Light-induced Reactions of *trans*-Chloro(cyanomethyl)bis(triphenylphosphine)palladium(II) and the Crystal and Molecular Structures of its Acetone, Acetonitrile, and Benzene Solvates

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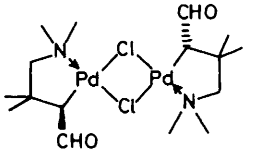
X-Ray structure determinations have been completed for the acetone, acetonitrile, and benzene solvates of [PdCl(CH_2CN)(PPh_3)$_2$] (2). Crystals of (2) • acetone and (2) • acetonitrile are isomorphous, monoclinic, space group $P2_1/n$ with four formula units in the unit cell. The acetone solvate has cell data: a = 12.679(4), b = 14.553(1), c = 19.506(5) Å, and β = 94.72(1)°; for the acetonitrile solvate a = 12.581(2), b = 14.323(2), c = 19.359(3) Å, and β = 93.85(1)°. The (2) • benzene crystals are also monoclinic, space group $P2_1/a$, with four formula units in a unit cell of dimensions a = 22.140(3), b = 10.058(1), c = 18.699(6) Å, and β = 114.78(2)°. The structures were solved by the heavy-atom method and refined by full-matrix least squares calculations to R = 0.026, 0.028, and 0.050 for 4 907 2,998, and 3 664 observed reflections for the acetone, acetonitrile, and benzene solvates, respectively. In all three complexes molecule (2) has slightly distorted square planar co-ordination with Pd–P 2.319—2.342(1), Pd–Cl 2.369(2)–2.394(1), and Pd–C 2.063(2)—2.088(6) Å. In (2) • acetone and (2) • acetonitrile the solvent molecules are trapped in polar pockets whereas in (2) • benzene the benzenes of solvation are in non-polar channels. The structures show little evidence of an interaction of the nitrile carbon atom with the metal atom nor any obvious structural features that might explain the photochromic behaviour of crystalline (2). Irradiation of (2) with u.v. or tungsten lamps, either in the solid state or in solution, leads to similar products. In the presence of oxygen, in benzene, the principal products are *trans*-[$PdCl_2(PPh_3)_2$] (3), [{PdCl(CH_2CN)(PPh_3)}$_n$] (4), [{$PdCl_2(PPh_3)$}$_2$] (5), PPh_3O (6), and acetonitrile. The accumulation of (4) and (5) results from a loss of PPh_3 [from (2) and (3) respectively], the oxidation of which is probably catalysed by a reduced palladium species generated by photolysis of (2). In the absence of oxygen, in benzene, the only products identified were (3) and acetonitrile whilst in chloroform essentially quantitative conversion of (2) into (3), acetonitrile, and some succinonitrile is observed. Although an e.s.r. investigation showed that radicals are generated upon irradiation of (2) the principal mode of formation of acetonitrile appears to involve proton abstraction from traces of water in the solvent. The red colour assumed by crystalline (2) upon irradiation is limited to the surface. Similar colours have been obtained by heating or irradiating (2) in solution and by treating ethanolic solutions of (3) with base. It is suggested that reduced palladium species are responsible for these colours.

IN an earlier paper, in which we reported [1] the structure of di-μ-chloro-bis[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-*CN*]dipalladium(II) (1), it was noted that the bond angle Pd–C(1)–C(formyl) is severely distorted (97.9°) from the tetrahedral valence angle. To account for this, it was suggested that there is some interaction between the metal atom and the formyl carbon atom. Such β-effects involving carbonyl and also nitrile carbon atoms are well known [2] and often have been signalled by the appearance at relatively low energies of the i.r. absorption band assigned to stretching of the multiple bond. In order to determine if a distortion similar to that observed for (1) could be detected in an α-cyanoalkylpalladium derivative we have performed *X*-ray crystallographic studies on three solvates of the previously reported [3] *trans*-[PdCl(CH_2CN)(PPh_3)$_2$] (2). We hoped that these studies might in addition shed some light (!) on the process(es) responsible for the observed [3,4] photochromism of (2).



(1)

RESULTS

We have determined the crystal and molecular structures for the acetone, acetonitrile, and benzene solvates of (2). The acetone and acetonitrile solvates are isomorphous; Figure 1 shows a view of (2) in (2) • acetone, Figure 2 of (2) in (2) • benzene, and Figures 3 and 4 show the packing diagrams for (2) • acetone and (2) • acetonitrile respectively. The conformation of (2) in (2) • benzene (shown in Figure 2) is quite different from that in Figure 1; the packing diagram for (2) • benzene is shown in Figure 5. Details of the principal dimensions of the three solvates are given in Table 1.

Since it was found that irradiation of (2) with long wavelength u.v. light (350 nm) brought about a more rapid and more extensive colour change than exposure to sunlight, we attempted to collect *X*-ray data on a single crystal which had been subjected to intense u.v. treatment. *X*-Ray photographs proved unambiguously that there was a marked structural change as additional reflections were produced, as well as powder lines, but the change was neither homogeneous nor complete enough to allow us to determine the structure or even the cell parameters of the product. On standing the colour faded and could be restored by re-irradiation but several cycles of this procedure caused marked deterioration of the crystal surface. Cleavage of a crystal after irradiation showed that the colour change was limited to surface layers.

The deterioration of the crystals of (2) upon u.v. irradiation in the course of these *X*-ray studies convinced us that contrary to the literature report [4] the photochromic changes are not reversible and this presumably reflects some associ-

TABLE 1

Principal dimensions with estimated standard deviations in parentheses for (2) • acetone, (2) • acetonitrile, and (2) • benzene

(*a*) Bond lengths (Å) [a]

	(2) · acetone	(2) · acetonitrile	(2) · benzene
Pd–Cl	2.370(1)	2.394(1)	2.369(2)
Pd–P(1)	2.332(1)	2.334(1)	2.342(1)
Pd–P(2)	2.320(1)	2.319(1)	2.324(1)
Pd–C(1)	2.063(2)	2.074(3)	2.088(6)
C(1)–C(2)	1.425(4)	1.404(6)	1.317(9)
N–C(2)	1.151(4)	1.154(5)	1.175(9)
P(1)–C(11)	1.827(2)	1.819(2)	1.817(6)
P(1)–C(21)	1.841(2)	1.843(2)	1.819(6)
P(1)–C(31)	1.823(2)	1.820(2)	1.820(6)
P(2)–C(41)	1.816(2)	1.812(2)	1.814(6)
P(2)–C(51)	1.817(2)	1.820(2)	1.816(6)
P(2)–C(61)	1.825(2)	1.824(2)	1.839(6)

(*b*) Bond angles (°)

	(2) · acetone	(2) · acetonitrile	(2) · benzene
P(1)–Pd–C(1)	94.6(1)	94.2(1)	91.1(2)
P(2)–Pd–C(1)	92.7(1)	92.5(1)	90.3(2)
Cl–Pd–C(1)	172.2(1)	173.6(1)	176.5(2)
Cl–Pd–P(1)	87.5(1)	87.4(1)	90.8(1)
Cl–Pd–P(2)	86.6(1)	86.7(1)	87.5(1)
P(1)–Pd–P(2)	167.4(1)	169.9(1)	173.6(1)
Pd–C(1)–C(2)	114.0(2)	113.1(2)	107.6(5)
Pd–P(1)–C(11)	110.6(1)	110.9(1)	107.6(2)
Pd–P(1)–C(21)	121.0(1)	121.7(1)	115.1(2)
Pd–P(1)–C(31)	112.5(1)	111.5(1)	118.6(2)
Pd–P(2)–C(41)	116.2(1)	115.9(1)	116.8(2)
Pd–P(2)–C(51)	105.6(1)	106.0(1)	108.2(2)
Pd–P(2)–C(61)	120.3(1)	120.3(1)	115.8(2)
C(11)–P(1)–C(21)	99.0(1)	98.5(1)	105.4(3)
C(11)–P(1)–C(31)	105.9(1)	106.9(1)	106.0(3)
C(21)–P(1)–C(31)	106.2(1)	106.0(1)	103.2(3)
C(41)–P(2)–C(51)	108.5(1)	109.3(1)	106.9(3)
C(41)–P(2)–C(61)	100.3(1)	99.8(1)	102.5(3)
C(51)–P(2)–C(61)	105.1(1)	104.8(1)	105.8(3)
N–C(2)–C(1)	180.0(1)	179.1(4)	177.7(8)

(*c*) Solvent dimensions

acetone	O–C(4)	1.201(5)	O–C(4)–C(3)	120.5(4)
	C(3)–C(4)	1.460(6)	O–C(4)–C(5)	122.6(4)
	C(4)–C(5)	1.514(7)	C(3)–C(4)–C(5)	117.0(4)
acetonitrile	N(1)–C(4)	1.125(7)	N(1)–C(4)–C(3)	179.3(7)
	C(3)–C(4)	1.410(7)		
benzene	C(3)–C(4)	1.37(1)	C(3)–C(4)–C(5)	122.0(10)
	C(4)–C(5)	1.34(1)	C(4)–C(5)–C(6)	118.4(9)
	C(5)–C(6)	1.37(1)	C(5)–C(6)–C(7)	121.3(9)
	C(6)–C(7)	1.37(1)	C(6)–C(7)–C(8)	119.8(8)
	C(7)–C(8)	1.37(1)	C(7)–C(8)–C(3)	119.0(9)
	C(8)–C(3)	1.38(1)	C(8)–C(3)–C(4)	119.5(9)

(*d*) Shorter intermolecular contacts <2.6 Å [b]

(2) • acetone solvate		(2) • benzene solvate	
O · · · H(23^{I})	2.53	N · · · H(53^{II})	2.56
O · · · H(63)	2.54		

(*e*) Distances from the best plane through Pd, Cl, P(1), P(2), and C(1)

	(2) • acetone	(2) • acetonitrile	(2) • benzene
Pd	−0.028	−0.019	−0.073
Cl	−0.175	−0.139	−0.016
P(1)	0.187	0.148	0.052
P(2)	0.192	0.152	0.053
C(1)	−0.177	−0.142	−0.017

[a] The phenyl rings were constrained to be regular planar hexagons with C–C 1.395 Å in (2) • acetone and (2) • acetonitrile. In (2) • benzene the phenyl C–C distances are in the range 1.321(12)—1.425(11) Å with a mean value 1.38 Å. [b] Roman numeral superscripts refer to the following transformations of the co-ordinates of the second atom: I $1 + x, y, z$; II $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

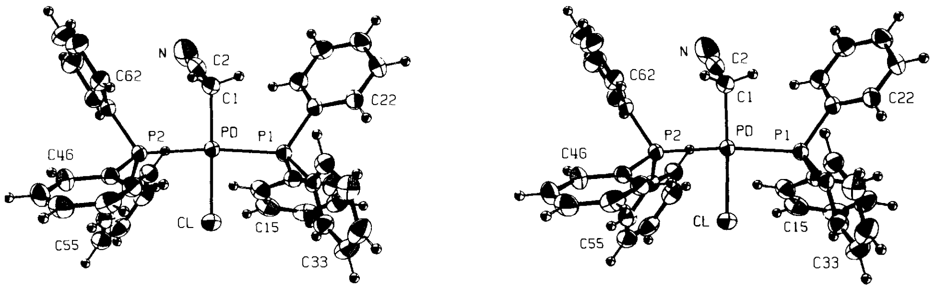


FIGURE 1 Stereoview of (2) in the acetone solvate

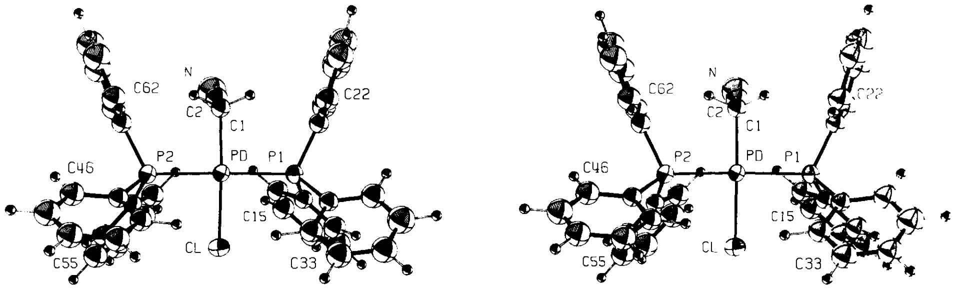


FIGURE 2 Stereoview of (2) in the benzene solvate

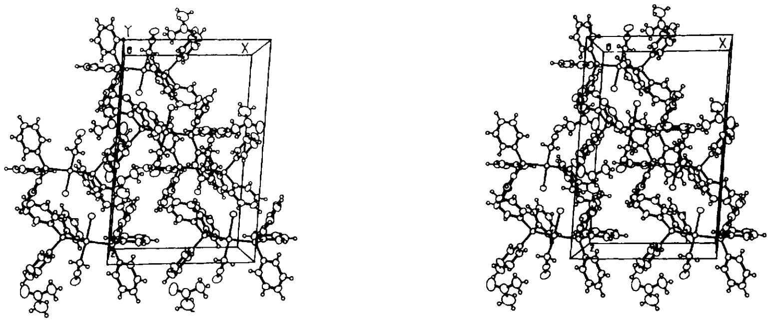


FIGURE 3 Stereoview of the (2) • acetone unit cell

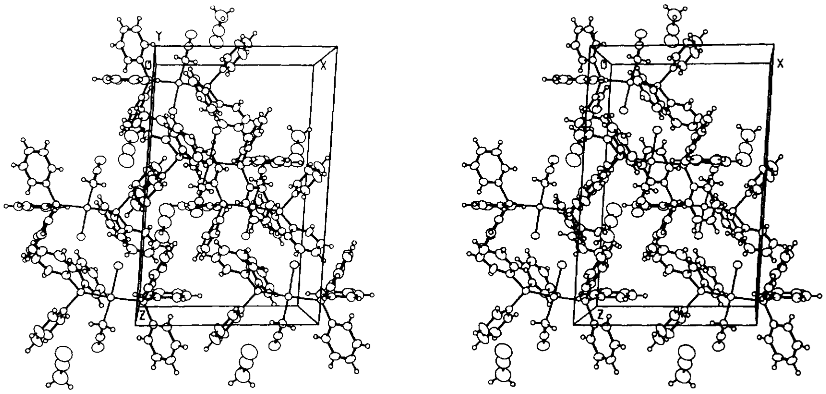


FIGURE 4 Stereoview of the (2) • acetonitrile unit cell

ated chemical transformation(s). The original report[3] of the preparation of (2) describes it as being white on deposition from the reaction mixture but yellow after crystallisation from acetone. In our hands, crystallisations performed in subdued light have given white or very pale yellow material. The yellow colour intensifies on further crystallisation or on storage. Exposure of the white material to light produces a pink colouration which slowly fades to yellow when the crystals are stored in the dark. Again, in contrast to the earlier workers,[4] we have noted colour changes in solution. Thus on exposure to light, virtually colourless solutions becomes increasingly yellow and indeed on occasions a transient pink colouration has been seen in the solution during the dissolution of (2) in hot

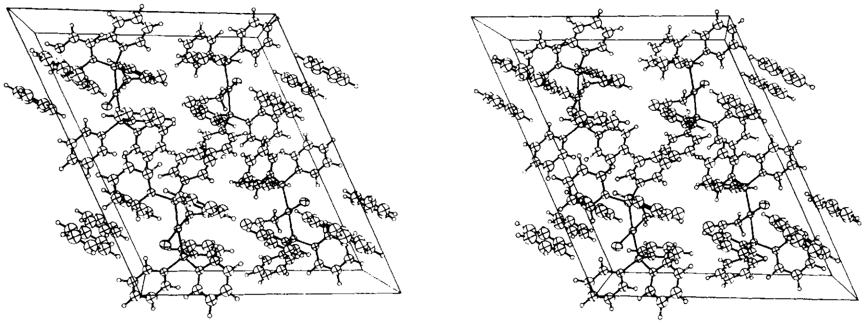


FIGURE 5 Stereoview of the (2) · benzene unit cell

acetone. These observations suggested that similar transformations may be occurring in both the solid state and in solution and led us to investigate the nature of the chemical changes involved.

Since these changes occur relatively slowly in ordinary light, we have examined the effect of irradiation with a tungsten lamp and with u.v. lamps having maximum output around either 350 or 250 nm. In our early experiments, air was not excluded. Spectroscopic and thin layer chromatography (t.l.c.) examinations indicated that irradiation at any of these frequencies initiates similar transformations, the rates of conversion increasing with increasing energy of the radiation. Thus, when (2) was irradiated as a Nujol mull, the following changes were observed in the u.v.–visible spectrum. First, loss of a band centred at 305 nm with growth of two new bands, one at 340 nm and the second at *ca.* 550 nm (associated with the red colour assumed by the sample), and secondly the development of bands at 270, 350, and 420 nm with the loss of those at 340 and 550 nm (sample at this stage is orange–yellow). Examination, by t.l.c., of the irradiated solid after dissolution in dichloromethane, showed the presence of a considerable amount of starting material, although the band at 305 nm in the u.v. spectrum associated with (2) had disappeared. This is consistent with reaction only in the surface layers of the solid. In addition, at least three other components could be detected by t.l.c. These appear to be identical with the products obtained on irradiation of (2) in benzene solution, and are discussed below.

Upon irradiation of (2) in benzene at 350 nm, the intensity of the lowest energy band at 285 nm decreases, whilst a new band builds up at 338 nm. Subsequently the intensity of the latter band shrinks and new bands appear at 353, 377, and 398 nm. Irradiation with a tungsten lamp led to similar spectroscopic behaviour initially, however, in the later stages only a very broad shoulder developed above 360 nm rather than well defined maxima. At this stage attempts were made to isolate the compounds responsible for these spectral changes. Accordingly, (2) was irradiated in benzene, using a tungsten lamp, for a period corresponding to that required for maximum development of the band at 338 nm. Analytical t.l.c. at this time showed the presence of three major products in addition to substrate. When this irradiated solution was allowed to stand in subdued light * the substrate gradually disappeared, although t.l.c. showed no new spots. When essentially all of (2) had reacted, the mixture was subjected to preparative t.l.c. and afforded, in order of increasing polarity, [$PdCl_2(PPh_3)_2$] (3) † (lowest energy u.v. band at 338 nm), a compound which could be formulated (see below) as [{$PdCl(CH_2CN)(PPh_3)$}$_n$] (4) (lowest energy u.v. band at 345 nm), and PPh_3O (6). Phosphorus-31 n.m.r. was used to confirm that these products were formed in solution in the presence of air and did not constitute chromatographic artefacts. The material of intermediate polarity, when freshly prepared, shows i.r. bands assignable [6] to both terminal and bridging CN groups, although these seem to be interchanging quite rapidly, since only a sharp singlet is present in its proton-decoupled ^{31}P n.m.r. spectrum and the methylene protons appear as a broad singlet in its ^1H n.m.r. spectrum. The addition of a small amount of pyridine to the sample causes the latter resonance to be replaced by a very clean doublet. Solutions of this material in solvents devoid of pyridine gradually deposit a pale yellow solid which is very insoluble in the common organic solvents. The i.r. spectrum (Nujol mull) shows only bridging CN groups and when it is dissolved in deuteriochloroform, with the aid of a small amount of pyridine, a clean doublet is again observed for the methylene protons in its ^1H n.m.r. spectrum. In accord with the formulation of this material as [{$PdCl(CH_2CN)(PPh_3)$}$_n$], a product of identical properties was obtained along with [$PdCl_2(PPh_3)_2$] (3) by mixing 2 molar equivalents of (2) with 1 molar equivalent of $PdCl_2{\cdot}2PhCN$.

When (2) (as either the acetone or benzene solvate) was irradiated with tungsten lamps in an n.m.r. tube in benzene solution and the progress of the reaction followed by ^1H n.m.r. spectroscopy, a gradual loss of the triplet arising from the methylene protons and the concomitant growth of a singlet ascribable to acetonitrile was observed. Since t.l.c. showed that at least two distinct decomposition pathways are operative, one involving loss of phosphine as the oxide and the other, cleavage of the cyanomethyl group, subsequent reactions were carried out under nitrogen in sealed n.m.r. tubes. Monitoring by ^1H n.m.r. demonstrated that cyanomethyl group cleavage still takes place under these conditions, while ^{31}P n.m.r. shows the build-up of a single resonance corresponding to [$PdCl_2(PPh_3)_2$] (3). Conversion of starting material was relatively slow, significant amounts of (2) remaining after irradiation for a week, and the orange-yellow solution obtained tended to turn somewhat murky on prolonged irradiation.

Similar changes were observed in the ^1H and ^{31}P n.m.r. spectra of benzene solutions of (2) under irradiation at 350 nm, but in this case, the starting material was completely consumed after *ca.* 1 d and the final solution was clear burbundy in colour. When such samples were opened to the air, the burgundy shade faded to give a murky solution, and some palladium was deposited. With hexadeuteriobenzene as solvent, the acetonitrile produced contains no deuterium.

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* Benzene solutions of (2) have been stored in subdued light for several weeks without significant changes occurring.

† Prolonged irradiation led to the conversion of (3) into [{$PdCl_2(PPh_3)$}$_2$] and PPh_3O (*cf.* ref. 5).

Integration against a $SiMe_4$ standard indicates that essentially all the available cyanomethyl groups are converted into acetonitrile, and that the additional hydrogen necessary comes from water in the solvent.

When a carefully degassed benzene solution of (2) was irradiated in an e.s.r. spectrometer, a short-lived radical with a *g* value of 2.015 was detected. The spectrum is very broad, being spread over almost 1 000 G,* and at least 12 ill defined lines are discernible with possible splittings of *ca.* 77 and 25 G. The breadth of this spectrum is suggestive of metal centred radicals. When irradiation was performed in the presence of the spin traps, nitrosodurene or phenyl-t-butylnitrone [*N*(α-t-butylbenzylidene)amine oxide], signals attributable [7] to the corresponding cyanomethyl radical adducts were readily detected ($a_N = 13.00$, $a_H = 8.58$ G and $a_N = 14.35$, $a_H^{CH} = 3.47$, and $a_H^{CH_2} = 0.64$ G respectively). No evidence was obtained for trapping of Cl atoms.

Compound (3) and acetonitrile were the major products detected when (2) was irradiated with either tungsten lamps or at 350 nm in carefully degassed deuteriochloroform solutions. In both cases the initial, almost colourless solution turned orange, remaining clear in the latter case but becoming quite cloudy in the former. On standing, (3) tends to crystallise out. Proton n.m.r. spectra of these solutions showed a new singlet, attributable to succinonitrile, in addition to that arising from the acetonitrile. Integration gave a mole ratio of *ca.* 1 : 5 for these two products. When (2) was irradiated in $CDCl_3$ containing either CD_3OD or CH_3OD (10% by volume) ^1H n.m.r. now showed that the acetonitrile produced consisted of monodeuteriated and undeuteriated material, the former predominating (*ca.* 80%).

DISCUSSION

X-Ray Structures.—In all three solvates there are discrete, well separated, molecules with no direct interaction between the solvent molecules and the complex (2). The arrangement of the molecules in the crystals of (2)·benzene (Figure 5) is such that columns of these molecules are generated in the *b* direction by two-fold screw axes ($x = 0.25$, $z = 0.5$, *etc.*) with the cyanomethyl moieties pointing inwards. This has the effect of producing non-polar channels (about two-fold screw axes at $x = 0$, $z = 0.25$ *etc.*) between these columns in which the benzene molecules of solvation are accommodated. No clear channels are found in the structures of the acetone and acetonitrile solvates of (2). Instead, in these structures, the solvent molecules are found in polar pockets but too far (⩾3.9 Å) from the cyanomethyl moieties for there to be any significant bonding interactions to them. In addition, in all three solvates, there are no unusually short intermolecular contacts; in particular the separation of the Pd atoms in the crystals rules out bridging of two Pd atoms by a cyanomethyl moiety without there being gross structural changes. In (2)·benzene the shortest intermolecular contact involves the cyanomethyl N atom and a proton on a nearby benzene ring [N ··· H(53) 2.56 Å]. This distance at best represents a very weak interaction.

In all three solvate structures the Pd atom has distorted square planar co-ordination; in (2)·acetone and (2)·acetonitrile the distortion is towards a tetrahedral conformation (Table 1) whereas in (2)·benzene the distortion leads to a pyramidal conformation.

The Pd–P [2.319(1)—2.342(1)], Pd–Cl [2.369(2)—2.394(1)], and Pd–C (sp^3) [2.063(2)—2.088(6) Å] distances (Table 1) are all in very good agreement with those reported for *trans*-$[PdCl(CH_2SCH_3)(PPh_3)_2]\cdot CH_2Cl_2$ [mean Pd–P 2.342(1), Pd–Cl 2.408(1), and Pd–C 2.061(3) Å].[8] For comparison, the distances in the related Pt complex, *trans*-$[PtCl(CH_2CN)(PPh_3)_2]$ are [9] mean Pt–P 2.309(3), Pt–Cl 2.390(3), and Pt–C 2.08(1) Å.

The dimensions of the $CH_2–C≡N$ moiety are similar in the acetone and acetonitrile solvates [C–C 1.425(4), 1.404(6); C≡N 1.151(4), 1.154(5) Å; Pd–C–C 114.0(2), 113.1(2); C–C–N 180.0(1), 179.1(4)°] and are in good agreement with the values found [9] in *trans*-$[PtCl(CH_2CN)(PPh_3)_2]$. In the benzene solvate the C≡N distance is longer [1.175(9)] and the C–C distance shorter [1.317(9) Å] implying a smaller amount of triple bond character in the C≡N bond, and greater bond character in the C–C bond. We noted above that this cyanomethyl nitrogen is involved in a weak intermolecular interaction with a phenyl hydrogen.

The orientations of the $CH_2–C≡N$ moieties with respect to the P_2PdClC framework are defined by the dihedral angles which the $Pd–CH_2–C≡N$ plane makes with the co-ordination plane. These angles are 107.1, 105.3, and 93.8° for the acetone, acetonitrile, and benzene solvates respectively. There is no evidence in any of the structures for an interaction between the Pd atom and the nitrile C atom; all Pd–C–C angles are close to or greater than tetrahedral [114.0(2), 113.1(2), and 107.6(5)° for acetone, acetonitrile, and benzene solvates respectively]. This contrasts with the Pd–C–C angle of 97.9(3)° found in (1).

In all three structures there are a number of short intramolecular Pd ··· H distances (in the range 2.88—3.22 Å) between *o*-hydrogen atoms of the phenyl rings and the Pd atoms. There are no intermolecular Pd ··· H contacts of this size. A recent paper [10] on $[\overline{PdI_2\{PPh_2(C_6H_4S}Me\text{-}o)\}]$ has commented on weak, axial, C–H ··· Pd interactions. In (2)·acetone and (2)·acetonitrile, one of the hydrogens is 2.88—2.89 Å from the Pd atom and occupies an octahedral site. This must at best be considered only a weak interaction as changing the solvent to benzene causes a considerable difference in Pd ··· H contacts (Table 1).

The other dimensions in the structure (Table 1) are in accord with accepted values and need no comment here.

Reactions induced by Radiation.—The nature of the products obtained on irradiation of (2) in solution depends on the availability of oxygen and moisture. Presumably, in the solid state reaction described by previous workers, atmospheric oxygen and moisture would intervene.

Reactions without Exclusion of Air.—In the presence of air, conversion of the substrate (2) into the bridged species (4) and PPh_3O competes with cleavage of the cyanomethyl group. However, products of the latter reaction are probably required to catalyse the former,

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* Throughout this paper: 1 G = 10^{-4} T.

which continues when the irradiation source is removed. The probable catalyst is a reduced palladium species formed by a reaction such as $2[PdCl(CH_2CN)L_2] \longrightarrow [PdCl_2L_2] + PdL_2 + 2(\cdot CH_2CN)$. It is well known [11] that $[Pd(PPh_3)_4]$ catalyses the oxidation of PPh_3 to the oxide, the reactive species being $[PdO_2(PPh_3)_2]$. Indeed when a catalytic amount of $[Pd(PPh_3)_4]$ is added to a solution of (2) in benzene, clean conversion to (4) and PPh_3O is observed.

Reactions in the Absence of Oxygen.—In the absence of oxygen, the only products which we have been able to identify for benzene solutions are *trans*-$[PdCl_2(PPh_3)_2]$ (3) and acetonitrile, although several other products * could be detected by analytical t.l.c. On the other hand, ^{31}P n.m.r. showed a single peak ascribable to (3), the presence of other phosphine-containing species only being indicated when irradiations were carried out with added PPh_3. In this case, the peak arising from (3) was again observed but significantly, that from PPh_3 suffered an increasingly marked downfield shift and then an upfield one during the course of the reaction. Several possibilities were considered for the source of the hydrogen abstracted by the cyanomethyl group. Solvent may be ruled out, since reaction in perdeuteriobenzene gave undeuteriated acetonitrile. Abstraction from a phosphine ligand to give, for example, a cyclometallated species is unlikely since no appropriate resonance could be detected in the relevant ^{31}P n.m.r. spectra, although successive abstraction from first the ligand, which in turn abstracts from solvent, cannot be discounted. Abstraction from a second cyanomethyl group is also a possibility and indeed such a process has been suggested [12] in the pyrolytic decomposition of (2). However, ^1H n.m.r. integration suggests that essentially all of the cyanomethyl groups are converted into acetonitrile, the predominant source of hydrogen being traces of water in the solvent. This observation would be most consistent with a polar mechanism in which the cyanomethyl group leaves as a carbanion, since it is unlikely that a cyanomethyl radical would abstract a hydrogen atom from a *free* water molecule. It may be possible for such an abstraction to take place from a palladium-co-ordinated water molecule (*cf.* suggested [13] abstraction of hydroxyl H from co-ordinated methanol). In any event, the use of water as the only source of hydrogen does not explain the formation of reduced palladium species, the presence of which is indicated by the oxidation catalysis and the deposition of palladium metal. Perhaps irradiation of (2) causes initial homolysis of the Pd–C bond, as indicated by our e.s.r. results, and then the initially formed radical pair may either decompose to give reduced palladium species or undergo internal single electron transfer to give $[PdClL_2]^+[CH_2CN]^-$.

Irradiations were then performed in deuteriochloroform in the expectation that if the radical pair $\cdot PdCl(PPh_3)_2 + \cdot CH_2CN$ were formed that the palladium atom would be able to abstract halogen from the solvent to give (3) while the cyanomethyl radical would abstract deuterium (*cf.* refs. 14 and 15). Indeed good yields of (3) and of acetonitrile were obtained, but surprisingly the latter was undeuteriated and had presumably abstracted hydrogen from traces of water present. In addition, a significant amount of succinonitrile was formed. When the irradiation was run in $CDCl_3$ containing CH_3OD the acetonitrile formed was mainly CH_2DCN, the remainder being CH_3CN. Again it appears difficult to rationalise these results. For example, the formation of (3) in essentially quantitative yield requires that chlorine be extracted from solvent. If this occurred by radical processes then the residual cyanomethyl radical would have to abstract a hydrogen atom presumably from free water (or methanolic hydroxyl) to form undeuteriated (or monodeuteriated) acetonitrile. This is unlikely in view of the observation [15] that methyl radicals when generated in deuteriochloroform containing water concentrations similar to those encountered in the present work abstracted deuterium from solvent. In any event, the resulting hydroxyl radicals would be expected to abstract deuterium atoms from the solvent and, since the concentration of water is minimal, some of this deuterium should appear in the acetonitrile formed. The formation of succinonitrile in the reaction cannot be taken as evidence for the production of free radicals since this product may derive from disproportionation of the substrate to give (3) and $[Pd(CH_2CN)_2(PPh_3)_2]$ followed by reductive elimination from the latter.

The participation of water in the cleavage of the cyanomethyl group from (2) appears to indicate that polar pathways predominate. It is however difficult to visualise how chloride can be abstracted from deuteriochloroform without the concomitant release of deuterium into the hydroxylic component of the solution.

We have also failed to obtain clear evidence for the structure(s) of the species reponsible for the photochromic behaviour of (2) in the solid state and the transient red colours sometimes observed when solutions of (2) are heated or irradiated. However, it would appear that the production of this colour requires the generation of reduced palladium species and may reflect a Pd^0–Pd^{II} interaction or indeed the formation of a Pd^I derivative. We have noted that particularly intense burgundy colours ($\lambda_{max.}$ 520 nm) are developed when toluene solutions of (2) containing ethanol or propan-2-ol are first irradiated at 350 nm and then heated, once the initial pink colour has developed. Indeed, the red solutions produced by irradiation maintain their colour for several days if kept at ambient, or lower temperature under nitrogen. A red colour also develops suddenly and then rapidly fades when (2) is heated in ethanol. The generation of a similar colour has also been noted [16] in dilute methanol solutions of dichlorobis(dimethyl-*o*-tolylphosphine)palladium(II). It seems likely that in these cases the alcohols are acting as reducing agents. Indeed, a red colour develops when *trans*-$[PdCl_2(PPh_3)_2]$ (3) is heated in ethanol in the presence of a small amount of solid potassium carbonate.

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* At least some of these probably represent artefacts produced when the solutions are opened to the atmosphere.

EXPERIMENTAL

Proton n.m.r. spectra were run on Bruker WH-400 (Southwestern Ontario NMR centre) or WP-60 or Varian EM360L spectrometers with $SiMe_4$ as internal standard and ^{31}P n.m.r. spectra on a Bruker WP-60 instrument with 85% phosphoric acid as external reference. Solvents for n.m.r. were used as obtained and contained water. Electron spin resonance spectra were run on a Varian E-104 instrument fitted with a u.v. lamp (Oriel Corporation of America model 8500 operating at 150 W, Xe; 200 W, Hg). Ultraviolet-visible and i.r. spectra were determined on a Varian DMS90 and a Beckman Acculab instrument respectively. The microanalysis was performed by Galbraith Laboratories Inc. Knoxville, Tennessee, and the mass spectrum was recorded on a Varian CH7 instrument. Thin layer chromatography plates were spread with Kieselgel G (Merck) and developed with benzene–acetone (9 : 1 for analytical and 37 : 3 for preparative purposes). Irradiations were carried out using (*i*) a Rayonet photochemical reactor fitted with lamps having a maximum output at 350 nm for solutions contained in n.m.r. tubes; (*ii*) a Gelman-Camag Universal u.v. lamp at either 350 or 254 nm for solutions in quartz u.v. cells or Nujol mulls between quartz plates; and (*iii*) tungsten lamps (2 × 60 W, 8 cm distant) for solutions in n.m.r. tubes or u.v. cells or powdered samples. The starting material (2) was prepared as outlined in ref. 3 and was recrystallised from either benzene, acetone, or acetonitrile in subdued light. The acetone or benzene solvates were used for the non-crystallographic studies.

Crystal Data for (2) • *Acetone*.—$C_{38}H_{32}ClNP_2Pd{\cdot}C_3H_6O$, $M = 762.55$, monoclinic, $a = 12.679(4)$, $b = 14.553(1)$, $c = 19.506(5)$ Å, $\beta = 94.72(1)^\circ$, $U = 3\,587.0$ Å^3, $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 1\,568$. Space group $P2_1/n$ (alternative setting of C_{2h}^5, no. 14) from systematic absences $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$.

Crystal Data for (2) • *Acetonitrile*.—$C_{38}H_{32}ClNP_2Pd{\cdot}C_2H_3N$, $M = 745.52$, monoclinic, $a = 12.581(2)$, $b = 14.323(2)$, $c = 19.359(3)$ Å, $\beta = 93.85(1)^\circ$, $U = 3\,480.5$ Å^3, $Z = 4$, $D_c = 1.42$ g cm^{-3}, $F(000) = 1\,528$. Space group $P2_1/n$ (C_{2h}^5, no. 14) from systematic absences $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$.

Crystal Data for (2) • *Benzene*.—$C_{38}H_{32}ClNP_2Pd{\cdot}C_6H_6$, $M = 784.6$, monoclinic, $a = 22.140(3)$, $b = 10.058(1)$, $c = 18.699(6)$ Å, $\beta = 114.78(2)^\circ$, $U = 3\,780.6$ Å^3, $Z = 4$, $D_c = 1.38$ g cm^{-3}, $F(000) = 1\,608$. Space group $P2_1/a$ (alternative setting of C_{2h}^5, no. 14) from systematic absences $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$.

For all complexes Mo-K_α radiation used with $\lambda = 0.710\,69$ Å and $\mu = 7.9$ cm^{-1}.

Preliminary Weissenberg and precession photographs provided space group information and unit cell dimensions. For (2) • acetone and (2) • acetonitrile, accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections (with θ in the range 10—15°) measured on an Enraf-Nonius CAD-4 diffractometer. For (2) • benzene the cell data were obtained from 12 reflections, with θ in the same range, measured on a Hilger and Watts Y-290 four-circle diffractometer. Three-dimensional intensity data were collected by the θ—2θ scan technique for (2) • acetone and (2) • acetonitrile on a CAD-4 diffractometer and for (2) • benzene on a Hilger and Watts Y-290 diffractometer.

For each crystal, measurements of three reflections were made periodically throughout data collection; the standards decayed by 2.2, 0.5, and 10.2% for the acetone, acetonitrile, and benzene solvates respectively. This was allowed for by appropriate scaling. After corrections for Lorentz, polarization, and absorption, the reflections with $I > 3\sigma(I)$ were labelled observed and used in structure solution and refinement. The number of independent reflections measured, those with $I > 3\sigma(I)$, and $\theta_{max.}$ were respectively 6 280, 4 907 (25°); 3 229, 2 998 (20°); 4 653, 3 664 (22°); for the acetone, acetonitrile, and benzene solvates.

Structure Solution and Refinement.—The structures of (2) • acetone and (2) • benzene were solved by the heavy-atom method once the co-ordinates of the Pd atom had been obtained from a Patterson synthesis. The co-ordinates of (2) in (2) • acetonitrile were taken from those of (2) • acetone. For (2) • acetone and (2) • acetonitrile, refinement (on an Amdahl V5 computer with the SHELX [17] programs) was by full-matrix least-squares calculations with anisotropic thermal parameters and the phenyl rings were constrained to be regular hexagons (C–C 1.395 Å). For (2) • benzene, refinement was by full-matrix least-squares calculations on an IBM 370 computer but because of space limitations only the Pd, Cl, and P atoms were allowed anisotropic motion, the remaining N and C atoms were only allowed isotropic vibration. Difference maps computed at intermediate stages in the refinement revealed maxima (0.3—0.6 e Å^{-3}) in positions expected for all protons, even those of the solvent molecules. The hydrogen atoms were then allowed for in geometrically idealised positions (C–H 0.95 Å) and included in the final rounds of calculations; only isotropic thermal parameters were refined for the protons.

In the final refinement cycles a weighting scheme of the form $\sqrt{w} = 1/[\sigma^2F + pF^2]^{\frac{1}{2}}$ was employed where the final p values are 0.001 9, 0.000 3, and 0.0 for the acetone, acetonitrile, and benzene solvates respectively. Scattering factors used in the structure factor calculations were taken from refs. 18 and 19 and allowance was made for anomalous dispersion.[20] Refinement converged with $R = \Sigma\Delta/\Sigma|F_o| = 0.026$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.030$ for (2) • acetone; the corresponding figures for (2) • acetonitrile are 0.028 and 0.038 and for (2) • benzene 0.050 and 0.056 respectively. Final difference maps were devoid of any significant features. Table 1 contains principal dimensions for the three solvates. Tables 2, 3, and 4 contain fractional co-ordinates with estimated standard deviations for (2) • acetone, (2) • acetonitrile, and (2) • benzene respectively. The hydrogen co-ordinates, phenyl ring distances of (2) • benzene, thermal parameters, and structure factor tables have been deposited as Supplementary Publication No. SUP 23330 (67 pp.).*

Irradiations in the Solid State.—(*i*) Mulled (Nujol) samples of (2) sandwiched between quartz plates were irradiated with the 8 W u.v. lamp (both wavelengths) and the progress of the ensuing reactions followed spectrophotometrically. The spectral changes observed are described in the Results section. (*ii*) Irradiation with a tungsten lamp gave similar colour changes, but over a much longer time span. A powdered sample of (2) (20 mg) was irradiated under N_2 for 3 d with two tungsten lamps, during which time the colour of the solid changed from creamy white, through red, to an orange–brown. This material was dissolved in benzene and examined by t.l.c. which showed the presence of much substrate in addition to spots corresponding to the presence of *trans*-$[PdCl_2(PPh_3)_2]$ (3) and small amounts of

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 2

Final fractional co-ordinates (Pd, Cl, and P ×10^5, the remainder ×10^4) with e.s.d.s in parentheses for [PdCl(CH_2CN)(PPh_3)$_2$] (2) • acetone

Atom	*x*	*y*	*z*
Pd	15 992(1)	22 906(1)	8 978(1)
Cl	13 609(6)	27 547(5)	20 393(3)
P(1)	−2 151(5)	19 998(5)	7 643(3)
P(2)	32 871(5)	29 089(4)	10 697(3)
O	5 386(2)	63(2)	−1 147(2)
N	2 156(3)	2 921(2)	−982(2)
C(1)	1 899(2)	1 726(2)	−37(1)
C(2)	2 040(2)	2 387(2)	−560(2)
C(3)	3 586(3)	−93(4)	−1 056(3)
C(4)	4 507(3)	288(3)	−1 359(2)
C(5)	4 295(5)	966(4)	−1 943(3)
C(11)	−965(1)	3 063(1)	836(1)
C(12)	−2 068(1)	3 039(1)	790(1)
C(13)	−2 642(1)	3 854(1)	821(1)
C(14)	−2 113(1)	4 692(1)	898(1)
C(15)	−1 009(1)	4 716(1)	945(1)
C(16)	−435(1)	3 901(1)	914(1)
C(21)	−850(1)	1 578(1)	−59(1)
C(22)	−1 602(1)	876(1)	−104(1)
C(23)	−2 151(1)	673(1)	−736(1)
C(24)	−1 946(1)	1 171(1)	−1 321(1)
C(25)	−1 194(1)	1 873(1)	−1 275(1)
C(26)	−646(1)	2 076(1)	−644(1)
C(31)	−647(1)	1 235(1)	1 426(1)
C(32)	−1 115(1)	1 586(1)	1 993(1)
C(33)	−1 424(1)	994(1)	2 502(1)
C(34)	−1 266(1)	49(1)	2 443(1)
C(35)	−798(1)	−302(1)	1 876(1)
C(36)	−489(1)	291(1)	1 367(1)
C(41)	4 162(1)	2 379(1)	1 740(1)
C(42)	3 837(1)	1 599(1)	2 081(1)
C(43)	4 540(1)	1 152(1)	2 558(1)
C(44)	5 568(1)	1 484(1)	2 693(1)
C(45)	5 893(1)	2 264(1)	2 352(1)
C(46)	5 190(1)	2 711(1)	1 875(1)
C(51)	3 100(1)	4 106(1)	1 295(1)
C(52)	2 427(1)	4 628(1)	847(1)
C(53)	2 235(1)	5 547(1)	997(1)
C(54)	2 715(1)	5 944(1)	1 595(1)
C(55)	3 388(1)	5 422(1)	2 042(1)
C(56)	3 580(1)	4 503(1)	1 893(1)
C(61)	4 154(2)	2 935(1)	368(1)
C(62)	4 650(2)	2 113(1)	217(1)
C(63)	5 304(2)	2 075(1)	−324(1)
C(64)	5 460(2)	2 860(1)	−714(1)
C(65)	4 964(2)	3 682(1)	−563(1)
C(66)	4 310(2)	3 720(1)	−22(1)

TABLE 3

Final fractional co-ordinates (Pd, Cl, and P ×10^5, the remainder ×10^4) with e.s.d.s in parentheses for [PdCl(CH_2CN)(PPh_3)$_2$] (2) • acetonitrile

Atom	*x*	*y*	*z*
Pd	15 052(2)	22 627(2)	8 714(1)
Cl	12 407(7)	27 541(6)	20 292(5)
P(1)	−3 221(6)	19 704(6)	7 420(4)
P(2)	32 293(7)	28 257(5)	10 539(5)
N	2 050(3)	2 937(3)	−1 015(2)
N(1)	3 714(4)	−34(4)	−959(3)
C(1)	1 808(2)	1 703(2)	−83(2)
C(2)	1 936(3)	2 385(3)	−592(2)
C(3)	3 889(4)	1 145(4)	−1 921(3)
C(4)	3 798(4)	488(4)	−1 387(3)
C(11)	−1 078(2)	3 043(1)	825(1)
C(12)	−2 187(2)	3 011(1)	808(1)
C(13)	−2 771(2)	3 837(1)	833(1)
C(14)	−2 245(2)	4 695(1)	876(1)
C(15)	−1 135(2)	4 726(1)	893(1)
C(16)	−552(2)	3 900(1)	868(1)
C(21)	−968(2)	1 554(1)	−84(1)
C(22)	−1 729(2)	844(1)	−125(1)
C(23)	−2 275(2)	638(1)	−758(1)
C(24)	−2 060(2)	1 142(1)	−1 349(1)
C(25)	−1 299(2)	1 852(1)	−1 308(1)
C(26)	−753(2)	2 058(1)	−675(1)
C(31)	−739(2)	1 173(1)	1 404(1)
C(32)	−1 224(2)	1 505(1)	1 983(1)
C(33)	−1 509(2)	886(1)	2 494(1)
C(34)	−1 309(2)	−67(1)	2 428(1)
C(35)	−824(2)	−400(1)	1 849(1)
C(36)	−540(2)	220(1)	1 337(1)
C(41)	4 066(1)	2 232(2)	1 714(1)
C(42)	3 705(1)	1 414(2)	2 012(1)
C(43)	4 383(1)	906(2)	2 472(1)
C(44)	5 422(1)	1 216(2)	2 633(1)
C(45)	5 782(1)	2 034(2)	2 335(1)
C(46)	5 104(1)	2 542(2)	1 876(1)
C(51)	3 103(2)	4 048(1)	1 290(1)
C(52)	2 438(2)	4 602(1)	853(1)
C(53)	2 288(2)	5 541(1)	1 010(1)
C(54)	2 803(2)	5 927(1)	1 604(1)
C(55)	3 467(2)	5 374(1)	2 041(1)
C(56)	3 617(2)	4 435(1)	1 884(1)
C(61)	4 122(2)	2 828(1)	350(1)
C(62)	4 621(2)	1 988(1)	203(1)
C(63)	5 300(2)	1 941(1)	−336(1)
C(64)	5 482(2)	2 735(1)	−729(1)
C(65)	4 984(2)	3 575(1)	−582(1)
C(66)	4 304(2)	3 622(1)	−43(1)

PPh_3O and [{PdCl(CH_2CN)(PPh_3)}$_n$] (4) (see below for their isolation from irradiations in solution). A similar experiment, this time in air and using the 8 W u.v. lamp (350 nm), gave analogous colour changes. When the resulting solid was dissolved in dichloromethane a small amount of (3) (2 mg) crystallised and the mother-liquors showed t.l.c. spots corresponding to substantial amounts of (2), (3), and (4) and phosphine oxide.

Reactions in Solution without the Exclusion of Air.—U.v.–visible spectra. Solutions of (2) (0.6 mg cm^{-3}) in benzene were irradiated in 1.0 mm cells using the tungsten lamps or the 8 W u.v. lamp at 350 nm (see Figure 6).

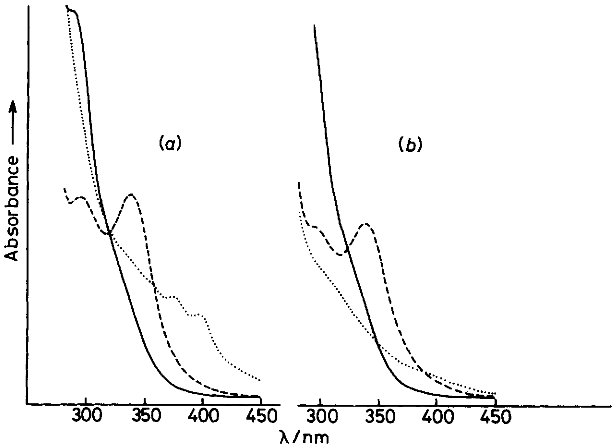

FIGURE 6 U.v. absorption of benzene solutions of (2) (0.6 mg cm^{-3}) after irradiation (*a*) at 350 nm: initial (——); after 25 min (— — —); after 28 h (· · · ·) and (*b*) with tungsten lamp: initial (——); after 45 min (— — —); after 3 h (· · · ·)

N.m.r. studies. These studies were carried out using *ca.* 10^{-2} mol dm^{-3} solutions of (2) in benzene. Attainment of such a concentration requires heating in subdued light, which does not lead to significant reaction of (2) (^1H n.m.r. and u.v.–visible spectra) even after several hours at 60 °C.

Proton n.m.r. Irradiations in [$^2H_6$]benzene led to the

TABLE 4

Final fractional co-ordinates (Pd, Cl, and P × 10^5, the remainder × 10^4) with e.s.d.'s in parentheses for [$PdCl(CH_2CN)(PPh_3)_2$ (2) : benzene

Atom	*x*	*y*	*z*
Pd	27 135(2)	60 650(5)	74 938(3)
Cl	31 598(9)	40 715(18)	81 895(12)
P(1)	37 854(8)	68 770(18)	78 026(11)
P(2)	16 675(8)	51 033(18)	70 882(11)
N	2 125(4)	7 265(9)	5 444(5)
C(1)	2 288(4)	7 752(7)	6 819(4)
C(2)	2 212(4)	7 509(8)	6 094(5)
C(3)	2 298(5)	68(11)	8 533(6)
C(4)	2 131(5)	−1 194(11)	8 652(7)
C(5)	1 812(5)	−1 446(12)	9 109(6)
C(6)	1 664(5)	−404(10)	9 476(6)
C(7)	1 827(5)	873(10)	9 375(6)
C(8)	2 143(5)	1 120(11)	8 898(6)
C(11)	4 189(3)	5 731(7)	7 389(4)
C(12)	4 846(4)	5 331(8)	7 800(5)
C(13)	5 120(5)	4 422(9)	7 447(6)
C(14)	4 749(5)	3 927(9)	6 719(6)
C(15)	4 100(4)	4 315(8)	6 306(5)
C(16)	3 814(4)	5 194(7)	6 644(4)
C(21)	3 818(3)	8 491(7)	7 381(4)
C(22)	3 701(4)	9 623(8)	7 742(5)
C(23)	3 618(5)	10 880(9)	7 366(6)
C(24)	3 648(5)	10 928(11)	6 658(7)
C(25)	3 768(5)	9 889(11)	6 305(7)
C(26)	3 857(4)	8 615(9)	6 669(5)
C(31)	4 354(3)	7 073(7)	8 835(4)
C(32)	4 221(4)	6 460(8)	9 412(5)
C(33)	4 671(4)	6 650(9)	10 204(5)
C(34)	5 252(4)	7 240(8)	10 407(5)
C(35)	5 387(5)	7 866(10)	9 842(6)
C(36)	4 398(4)	7 792(8)	9 054(5)
C(41)	1 382(3)	4 758(7)	7 848(4)
C(42)	1 807(3)	4 875(7)	8 633(4)
C(43)	1 575(4)	4 642(8)	9 207(5)
C(44)	931(4)	4 256(8)	8 999(5)
C(45)	504(4)	4 115(9)	8 237(5)
C(46)	722(4)	4 372(8)	7 643(5)
C(51)	1 672(3)	3 531(7)	6 613(4)
C(52)	1 944(4)	3 509(8)	6 069(5)
C(53)	1 974(4)	2 314(9)	5 703(6)
C(54)	1 752(5)	1 162(10)	5 908(6)
C(55)	1 496(4)	1 169(9)	6 452(5)
C(56)	1 452(4)	2 358(7)	6 807(5)
C(61)	972(3)	6 062(7)	6 366(4)
C(62)	694(4)	7 061(8)	6 647(5)
C(63)	203(5)	7 882(10)	6 112(6)
C(64)	16(5)	7 689(10)	5 325(6)
C(65)	277(5)	6 721(10)	5 049(6)
C(66)	760(4)	5 884(8)	5 574(4)

release of apparently undeuteriated acetonitrile with the concomitant loss of the resonance arising from the methylene protons. No other non-aromatic protons were detected.

Phosphorus-31 *n.m.r.* Irradiation for 6 h resulted in the build-up of resonances due to (3) (δ 22.8), (4) (33.6), and (6) (24.0) in addition to one (26.1 p.p.m.) from substrate (2). Upon standing the resonance due to (2) gradually shrank and those arising from (4) and (6) grew.

Thin layer chromatography studies. An almost colourless solution of (2) (52 mg) in benzene (50 cm^3) was irradiated with a 40 W tungsten lamp for 6 h while immersed in a water-bath, the temperature of which rose from 22 to 35 °C during that period. Analytical t.l.c. of the resulting yellow solution revealed the presence of a substantial amount of substrate and smaller quantities of at least three products. When this solution was allowed to stand in air in subdued light for 5 d, periodic monitoring by t.l.c. revealed the gradual disappearance of substrate (2) although no additional spots appeared. Preparative t.l.c. of the resulting mixture afforded, in order of increasing polarity, [$PdCl_2(PPh_3)_2$] (3) (9 mg), material formulated as [$\{PdCl(CH_2CN)(PPh_3)\}_n$] (4) (19.5 mg), PPh_3O (6) (18.5 mg), and a non-mobile fraction (3.5 mg). Compounds (3) and (6) were identified by comparison (^{31}P n.m.r., u.v.–visible spectra, and t.l.c.) with authentic samples. Compound (3) shows a long wavelength maximum at 340 nm (*cf.* irradiation in u.v. cells, see Figure 6). Compound (4), as initially obtained, was a yellow gum which had ν(C≡N)($CHCl_3$) at 2 210, 2 250 cm^{-1}; $\lambda_{max.}$ (CH_3CN) 345 nm; ^1H n.m.r. δ ($CDCl_3$) 1.32 (2 H, br s), ($CDCl_3$ + C_5H_5N) 1.28 (2 H, d, *J* = 3.8 Hz); ^{31}P n.m.r. δ (C_6D_6) 33.6 p.p.m. On standing in chloroform a pale yellow solid was deposited. This had ν(C≡N) (Nujol mull) 2 242 cm^{-1}; δ ($CDCl_3$ + C_5H_5N) 1.28 (2 H, d, *J* = 3.8 Hz); decomposes without melting above 200 °C (Found: C, 50.95; H, 3.95; N, 2.8. $C_{20}H_{17}ClNPPd{\cdot}0.3CHCl_3$ requires C, 50.8; H, 3.65; N, 2.9%). The presence of $CHCl_3$ in the analytical sample was confirmed by mass spectroscopy. When a benzene (25 cm^3) solution of (2) (25 mg) was irradiated under similar conditions for 36 h a new product (6 mg) was separated by preparative t.l.c. and identified as bis[dichloro(triphenylphosphine)palladium(II)] by comparison with an authentic sample (t.l.c. and u.v.–visible spectrum).

Preparation of Compound (4).—A solution of bis(benzonitrile)dichloropalladium(II) (38.4 mg) in dichloromethane (1 cm^3) was filtered into a solution of (2) (141.3 mg) in the same solvent (4 cm^3). Within a few minutes (3) (71 mg) crystallized and was recovered by filtration. Preparative t.l.c. of the mother-liquors gave (4) (72 mg) as a pale yellow powder with spectroscopic properties identical to those described above. This material could not be crystallized as its solutions again deposited insoluble material.

Catalysis of the Air Oxidation of Compound (2) *with* Pd^0.—A benzene (5 cm^3) solution containing (2) (14.3 mg, 0.020 mmol) and tetrakis(triphenylphosphine)palladium(0) (2.1 mg, 0.0020 mmol) was allowed to stand at ambient temperature in subdued light. T.l.c. showed the disappearance of (2) and the accumulation of (4) and triphenylphosphine oxide, complete conversion requiring about 24 h. Little or no change was observed over 48 h in related experiments on solutions of (2) alone or (2) in the presence of (3).

Irradiations of Degassed Solutions of Compound (2).—*In benzene.* When degassed C_6D_6 solutions of (2) (*ca.* 10^{-2} mol dm^{-3}) containing water (*ca.* 2 × 10^{-2} mol dm^{-3}) were irradiated with either tungsten lamps or at 350 nm, ^1H n.m.r. spectroscopy showed consumption of (2) (loss of triplet at δ 1.07) and of water with formation of undeuteriated acetonitrile (δ 0.62). Integration suggested that most of the cyanomethyl residues were converted into acetonitrile. Phosphorus-31 n.m.r. showed loss of the peak corresponding to substrate and growth of one attributable to (3). Preparative t.l.c. of the products from one such experiment, which had been allowed to proceed (at 350 nm) until consumption of (2) (17 mg) was almost complete, gave (3) (5 mg) and less polar (2 mg) and more polar (7 mg) material. When irradiation was repeated on a sample containing PPh_3 (mole ratio, phosphine : (2) *ca.* 2.5 : 1), similar changes were observed in the ^1H and ^{31}P n.m.r. spectra. In the latter, the peak due to phosphine, which appeared initially at δ −6.0, moved downfield to positive chemical shift values and then upfield again as the reaction was allowed to proceed.

In deuteriochloroform. Reaction of (2) upon irradiation (tungsten lamps or 350 nm) in degassed deuteriochloroform solution (4×10^{-2} mol dm^{-3}) was followed by ^{1}H and ^{31}P n.m.r. spectroscopy, the only products detected being (3), undeuteriated acetonitrile, and undeuteriated succinonitrile, the latter two in a mole ratio of *ca.* 5 : 1. Preparative t.l.c. of the products when virtually all of (2) (30 mg) had reacted afforded (3) (29 mg) and a trace of more polar material. When a solution of (2) in $CDCl_3$–CH_3OD (9 : 1) was irradiated at 350 nm the acetonitrile was mainly (*ca.* 80%) monodeuteriated, the remainder being undeuteriated.

Generation of Red Species in Solution.—Red solutions were observed in the following situations. Fleeting pink colours often developed when (2) was dissolved in hot acetone. A much more intense colour was produced upon heating (2) in ethanol. This colour faded rapidly and palladium was deposited. Irradiation of toluene, benzene, and acetone solutions of (2) at 254 or 350 nm often led to the development of a pink colouration. When ethanol was present, deeper shades were produced and could be further intensified by heating. The red colour persisted in degassed solutions but faded rapidly in air giving murky suspensions. When a reaction of this type was carried out in benzene–ethanol (10 : 1) in a u.v. cell (purged with nitrogen) the following spectral changes were noted: (*i*) loss of the peak at 285 nm and growth of one at 340 nm and (*ii*) development of a peak at 520 nm which intensified upon heating and was gradually replaced by one at 420 nm. Red solutions were also generated from (3) in benzene–ethanol by adding a trace of sodium ethoxide in ethanol or by heating with solid potassium carbonate. Such solutions also showed bands at 420 and 520 nm in addition to one at *ca.* 470 nm.

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