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CYCLIC ACYL COMPLEXES OF PALLADIUM(II). SYNTHESIS AND NMR SPECTROSCOPY OF ACYL COMPLEXES DERIVED FROM QUINOLINE-8-CARBALDEHYDE AND 2-(DIMETHYLAMINO)BENZALDEHYDE

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Summary

The room temperature syntheses of new chelating acyl palladium(II) complexes, $[Pd(\mu\text{-}Cl)(C(O)C_9H_6N)]_2$ and $[Pd(\mu\text{-}Cl)(C(O)C_6H_4N(CH_3)_2)]_2$, derived from quinoline-8-carbaldehyde and 2-(dimethylamino)benzaldehyde are described. These chloro bridged dimers may be cleaved with neutral phosphine and nitrogen ligands, L, to give the monomeric $[PdCl(C(O)C_9H_6N)L]$ and $[PdCl(C(O)C_6H_4N(CH_3)_2)L]$ compounds. ^1H-, ^{13}C- and ^{31}P-NMR data for the new complexes are reported.

Introduction

Acyl complexes of transition metals are known to be intermediates in the hydroformylation reaction [1], and an increasing number of studies have been dedicated to their reactivity [2]. As part of our interest in this area we have synthesized Pd^{II} and Pt^{II} complexes containing cyclic acyl ligands of the general type $[\overline{M(O \sim CO)}L_2]$, (L = tertiary phosphine) derived from salicylaldehyde [3,4]. These can be prepared by deprotonation of the phenol oxygen, followed by oxygen coordination to the metal, and subsequent activation of the aldehyde. A similar type of aldehyde activation has been reported for the ligand 2-diphenylphosphinobenzaldehyde [5], using Ir^I and Pt^{II} precursors.

Having noted that prior coordination of either oxygen or phosphorus leads to formation of cyclic acyl complexes, we have investigated the products of the reaction of palladium salts with organic aldehydes which contain nitrogen coordination sites, and describe below the synthetic and spectroscopic results for quinoline-8-carbaldehyde and 2-(dimethylamino) benzaldehyde.

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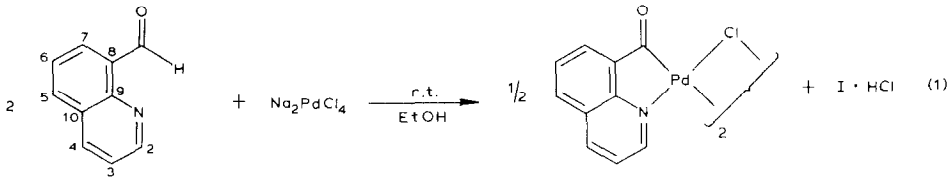
Results and discussion

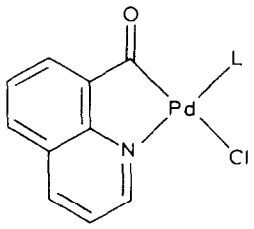
Quinoline-8-carbaldehyde derivatives

The binuclear complex (II) was prepared from ligand (I) as shown in eqn. 1. Two



(I) (II)

equivalents of I are required since HCl is formed during the reaction and protonates the quinoline. As the reaction progresses the product precipitates out as a stable yellow solid which may be isolated by conventional means. The derivatives III–V are easily prepared by reaction of two equivalents of the appropriate ligand, with one



(L = PPh_3 (III); PEt_3 (IV); 4-$NC_5H_4CH_3$ (V))

equivalent of dimer in CH_2Cl_2, and these are also stable yellow complexes. The new cyclic compounds were characterized by microanalytical, IR (Table 1), ^1H (Table 2) and ^{13}C (Table 3) NMR spectroscopy. Where appropriate ^{31}P NMR spectra were also recorded. The ν(C=O) stretches, 1670–1700 cm^{-1}, are in the region expected for an acyl coordinated to Pd^{II} [4], and lie on both sides of that found for the free ligand, 1685 cm^{-1}. For II and V where the carbonyl is *trans* to a relatively poor donor, the carbonyl stretch is found at higher frequency. Unfortunately, II is extremely insoluble in non-coordinating solvents, such as $CDCl_3$ and CD_2Cl_2, so that NMR data are unavailable for this complex; however, the presence of the coordinated chelating acyl is clearly shown by the ^1H NMR spectrum of IV. The high field region contains the $P(CH_2CH_3)_3$ signals at δ (ppm) 1.23 (CH_3) and 2.01 (CH_2), whereas the low field portion of the spectrum shows six groups of signals for the protons H_2–H_7. The aldehyde proton, initially observed in the ligand at δ 11.48 ppm, is absent. The assignment of the proton signals was made using homonuclear decoupling techniques combined with spin-spin coupling patterns.

We note that the ^1H signals from H_2–H_4 are deshielded upon complexation, as expected as a result of development of some positive charge on nitrogen due to complexation. Interestingly, for III, IV and VI, we observe long-range coupling (1–3 Hz) of the ^{31}P nucleus through the metal to H_2 and H_3; however, this is not unprecedented as we have made similar observations in the chemistry of coordinated

TABLE 1

ANALYTICAL AND IR DATA

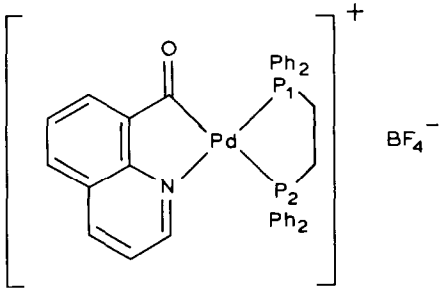
Complex	Analysis found (calcd.) (%)					IR (ν(CO)) [a]
	C	H	N	Cl	P	
II	40.15 (40.30)	2.08 (2.03)	4.64 (4.70)	11.89 (11.92)	–	1700
III	59.57 (59.14)	3.82 (3.86)	2.45 (2.55)	7.18 (6.47)	5.34 (5.65)	1670
IV	47.20 (46.17)	5.33 (5.09)	3.18 (3.36)	–	6.78 (7.45)	1670
V [b]	48.13 (49.13)	4.06 (4.04)	7.16 (6.79)	9.67 (9.06)	–	1680
VI [b]	55.29 (57.82)	4.04 (4.06)	1.69 (1.87)	–	–	1674
VIII	37.58 (37.27)	3.40 (3.47)	4.66 (4.83)	12.43 (12.22)	–	1675
IX	58.83 (58.71)	4.63 (4.56)	2.50 (2.54)	6.64 (6.42)	4.73 (5.61)	1658
X	44.85 (44.13)	6.23 (6.17)	3.20 (3.43)	8.39 (8.68)	6.96 (7.59)	1656
XI [b]	45.71 (47.13)	4.32 (4.47)	7.00 (7.31)	–	–	1681
XII [b]	56.03 (56.82)	4.80 (4.63)	1.75 (1.89)	–	–	1660

[a] As KBr pellets, in cm^{-1}. [b] These complexes show a tendency to lose CO when heated. Consequently the %C found is often slightly low.

Schiff's bases [6]. A similar ^1H assignment was made for the PPh_3 complex III, and by analogy for the remaining complexes.

The ^{13}C spectra for III and IV show signals for C(2), C(9) and the acyl carbonyl which are readily assignable using literature data [7]. Of primary interest is the $\simeq$ 15 ppm low field coordination shift of the carbonyl carbon, a value similar to that found for the salicylaldehyde acyl complexes [3].

The ^{31}P spectra for III and IV reveal the expected single resonances at 39.1 and



(VI)

(Continued on p. 107)

TABLE 2

^{1}H NMR DATA [a] FOR THE LIGANDS AND COMPLEXES (δ(ppm), J(Hz))

Compound	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	others
I	δ 9.05 J(H(2),H(3)) 4.1 (H(2),H(4)) 1.8	7.45 (H(3),H(4)) 8.3	8.25	8.12 (H(5),H(6)) 8.1 (H(5),H(7)) 1.5	7.70 (H(6),H(7)) 7.0 (H(6),C*H*O) 0.8	8.35	C*H*O 11.48
III	δ 10.14 J(H(2),H(3)) 4.8 (H(2),H(4)) 1.4	7.72 (H(3),H(4)) 8.3	8.49	7.92 (H(5),H(6)) 8.0 (H(5),H(7)) 1.2	7.62 (H(6),H(7)) 7.3	8.06	PPh_3 7.8 & 7.41 multiplets
IV	δ 10.02 J(H(2),H(3)) 4.9 (H(2),H(4)) 1.4 (P,H(2)) 3.4	7.70 (H(3),H(4)) 8.2 (P,H(3)) 1	8.47	8.08/8.04 [b] (H(5),H(7)) 1.2	7.68 (H(6),(H(5/7)) 7.3/7.9	8.04/8.06 [b]	P-C-CH_3 1.23 (H,H) 7; (P,H) 17 P-CH_2-C 2.07 (P,H) 10
V	δ 10.08 J(H(2),H(3)) 5.2 (H(2),H(4)) 1.3	7.68 (H(3),H(4)) 8.2	8.49	8.14/8.09 [b] (H(5),H(7)) 1.3	7.67 (H(6),H(5/7)) 7.1/8.3	8.90/8.14 [b]	
VI	δ 8.55	c)	8.79	8.23/8.02 [b]	[c]	8.02/8.23 [b]	-PPh_2 7.5 ≠ 7.8 multiplet

	J(H(2),H(3)) 4.9 (H(2),H(4)) 1.4 (P(1),H(2)) 3.5 (P(2),H(2)) 1			(H(5),H(7)) 1.2			
VII	δ 2.92 *J*	7.04 (H(3),H(4)) 8.9 (H(3),H(5)) 1.3	7.46 (H(4),H(5)) 7.1 (H(4),H(6)) 1.7	7.00 (H(5),H(6)) 7.7	7.76	*CHO*	10.23
VIII	δ 3.44 *J*	7.50 (H(3),H(4)) 7.8 (H(3),H(5)) 1.2	7.60 (H(4),H(5)) 6.9 (H(4),H(6)) 1.4	7.27 (H(5),H(6)) 7.7	7.65		
IX	δ 3.48 *J* (H,P) 1.7	[d]					
X	δ 3.35 *J*						
XI	δ 3.58 *J*						
XII	δ 3.12 *J* broad						

[a] $CDCl_3$ solutions at room temperature. [b] Resonances not assigned: H(5) and H(7) respectively. [c] Resonances under PPh_2 multiplet. [d] The aromatic resonances of the compounds IX–XII were either not resolved or lie under the signals of the phenyl groups of the phosphine ligands.

TABLE 3

^{13}C NMR CHEMICAL SHIFT DATA [a]

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	CO
I	151.3	121.8	136.3	134.3	126.2	129.2	131.5	147.5	128.2	192.6
III	152.8	128.5	138.5	131.0	123.0	126.5	143.8	149.1	128.9	206.6 (8.5)
IV	152.1	128.4	138.3	131.2	128.8 (2.5)	125.7	144.3 (5.5)	149.1	128.9 (2.8)	212.9 (6.2)

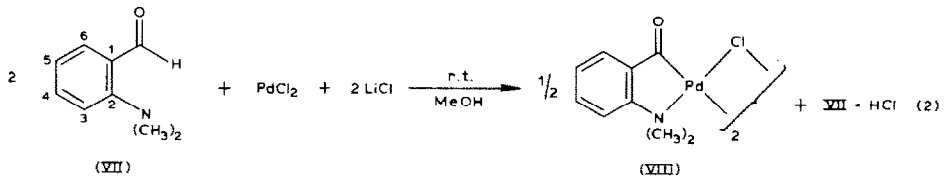
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CO	NCH_3
VII	127.5	156.0	117.8	134.6	120.8	131.1	191.2	45.6
VIII	137.5	157.9	119.9	134.5	129.4	125.7	194.8	54.4
IX	142.3 (7.4)	157.4 (3.3)	120.9 (3.6)	134.0	128.7	125.6	210.7 (10.2)	52.6

[a] All measurements in $CDCl_3$ at 62.89 MHz; assignments made by utilizing selective ^{1}H decoupling and literature substituent effects. Chemical shifts in ppm relative to external TMS, J values in Hz. Values in parentheses are ^nJ(P,C) coupling constants.

35.4 ppm, whereas the bisdiphenylphosphinoethane, dppe, complex VI shows an AX spectrum, with signals at 50.6 and 32.6 ppm (^2J(P,P) 35 Hz).
We assign these resonances to P(1) and P(2), respectively, based on: (a) the relationship between δ (^{31}P) and the *trans* influence in Pd^{II} complexes [8,9] and (b) the assumption that the larger $^4J(P,H_2)$ coupling constant results from the *trans* phosphorus atom. (Selective $^1H\{^{31}P\}$ experiments show ^4J(P(1), H(4)) 3 Hz, ^4J(P(2),H(4)) 1 Hz). We note that the phosphorus atoms in VI experience an upfield shift, relative to [$PdCl_2$(dppe)], δ 63.5 ppm.

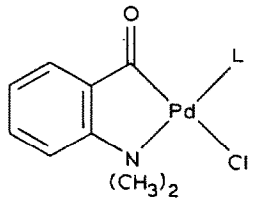
(Dimethylamino)benzaldehyde derivatives

The dimethylamino acyl complexes (VIII–XII) were prepared as shown in eq. 2. This reaction is considerably slower than that for the quinoline aldehyde, with the



product slowly precipitating over a period of several days. Once again two equivalents of base were used, one of which served to trap the acid which formed. The use of the lithium salt of $PdCl_4^{2-}$ (generated in situ from $PdCl_2$ and LiCl) is important since the reaction does not proceed if solid Na_2PdCl_4 is used.

Further, we find $Pd(OAC)_2$ is also ineffective as starting material for this reaction. The source of these differing reactivities is not clear; however, as described in the experimental reaction, VIII can be obtained in 81% yield using LiCl. The complexes IX–XI were prepared in the same way as III–V.



(L = PPh_3, (IX); PEt_3, (X); 4-$NC_5H_4CH_3$, (XI))

In contrast to II, the dimer VIII is reasonably soluble in $CDCl_3$, so that ^{1}H and ^{13}C spectra were obtainable. The four ^{1}H resonances H_3–H_6 appear at δ 7.50, 7.60, 7.27, 7.65 ppm, respectively. Once again, the aldehyde proton is absent. The $N(CH_3)_2$ resonance is shifted to δ 3.44 from its position at δ 2.92 ppm in the free ligand, presumably due to the partial positive charge on nitrogen. This same effect is probably responsible for the low field shifts of H(3) and H(5). The ^{13}C spectrum of VIII shows the acyl carbon at δ 194.8 ppm, again at lower field than the free ligand carbonyl, δ 191.2 ppm, as well as C(1) and C(2) resonances at 137.5 and 157.9 ppm, respectively. The dimethylamino resonances move downfield on complexation from 45.6 to 54.4 ppm. A complete listing of ^{1}H and ^{13}C data is given in Tables 2 and 3, and microanalytical and IR data are shown in Table 1. For the complexes IX and X

the ^{31}P-spectra show resonances at 40.2 and 37.7 ppm, respectively. The dppe-complex XII gives the expected AX spectrum with signals at 53.8 and 35.4 ppm (^{2}J(P,P) 28 Hz) and these resonances are assigned by analogy with those of complex VI.

Surveying our results, we note first that aldehyde carbon atoms are readily activated by various transition metals especially when kept close to the metal by prior coordination. Moreover, our systems are of additional interest in that the products arise from reactions which proceed at room temperature under mild conditions. We have no data on the mechanism of this activation; however, since we know of no published results which might lead us to suspect oxidative oxidation for palladium(II) we lean towards simple acid-base chemistry in which the metal assists by making the aldehyde proton more acidic through some form of coordination of the carbonyl. Further studies in this area are in progress.

Experimental

$PdCl_2$ was obtained from Johnson Matthey Ltd., London. 8-methylquinoline, 4-picoline, dppe, PPh_3 and PEt_3 were purchased from Fluka AG, Buchs, and used directly. Ethyl-2(dimethylamino)benzoate was obtained from EGA Chemie, Sternheim, BRD, and 2-(dimethylamino)benzaldehyde was prepared according to the literature [10].

NMR spectra were recorded with $CDCl_3$ solutions using Bruker HX 90 and WM-250 NMR spectrometers. Details are given in the Tables. IR spectra were recorded using a Beckmann IR 4250-spectrometer as KBr disks. Microanalyses were carried out by the analytical laboratory of the E.T.H. Zürich.

Preparation of quinoline-8-carbaldehyde (I)

N-Bromosuccinimide (NBS, 25 g, 0.14 mol) was added to 8-methylquinoline (10 g, 0.07 mol) in 40 ml CCl_4. A catalytic amount of dibenzoyl peroxide was added to initiate the reaction, and the mixture refluxed until all the NBS had reacted. The mixture was cooled to 0°C and the succinimide was filtered off. The CCl_4 layer was then extracted with 2*N* NaOH, washed with water and dried over Na_2SO_4. Concentration i.v. was followed by recrystallization from ligroin to afford 17.3 g (82%) of 8-(dibromomethyl)quinoline as colorless needles. 8-(dibromomethyl)quinoline (12.4 g, 0.04 mol) was refluxed in 150 ml water for 1 h. The solution was then filtered hot, cooled, and treated with 2*N* NaOH, from which the crude product separated. This was extracted with ether and the organic layer washed to neutrality with water. Concentration and recrystallisation from water yielded 5.2 g (80.6%) of I as fine colourless needles.

Preparation of II

Quinoline-8-carbaldehyde (200 mg, 1.27 mmol) in 5 ml ethanol was added slowly to Na_2PdCl_4 (187 mg, 0.636 mmol) dissolved in 20 ml absolute ethanol. The yellow solid which separated over a 20 min period was collected by filtration and dried i.v. (188 mg, 99%). The second equivalent of aldehyde may be recovered from the solution by treatment with NaOH.

Preparation of III–V

All the bridge cleavage reactions were carried out in an essentially identical way.

Typically, a suspension of II in CH_2Cl_2 was treated with two equivalents of ligand. The solid dissolved immediately. Concentration followed by recrystallization from CH_2Cl_2/hexane gave quantitative yields of the monomeric products.

Preparation of VI

A suspension of II (32 mg, 0.053 mmol) in acetone was treated with $Ph_2PCH_2CH_2PPh_2$ (42 mg, 0.106 mmol) and $AgBF_4$ (20.5 mg, 0.106 mmol). The AgCl which separated was filtered off and the solution evaporated in vacuo. The crude product was recrystallized from acetone/ether to yield 59 mg (75%) of orange crystals.

Preparation of VIII

To a solution of $PdCl_2$ (276 mg, 1.56 mmol) and LiCl (132 mg, 3.12 mmol) in 30 ml MeOH was added neat 2-(dimethylamino)benzaldehyde (464 mg, 3.12 mmol). After three days at room temperature yellow crystals had separated and these were filtered off (221 mg, 49%). If the reaction mixture is kept for three weeks, there is a gradual precipitation of additional product. Total yield 367 mg (81%). The complex may be recrystallized from CH_2Cl_2/MeOH.

Compounds IX–XII were prepared as described for III–VI.

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