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Platinum Induced C–H Activation in Aromatic Aldehydes. Unusual *J*(Pt, H) Coupling Constants and Structure of *trans*-Dichloroquinoline-8-carboxaldehyde Triethylphosphine Platinum(II)

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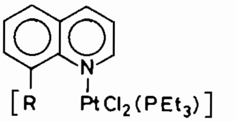
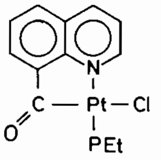
Carbon–hydrogen bonds of aldehydes may be activated by transition metals [1] to give cyclometallated complexes. In analogy with its Pd(II) counterpart [2] we find that *sym-trans*-[Pt(μ-Cl)-Cl(PEt$_3$)$_2$]$_2$, **(I)**, reacts quantitatively at room temperature with quinoline-8-carboxaldehyde, **(II)**, via **(IIIa)** to give **(IV)** and the salt [**(II)**·H$^+$][PtC$_3$-(PEt$_3$)]$^-$, **(V)**, each in 50% yield. If the reaction is performed in refluxing chloroform, thereby allowing HCl to escape, the yield of **(IV)** is much higher. The intermediate **(IIIa)** is isolatable and has interesting NMR and structural properties. The ^{1}H-resonance for the aldehyde proton is at δ 13.09 shifted *downfield* by 1.62 ppm, relative to the free ligand and has an unusually large $J(^{195}\text{Pt}, {}^1\text{H})$ value of 13.7 Hz. In the absence of a Pt–H–C(=O) interaction this would be a five-bond coupling constant.

$$\text{(I)} + \text{(II)} \longrightarrow \text{(III)} \longrightarrow \text{(IV)} + \text{(V)}$$

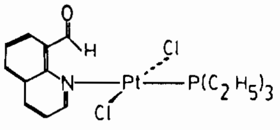


(III) a R = CHO
b R = CHBr$_2$



(IV)

The aldehyde carbon-13 resonance appears at δ 188.1 and also shows a relatively large coupling to platinum, $J(^{195}\text{Pt}, {}^{13}\text{C}_{10})$ = 31.6 Hz. For comparison, the two-bond coupling constant, $^2J(^{195}\text{Pt}, {}^{13}\text{C}_1)$ = 20.7 Hz. The ^{31}P parameters, δ^{31}P = 1.0, $^1J(^{195}\text{Pt}, {}^{31}\text{P})$ = 3467 Hz, and the ^{195}Pt chemical shift, δ – 3529, are not exceptional [3, 4].



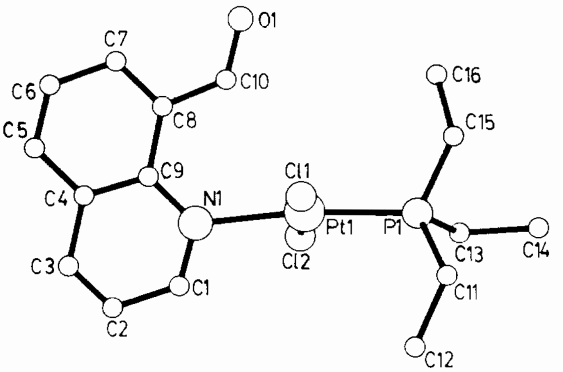


Fig. 1. PLUTO drawing of compound (IIIa).

The X-ray structure of **(IIIa)** (see Fig. 1) reveals a slightly distorted square planar geometry with the aldehyde C–H bond directed *toward* the platinum *ca.* 2.3 Å away.* Typical M–H separations in C–H–M bridges are 1.64–2.29 Å [5]. This orientation is important, as it is conceivable that the carbonyl oxygen coordinated the platinum (*i.e.*, Pt–O=CH–), thereby reducing the coupling pathway to three bonds. The platinum–oxygen separation is *ca.* 4 Å and Table I shows a selection of bond lengths and bond angles. These bond distances and angles are normal for this type of platinum phosphine complex [6]. The IR spectra of **(IIIa)** in both the solid and solution states show ν(C=O) at 1682 cm^{-1} and when deuterated at the aldehyde carbon, **(IIIa)** shows a 40 cm^{-1} shift to lower energy for ν(C–D) relative to the uncomplexed deuterated aldehyde **(II)**. Taken

TABLE I. Some Bond Lengths (Å) and Bond Angles (°) for (IIIa).

Pt–Cl(1)	2.286(5)	Cl(1)–Pt–Cl(2)	177.0(4)
Pt–Cl(2)	2.287(5)	Cl(1)–Pt–P	88.4(2)
Pt–P	2.222(4)	Cl(2)–Pt–N	88.6(4)
Pt–N	2.155(13)	Cl(2)–Pt–P	94.5(5)
P–C^a	1.83(2)	P–Pt–N	171.7(6)
C(1)–N	1.30(2)	C(8)–C(10)–O	118.0(1)
C(9)–N	1.37(2)		
C(8)–C(10)	1.49(2)		
C–O	1.28(2)		

^{a} Average value.

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*The H-atom was placed in its idealized position assuming sp^2 carbon hydridization and a C–H separation of 1.08 Å.

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together, the physical data suggest a weak aldehyde C–H··M interaction although they do not support hydridic character for the hydrogen.

This is the first example of a close platinum–hydrogen interaction which leads directly to aldehyde C–H activation, and eventual cyclometallation, under mild conditions. Moreover, **(IIIa)** is controversial in that although the aldehyde proton–platinum coupling is relatively large (and exceptionally large at 39 Hz for the complex with R = $CHBr_2$), $^1J(^{13}C, ^1H)$ at 183 Hz is normal [7] and essentially identical to that observed in **(II)**, 185 Hz. These one-bond $^{13}C-^1H$ coupling constants suggest that the C–H bond is still substantially aldehydic in nature. This contrasts with observations for 'agostic' [5] covalent M–H–C interactions in which a) $^1J(^{13}C, ^1H)$ decreases more than 20% and b) the proton resonance shifts to higher[§] field as the hydrogen takes on hydride-like character. However, since none of the known bridging C–H–M interactions involve an aldehyde, perhaps these existing NMR empiricisms are not pertinent for **(IIIa)**. The aldehyde C–H activation of **(II)** is dependent on the remaining ligands in the coordination sphere and we shall expand on this theme elsewhere.

Experimental

Quinoline-8-carboxaldehyde (40.9 mg, 0.26 mmol) was added to a $CHCl_3$ solution of $[Pt_2Cl_4(PEt_3)_2]$ (100 mg, 0.13 mmol). The formation of the product **(IIIa)** was immediate and indicated by a change in solution colour from dark to light yellow. **(IIIa)** was isolated quantitatively by removal of the solvent and recrystallisation from methylene chloride/hexane. *Anal.* Found (calcd): C, 35.56 (35.49); H, 4.21 (4.13); N, 2.64 (2.59); Cl, 13.39 (13.09) %. Compound **(IIIa)** is monoclinic; space group $P2_1/c$; $a = 14.411(3)$, $b = 9.172(2)$, $c = 15.217(4)$ Å, $\beta = 107.07(2)°$, $V = 1929.5$ Å^3; $Z = 4$. Data were collected on an automated CAD4 diffractometer, using Mo$K\bar{\alpha}$ radiation up to $2\theta = 50°$. 2362 observed reflections, ($I \geqslant 3\sigma(I)$) corrected for absorption, were used for the structure determination. Atomic positions were obtained by Patterson and Fourier methods and refined by block-diagonal least squares, using anisotropic temperature factors for Pt, P and Cl atoms, and isotropic for the others. The present conventional R factor is 0.048.

Acknowledgements

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[§] Low field alkylproton shifts on coordination are known for palladium complexes of 8-alkylquinolines [8].