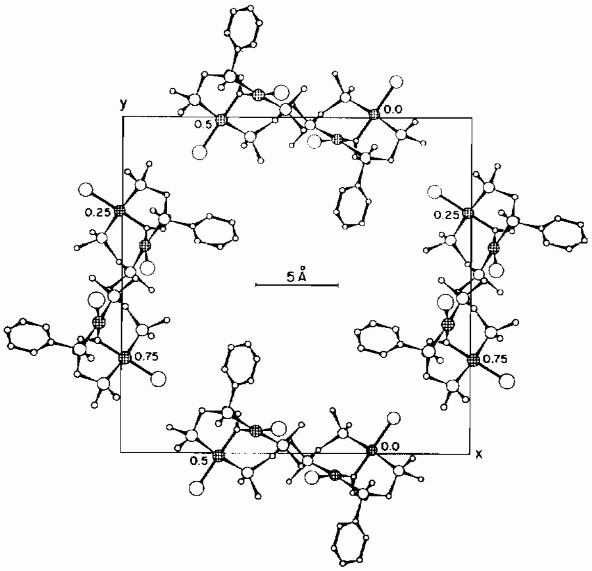

Fig. 4. Packing diagram for **1**. For the sake of clarity all the phenyl groups are omitted, except one which protrudes into the channel. Fractional *z*-coordinate of the Pd(1) atom is shown.

The molecular structure of **1** (Fig. 3) is similar to that of other 'A-frame' complexes [5, 6, 10, 17–20]. The Pd···Pd distance of 3.188(4) Å in **1** is comparable to the distance of 3.198(4) Å found in **7** [10]. The configuration around each Pd atom is slightly distorted from square planar as reflected in the bond angles. The bridging isocyanide moiety has the typical bent geometry with an angle of 129.3(9)° at the N atom. The value is comparable with 131(2)° and 133(3)° reported for $[Pd_2(dppm)_2(\mu\text{-CNMe})(CNMe)_2]^{2+}$ [17] and **7** [10] respectively. An interesting feature of the isocyanide coordination in **1** is the significant difference between the Pd–C–N angles which are 132.5(8)° and 120.0(7)° for Pd(1) and Pd(2) respectively. This difference is presumably due to the steric requirements of the phenyl ring, which lies on the side with the larger Pd–C–N angle.

Crystals of **1**, although more stable than those of **7**, also proved to be light sensitive. Thus, darkening was observed after a few days in a batch which had been stored at ambient temperature without protection from light, while batches which were stored in the dark at 0 °C appeared to be unchanged. A sample stored for 8 months under the latter conditions showed no change of colour or crystallinity. During X-ray data collection (*ca.* 15 d) only a 1% random fluctuation of the intensity of the standard reflections was observed, but over a further month a gradual decline of *ca.* 50% occurred, at which stage the crystal had become dark and translucent. That chemical change, as opposed to breakdown of an unstable crystal lattice, was occurring was demonstrated by comparison of the electronic spectrum of freshly-prepared **1** (Fig. 1a) with the spectrum of a sample of **1** which had been stored for some time without protection from light (Fig. 1b), and of the latter sample after irradiation with a 100 W tungsten lamp (Fig. 1c). The spectra show the decay of the absorption bands of **1** with concomitant build-up of a new band at *ca.* 340 nm. Tungsten lamp irradiation of a solution of **1** in dichloromethane resulted in fading of the orange colour of the solution and disappearance of the absorption bands due to **1** within 0.5 h, again accompanied by growth of a band at 340 nm (Fig. 1d). Analytical t.l.c. of the solutions from these irradiations showed the presence of several components including one with an R_F corresponding to $Pd(dppm)Cl_2$. When irradiation of a dichloro-

TABLE III. Vol/non-H Atom for Selected Compounds.

Compound	Vol (A^3)	Ref.	Compound	Vol (A^3)	Ref.
1 $Pd_2(dppm)_2(\mu\text{-CNPh})Cl_2$	24.34	–	1 $Rh_2(dppm)_2(\mu\text{-S})(CO)_2$	18.97	4
2 $Pd_2(dppm)_2(\mu\text{-S})Cl_2 \cdot 3CH_2Cl_2$	23.18	6	2 $Pd_2(dppm)_2(\mu\text{-SO}_2)Cl_2 \cdot \frac{1}{2}CH_2Cl_2 \cdot CH_3OH$	19.06	6
3 $Pd_2(dppm)_2(\mu\text{-C}_4F_6)Cl_2$	23.60	7	3 $Rh_2(dppm)_2(\mu\text{-SO}_2)Cl_2$	19.19	18
4 $Rh_2(dppm)_2(\mu\text{-C}_4F_6)Cl_2$	23.74	8	4 $Rh_2(dppm)_2(\mu\text{-CO})Br_2$	18.79	19
5 $Rh_2(dppm)_2(\mu\text{-CH}_2)(\mu\text{-C}_4F_6)Cl_2$	24.03	9	5 $Rh_2(dppm)_2(\mu\text{-CO})(\mu\text{-CH}_3O_2CC_2CO_2CH_3)Cl_2$	20.74	20
6 $Pd_2(dppm)_2(\mu\text{-CNR})Cl_2$	23.04	10			
MEAN	23.7(5)		MEAN	19.3(8)	

$\Delta V = 4.3$ A^3/non-H atom and 1137.8 A^3/U-cell (266 atoms)

methane solution of **1** was carried out under nitrogen in freshly distilled, dried solvent, photolysis again took place, and the new electronic spectral maximum (Fig. 1e) appeared at 352 nm. Again, analytical t.l.c. indicated that $Pd(dppm)Cl_2$ was formed along with other products.

Samples of **9** also became discoloured when stored without protection from light. Irradiation of solutions of **9** in dichloromethane causes fading of their orange colour. Electronic spectra (Fig. 2) show the disappearance of the absorption bands due to **9** and the growth of a new maximum at 347 nm, while t.l.c. indicates that a mixture of products, including $Pd(dppm)Cl_2$, is formed. It is surprising that there appears to be no previous report of the sensitivity of **1** and **9** to light. Indeed the olefinic isomerisation observed [10] in the course of reaction of isocyanide **8** with **9** could have been catalysed by a product of photolysis of the latter. It has been reported that the platinum analogue of **9**, on standing in dichloromethane solution for several days, gives appreciable amounts of $Pt(dppm)Cl_2$ along with other unidentified products, but there is no indication of whether or not the solutions were protected from light [22].

The foregoing results suggest that the open crystal structure adopted by complexes **1**–**7** does not require any solvent of crystallisation to stabilise it as surmised earlier [5, 6]. In fact the evidence indicates that the relative stabilities of 'A-frame' complexes of types **1**–**7** depend mainly on the readiness with which the bridging (CO, S, isocyanide, acetylene) ligand is lost, and on the possibility of escape or further reaction of the resulting fragments. In the case of the CO-bridged complex **2**, the observed [12, 21] ready reversibility of formation of analogues of general formula $Pd_2(dppm)_2(\mu\text{-CO})X_2$ suggests that extrusion of CO, and its subsequent escape from the lattice, constitute the principal decomposition route for this complex. The stabilising effect of solvent may then be ascribed to its blocking the channels in the crystals of **2**, thereby hindering the escape of CO, which therefore has the opportunity to reform the original complex. Although the insertion of sulphur into $Pd_2(dppm)_2Cl_2$ to form **3** has not been reversed [2, 6], the crystal structure analysis of **3** was performed under conditions designed to preserve solvent in the channels [6]. Our results indicate that such a procedure should not have been necessary to maintain crystallinity. Formation of isocyanide-bridged complexes such as **1** and **7** from **9** is also not readily reversible [2]. Extrusion of isocyanide ligand could however be promoted by irradiation, net decomposition of the complexes **1** and **7** resulting since **9** thus formed is itself susceptible to photolysis. The greater stability of **1** compared to **7** presumably reflects the intrinsic lability of the isocyanide ligand in the latter complex. Finally, while crystals of the acetylene-bridged complexes **4**–**6** appear to have been well-behaved during data collection, it has been observed [2] that the complex $Pd_2(dppm)_2(\mu\text{-MeO}_2CC{\equiv}CCO_2Me)Cl_2$ undergoes photodissociation. It is therefore likely that **4**–**6** will undergo a similar reaction.

The volume/non-H atoms values for the complexes **1**, **3**–**7** and for five similar compounds with more efficient crystal packing [4, 6, 18–20] are given in Table III. The difference in mean vol/non-H atoms ratio between these two groups of complexes is 4.3 Å/atom and 1138 Å/unit cell. The channels, therefore, can accommodate a fairly large number of guest molecules. For example this space is sufficient for ~13 benzene or 33 methanol molecules (vol of benzene = 85.4 Å^3 and methanol = 34.9 Å^3 [23]). Such systems appear to have good potential for studying solid-state reactions.

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