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Crystal Structure and Reactivity in Solution of *o*-Cyanobenzylbis(diphenylphosphino)ethyleneplatinum(II) Tetrafluoroborate

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X-ray analysis of crystalline o*-cyanobenzylbis(diphenylphosphino)ethyleneplatinum(II) tetrafluoroborate shows that the complex is a dimer* $[Pt(o\text{-}CH_2C_6H_4CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ *having linear* $Pt\text{–}N{\equiv}C$ *bonds, even though molecular models indicate a favourable geometry for π-coordination of the nitrile moiety. The CN group remains σ-coordinated to the metal in solution and is very prone to nucleophilic attack by water, alcohols and amines, giving imide, iminoether and amidine complexes, respectively.*

Introduction

We previously reported the preparation, spectroscopic properties and reactivity of various cyanoalkyl complexes of platinum(II) of the type $PtX(RCN)L_2$, *1* (L = tertiary phosphine or arsine; R = $(CH_2)_n$, n = 1,2,3,-*o*-$CH_2C_6H_4$; X = Cl, Br) and their cationic derivatives [1]. The latter, obtained by halide abstraction from the parent neutral complexes *1* with $AgBF_4$ in dichloromethane, have a CN group occupying the fourth coordination site. Molecular models of two cationic cyanobenzyl complexes – the title compound $[Pt(o\text{-}CH_2C_6H_4CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$, *2* and the bis(triphenylphosphine) analog – indicate a favourable geometry for monomer formation with π-coordination of the CN group. Side-on coordination of CN to transition metals is seldom encountered [2]. In the case of platinum, Clark *et al.* [3] have proposed that initial π-CN–Pt bond formation is essential for nucleophilic attack on pentafluorobenzonitrile and 2,3,5,6-tetrafluoroterephthalonitrile complexes. We have found that the CN group of *2* is very prone to nucleophilic attack by water, alcohols and amines and report here its crystal structure together with some aspects of its reactivity in solution.

Crystal Structure of $[Pt(o\text{-}CH_2C_6H_4CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$, *2*

Suitable crystals for X-ray examination were grown from toluene/dichloromethane solution by slow evaporation. A multifaced crystal of approximate dimensions 0.21 × 0.13 × 0.12 mm was mounted on a Syntex $P2_1$ automated diffractometer and determined to be orthorhombic with cell dimensions a = 34.322(12), b = 21.216(4), and c = 18.158(3)Å, and space group Pcab (by systematic absences: Okl, l = 2n; hOl, h = 2n; hkO, k = 2n). The measured density was 1.626 g cm^{-3} (d_{calc} = 1.619 g cm^{-3} for Z = 8). Attempts to cool the crystal always led to a serious reduction in its quality, hence the measuremements were carried out at room temperature.

The intensities of 6207 independent reflections, 2805 of which were below the 3σ limit, were measured with niobium filtered Mo-K_α radiation (λ = 0.71069Å) to $(\sin\theta/\lambda)_{max}$ = 0.482. Backgrounds were obtained by analysing the 2θ–θ scan profile [4]. The form of the crystal was accurately measured by means of a special telescope mounted on the 2θ arm of the diffractometer, and was used to correct the intensities for absorption ($\mu_{Mo\text{-}K\alpha}$ = 47.0 cm^{-1}).

Computer programs were taken from the "X-RAY 72" program system [5], and the figures were prepared by the program ORTEP [6]. Scattering factors for the neutral atoms were taken from Cromer and Mann [7], and anomalous dispersion factors for Pt and P were taken from Cromer [8]. The severely disordered BF_4^- ions were treated as freely rotating groups with the spherical scattering factor:

$$f_{BF} = f_B + 4f_F \frac{\sin 4\pi \sin\theta/\lambda \cdot r}{4\pi \sin\theta/\lambda \cdot r}$$

The two independent platinum atoms were found from the interpretation of a three dimensional Patterson map. A difference Fourier synthesis phased with these atoms revealed the four phosphorus atoms. Two more difference maps located all the other non-hydrogen atoms except for two phenyl rings attached to P2. The BF_4^- ions were rather diffuse and for this

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TABLE I. Atomic coordinates and thermal parameters (the error of the last significant digit is given in parentheses). The temperature factor has the form e^{-T} where $T = 8\pi^2 U\sin^2\theta/\lambda^2$ for isotropic atoms and $T = 2\pi^2 \Sigma h_i h_j U_{ij} a_i^* a_j^*$ for anisotropic atoms.[a]

ATOM	X	Y	Z	U11(U)	U22	U33	U12	U13	U23
PT1	.03087(3)	.23657(5)	.36596(6)	.0446(6)	.0527(7)	.0551(7)	–.0072(7)	–.0074(7)	.0034(7)
PT2	.20643(3)	.32188(5)	.34054(6)	.0430(6)	.0602(7)	.0368(6)	–.0041(7)	.0026(7)	.0003(7)
P1	–.0311(2)	.2541(3)	.3404(4)	.050(5)	.071(6)	.059(5)	–.008(5)	–.008(5)	.009(5)
P3	.2258(2)	.4232(4)	.3609(4)	.062(6)	.067(6)	.055(6)	–.008(5)	.005(5)	.002(5)
P4	.2610(2)	.3111(4)	.2774(4)	.049(5)	.063(6)	.047(5)	–.007(5)	.005(4)	–.004(5)
P12	.0099(7)	.134(1)	.381(1)	.07(1)					
P22	.0157(6)	.131(1)	.357(1)	.056(8)					
N1	.0868(6)	.2144(9)	.388(1)	.051(6)					
N2	.01560(6)	.3344(9)	.398(1)	.057(7)					
C1	–.0546	.3130	.3941	.054(8)					
C2	–.0580	.3743	.3670	.067(9)					
C3	–.0736	.4216	.4114	.08(1)					
C4	–.0857	.4077	.4829	.09(1)					
C5	–.0823	.3465	.5100	.10(1)					
C6	–.0667	.2991	.4656	.08(1)					
C7	–.0405	.2678	.2448	.070(9)					
C8	–.0798	.2769	.2286	.09(1)					
C9	–.0922	.2788	.1555	.12(1)					
C10	–.0653	.2716	.0986	.08(1)					
C11	–.0260	.2625	.1148	.10(1)					
C12	–.0136	.2606	.1879	.09(1)					
C13	–0.596(7)	.182(1)	.360(1)	.064(8)					
C14	–.0399(8)	.130(1)	.371(1)	.067(9)					
C27	.1181(7)	.199(1)	.407(1)	.041(8)					
C28	.1562(7)	.177(1)	.434(1)	.045(7)					
C29	.1543(8)	.139(1)	.498(1)	.051(8)					
C30	.1872(9)	.113(1)	.521(2)	.07(1)					
C31	.2245(9)	.123(1)	.481(2)	.09(1)					
C32	.2243(8)	.160(1)	.413(1)	.061(9)					
C33	.1900(7)	.189(1)	.389(1)	.040(7)					
C34	.1897(6)	.227(1)	.319(1)	.040(7)					
C35	.2298	.4481	.4576	.051(8)					
C36	.2649	.4411	.4955	.08(1)					
C37	.2670	.4561	.5702	.09(1)					
C38	.2341	.4781	.6070	.11(1)					
C39	.1990	.4852	.5691	.10(1)					
C40	.1969	.4702	.4944	.11(1)					
C41	.1988	.4826	.3169	.09(1)					
C42	.1737	.4651	.2599	.09(1)					
C43	.1528	.5110	.2217	.12(1)					
C44	.1569	.5744	.2404	.17(2)					
C45	.1820	.5919	.2974	.15(2)					
C46	.2029	.5460	.3356	.12(1)					
C47	.2746(8)	.431(1)	.323(2)	.08(1)					
C48	.2890(8)	.380(1)	.288(1)	.07(1)					
C49	.2931	.2484	.3027	.064(8)					
C50	.3141	.2542	.3681	.08(1)					
C51	.3351	.2029	.3953	.11(1)					
C52	.3351	.1459	.3571	.11(1)					
C53	.3141	.1401	.2916	.11(1)					
C54	.2931	.1914	.2644	.08(1)					
C55	.2554	.3021	.1798	.059(9)					
C56	.2887	.3036	.1358	.09(1)					
C57	.2855	.2953	.0598	.09(1)					
C58	.2491	.2853	.0279	.066(9)					
C59	.2158	.2838	.0719	.09(1)					
C60	.2189	.2922	.1479	.072(9)					
C61	.1261(8)	.344(1)	.426(1)	.040(7)					

ATOM	X	Y	Z	U11(U)	U22	U33	U12	U13	U23
C62	.0939(8)	.362(1)	.470(1)	.048(8)					
C63	.1033(8)	.382(1)	.544(2)	.07(1)					
C64	.0704(9)	.400(1)	.591(2)	.08(1)					
C65	.0334(9)	.395(1)	.560(2)	.075(9)					
C66	.0269(9)	.378(1)	.488(2)	.072(9)					
C67	.0546(8)	.356(1)	.440(1)	.054(8)					
C68	.0474(7)	.333(1)	.361(1)	.056(8)					
C115	.0222	0.960	.4694	.05(2)					
C116	–.0049	.1015	.5263	.06(2)					
C117	.0054	.0842	.5979	.06(2)					
C118	.0428	.0614	.6124	.08(2)					
C119	.0698	.0559	.5554	.04(2)					
C120	.0595	.0732	.4839	.09(2)					
C121	.0379	.0791	.3198	.21(4)					
C122	.0341	.0144	.3319	.27(5)					
C123	.0366	–.0275	.2729	.13(3)					
C124	0.428	–.0047	.2018	.17(4)					
C125	.0466	.0599	.1897	.18(4)					
C126	.0442	.1018	.2487	.07(2)					
C215	.0349	.0849	.4332	.07(2)					
C216	.0265	.0969	.5070	.12(3)					
C217	.0474	.0663	.5623	.08(2)					
C218	.0768	.0238	.5437	.06(2)					
C219	.0852	.0118	.4699	.12(3)					
C220	.0643	.0423	.4146	.06(2)					
C221	.0337	.0938	.2828	.07(2)					
C222	.0108	.0409	.2691	.10(2)					
C223	.0183	.0031	.2078	.09(3)					
C224	.0488	.0183	.1603	.07(2)					
C225	.0718	.0713	.1740	.05(2)					
C226	.0642	.1090	.2353	.09(3)					
BF1	.1034(7)	.297(1)	.148(1)	.14(1)					
BF2	.3775(5)	.4800(9)	.273(1)	.070(8)					

[a] The atoms C1–C6, C7–C12, C35–C40, C41–C46, C49–C54, C55–C60, C115–C120, C121–C126, C215–C220, C221–C226 were refired as ideal phenyl groups. The ordered (disordered groups have average standard deviations in x, y, z and the three orientation angles of 0.0004(0.0007), 0.0006(0.001), 0.0007(0.002), 0.7(1.9), 0.8(1.9), 1.7(2.6).

reason the group form factor described above was used. The model at this stage was refined on the |F|'s by block diagonal least squares in two parts. First the core of the complex was refined while keeping the contribution from the phenyl groups and the BF_4^- ions constant, then the phenyl rings (as ideal groups with bond lengths and angles of 1.395Å and 120° respectively) and the BF_4^- ions were then adjusted, and then the cycle repeated. Using the weights $1/\sigma^2$ (where the esd's of the structure factors were derived from counting statistics and the variations in the intensities of the periodically measured check reflections), with anisotropic temperature factors for platinum and phosphorus and isotropic temperature factors for all the light atoms. The model was refined to R = 0.10. A difference Fourier synthesis now revealed diffuse electron density in the region expected for the missing phenyl groups, indicating strong disorder which explains in part the large number of unobserved reflections. A model was chosen in which both phenyl groups were allowed to take up two different orientations and the four half phenyls refined as ideal groups as above, keeping the contribution from the rest of the molecule constant. A further refinement cycle of the complex core now revealed P2 to have an elongated thermal ellipsoid, and this atom was subsequently also treated as disordered. Final refinement in three parts *viz.* complex core, ordered phenyls, disordered atoms and BF_4^- ions, gave the residual R = 0.072.

Final atomic parameters are listed in Table I, and chemically significant bond lengths and angles in Table II. A perspective drawing of the molecule is shown in Fig. 1 (only the average positions of the disordered atoms are shown), and the disordered part of the molecule in Fig. 2. A table of observed and calculated structure factors is available as supplementary material.

It is to be noted that the standard deviations on the bond lengths and angles are rather high. This is

TABLE II. Bond Lengths (Å) and Angles (°) in *2* (the error of the last significant digit is given in parentheses).

Pt1–N1	2.02(2)	Pt2–N2	2.04(2)
Pt1–C68	2.13(2)	Pt2–C34	2.12(2)
Pt1–P1	2.208(7)	Pt2–P4	2.207(7)
*Pt1–P2	2.31(2)	Pt2–P3	2.279(8)
P1–C13	1.84(3)	P4–C48	1.76(3)
*P2–C14	1.83(3)	P3–C47	1.82(3)
N1–C27	1.17(3)	N2–C61	1.16(3)
C27–C28	1.47(3)	C61–C62	1.41(4)
C28–C33	1.45(3)	C62–C67	1.46(4)
C33–C34	1.51(3)	C67–C68	1.54(4)
N1–Pt1–C68	88.8(8)	N2–Pt2–C34	89.4(8)
N1–Pt1–P1	176.2(6)	N2–Pt2–P4	178.5(6)
*N1–Pt1–P2	91.6(8)	N2–Pt2–P3	92.4(6)
C68–Pt1–P1	95.0(7)	C34–Pt2–P4	92.0(6)
*C68–Pt1–P2	174.0(9)	C34–Pt2–P3	178.2(6)
*P1–Pt1–P2	84.7(6)	P3–Pt2–P4	86.3(3)
Pt1–P1–C13	109.5(9)	Pt2–P4–C48	109(1)
*Pt1–P2–C14	107(1)	Pt2–P3–C47	107(1)
P1–C13–C14	117(2)	P4–C48–C47	121(2)
*P2–C14–C13	118(2)	P3–C47–C48	116(2)
Pt1–N1–C27	174(2)	Pt2–N2–C61	174(2)
N1–C27–C28	176(2)	N2–C61–C62	170(3)
C27–C28–C33	118(2)	C61–C62–C67	119(2)
C28–C33–C34	125(2)	C62–C67–C68	122(2)
C33–C34–Pt2	110(1)	C67–C68–Pt1	108(2)

*Average value from the two half atoms P12 and P22 of the disordered model.

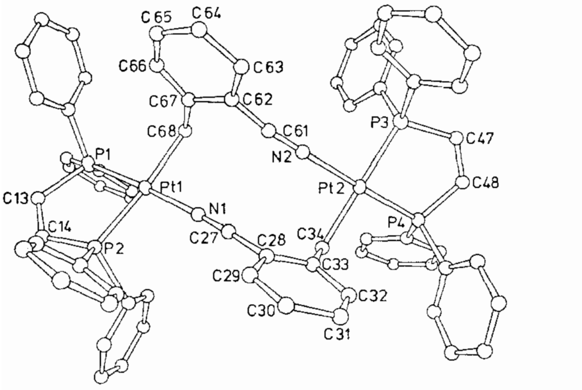

Figure 1. ORTEP plot of *o*-cyanobenzylbis(diphenylphosphino)ethyleneplatinum(II) fluoroborate (the average positions of the disordered atoms are shown, see text).

due in part to the serious approximations used in our model to describe the disordered phenyl groups and BF_4^- ions. A second important contribution to the imprecision of the light atom positions is the presence of the very heavy platinum atoms. Indeed, the platinum and phosphorus atoms alone give a residual R = 0.19 with an overall temperature factor.

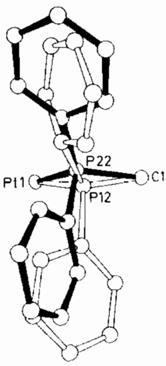

Figure 2. ORTEP plot showing the disordered part of the complex (P2 and phenyl groups attached to it).

Both platinum atoms are square planar and the twist in the molecule due to the constraints in the bridge inclines the two planes at 45.4° to each other. Around Pt2 the maximum deviation out of the plane Pt2–P3–P4–N2–C34 is 0.01 Å. Aroud Pt1 the disordered phosphorus atoms P12 and P22 are shown to be 0.23 Å above and below the plane described by Pt1–P1–N1–C68. This distortion from planar geometry is associated with two different orientations of the associated phenyl groups. At present, the origin of this disorder, and of the distortion from the planar configuration are not clear.

The Pt2–N2–C61 angle and N2–C61 bond distance correspond to a σ-coordination of the CN group and sp hybridization of the nitrogen atom and not to π-coordination as was suggested by molecular models. The Pt2–N2 bond distance is longer than the Pt–NC bond distance (1.950(15)Å) [9] in *trans*-dichlorobis(benzonitrile)platinum(II) probably because of the higher *trans* influence of phosphorus compared to that of nitrogen. The Pt2–C34 bond distance corresponds to a σ-coordinated benzyl group (this distance seems not much affected by the nature of the atom in the *trans* position, 2.11(2)Å for carbon [10], 2.12(2) (this work) or 2.09(4) [11] for phosphorus). Alkyls are known to have a high *trans* influence. This is refelcted in the longer Pt2–P3 bond distance (2.279(8)Å) than Pt2–P4 (2.207(7)) where P3 is *trans* to carbon and P4 *trans* to nitrogen, as well as in the greater ^{1}J(Pt–P4) coupling constant compared to ^{1}J(Pt–P3) (Table III). The same observations can be made for the coordination of Pt1.

Reactivity in Solution

The mode of bonding of CN observed in the crystalline state is conserved in solution. Indeed, I.R. spectra of a dichloromethane solution of *2* show a band attributable to ν(C≡N) at the same frequency

TABLE III. ^1H, ^{31}P FTNMR and Infra-red Spectral Data.

Complex	$\delta(CH_2)^a$ (ppm)	$^2J(PtCH)$ (Hz)	$^3J(PPtCH)$ (Hz)	$\delta(P)^b$ (ppm)	$^1J(PtP)$ (Hz)	$^2J(PP)$ (Hz)	I.R. (nujol) (cm^{-1})
1 $PtCl(CH_2C_6H_4CN)(C_2H_2P_2Ph_4)$	3.1 (dd)^c	78	4.5 (*cis*) 11 (*trans*)	47.2 54.8	3919 2165^d	7.4	ν(CN) 2218 ν(PtCl) 320, 316
2 $[Pt(CH_2C_6H_4CN)(C_2H_2P_2Ph_4)]_2(BF_4)_2$	3.1 (dd)	77	4 (*cis*) 10 (*trans*)	38.2 51.1	3996 2195	8.4	ν(CN) 2258^e ν(BF_4) 1050^f
3 $[Pt\{CH_2C_6H_4C(=NH)OC_2H_5\}(C_2H_2P_2Ph_4)]BF_4$	2.9 (dd)^g	62	5 (*cis*) 9 (*trans*)	41.0 58.2	3550 2310	8.3	ν(C=N) 1605^h ν(NH) 3310
4 $[Pt\{CH_2C_6H_4C(=NH)N(CH_3)Ph\}(C_2H_2P_2Ph_4)]BF_4$	2.8 (dd)^i	63	5 (*cis*) 9 (*trans*)	41.1 56.1	3561 2307	8.3	ν(C=N) 1575, 1545 ν(NH) 3340
5 $[Pt(CH_2C_6H_4CONH)(C_2H_2P_2Ph_4)]_2$	2.7 (dd)	81	6 (*cis*) 8 (*trans*)	44.9 56.8	3130 2211	7.9	ν(CONH) 1590, 1555 ν(NH) 3345

[a] In $CDCl_3$, TMS as internal standard. [b] In CD_2Cl_2, positive sign for a resonance at lower field than 85% H_3PO_4 (external reference). [c] Triplet (1/4/1) of doublet of doublets. [d] Smaller coupling constant attributed to P *trans* to CH_2. [e] Raman 2260 cm^{-1}. [f] Broad. [g] $\delta(OCH_2)$ 3.2 (q), $\delta(CH_3)$ 1.3 ppm (t). [h] $\nu(COC)_{as}$ 1230 cm^{-1}. [i] $\delta(NCH_3)$ 2.7 ppm (s).

(2258 cm^{-1}) as that observed in the solid (IR and Raman). It occurs 40 cm^{-1} higher than the ν(C≡N) of the uncoordinated cyanobenzyl of *1* (Table III), and is characteristic of an N-coordinated CN group [3] (π-coordination gives rise to a band at lower frequency than that of the free nitrile [2]). The identity of the dimer is maintained in solution as shown by its spectral data (Table III): a broad I.R. band around 1050 cm^{-1} is indicative of ionic BF_4^-; the $^{31}P\{^1H\}$FTNMR spectrum present an AX pattern indicating two non-equivalent phosphorus with different $^1J(PtP)$ coupling constants, which are preserved upon heating the solution. Following Pidcock *et al.* [12], the smaller coupling constant is associated with a Pt–P bond of lower s-character and corresponds here to the phosphorus *trans* to carbon. The methylene resonance is split into a doublet of doublets by two non-equivalent phosphorus nuclei with satellites due to coupling with ^{195}Pt.

Nucleophilic attack of the CN group is observed on heating *2* in ethanol Two new IR bands appear in the ν(NH) and ν(C=N) regions together with a parallel decrease of the intensity of the ν(C≡N) band. The product (80% yield) is the iminoether complex $[Pt\{o\text{-}CH_2C_6H_4C(=NH)OC_2H_5\}(Ph_2PCH{=}CHPPh_2)]BF_4$, *3*, a yellow crystalline solid stable in air which behaves as a 1/1 electrolyte in nitromethane. Direct attack of the σ-coordinated CN by free ethanol seems to be the sole reaction path. A similar reaction takes place on heating *2* in acetone in the presence of *p*-toluidine, yielding $[Pt\{o\text{-}CH_2C_6H_4C(=NH)N(CH_3Ph\}(Ph_2PCH{=}CHPPh_2)]BF_4$, *4*. On monitoring the spectrum of the isolated mixture of complexes during the course of the reaction, a small peak at 2220 cm^{-1} is observed beside the band at 2258 cm^{-1}. This indicates that substitution of CN by *p*-toluidine occurs partially giving a 4-coordinate complex which apparently does not rearrange into the final amidine complex. Here again there is no indication of transient π-coordination of CN during the course of the nucleophilic attack. On heating *2* in acetone/water with or without an equimolar quantity of NaOH, the imide complex $[Pt(o\text{-}CH_2C_6H_4CONH)(Ph_2PCH{=}CHPPh_2)]_2$, *5* is obtained (vapour pressure osmometry indicates a dimeric structure). *o*-toluoamide is liberated on treating a dichloromethane solution of *5* with HCl.

All complexes were characterized by elemental analysis, IR, ^1H- and ^{31}P-NMR (Table III). As shown by the decrease of $^1J(PtP)$ (3996 to 3130 Hz), the *trans* influence of the fourth ligand increases with the sequence nitrile < chloride < iminoether ~ amidine < imide. The imide group is indeed strongly bonded to platinum: *5* does not react with PPh_3 in dichloromethane, whereas the CN group of *2* is displaced quantitatively by the phosphine.

In conclusion, σ-coordination of CN to platinum is preferred to side-on coordination even in the favourable case of the cyanobenzyl chelate and there is no evidence in this case that π-coordination is needed for nucleophilic attack.

Experimental

The spectroscopic techniques were described earlier [1].

Preparation of Complexes

1, 2: see [1].

3: a suspension of *2* (0.2 g) in ethanol was stirred for 4 h at 65 °C; a yellow precipitate formed on addition of ether/hexane, and was recrystallized from methanol/ether to give pale yellow needles (yield 80%). $BC_{36}F_4H_{34}NOP_2Pt$: found (calc.) C 51.02 (51.44), H 4.29 (4.08).

4: *2* (0.2 g) was stirred for 10 h in acetone (10 ml) with a twofold excess of *p*-toluidine at room temperature. The volume was reduced to 4 ml, the complex was precipitated by adding ether, and was recrystallized from dichloromethane/pentane (yield 70%). $BC_{41}F_4H_{37}N_2P_2Pt$: C 55.49 (54.62), H 4.39 (4.14).

5: a suspension of *2* (0.2 g) in acetone (40 ml) and water (10 ml) containing an equimolar quantity of NaOH was stirred at 40 °C for 5 h. The white solid was washed with water, then methanol, and was recrystallized from dichloromethane/ether (yield 80%). $C_{34}H_{29}NOP_2Pt$: C 60.02 (60.63), H 4.24 (4.34).

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