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Facile cycloplatination of nitrogen compounds. Crystal structure of the cycloplatinated Schiff's base tetralone derivative $PtCl\{(cyclohexyl)N{=}C(CH_2)_3C_6H_3\}(CO)$

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Abstract

Facile preparative methods for the cycloplatination of benzo[*c*]quinoline (**1**), two Schiff's base tetralone compounds, $R^1N{=}C(CH_2)_3C_6H_4$ (R^1 = cyclohexyl (**2**), $CH_2(p\text{-}C_6H_4OCH_3)$ (**3**)), and 8-methylquinoline (**4**), are given. An extension of these methods leads readily to new cycloplatination chemistry involving use of **1** or **3** or quinoline-8-carboxaldehyde and the cycloplatinated phosphite complex $[Pt(\mu\text{-}Cl)\{(R^2O)_2POC_6H_4\}]_2$, R^2 = Et, Ph, to give the complexes $Pt(NO_3)(\widehat{CN})\{P(OPh)(OR)_2\}$, where $\widehat{CN}$ denotes the cycloplatinated nitrogen-ligand. The molecular structure of $PtCl\{(cyclohexyl)N{=}C(CH_2)_3C_6H_3\}(CO)$ has been determined by X-ray diffraction.

Introduction

Cyclometallation chemistry is widely studied and continues to attract much interest [1,2]. The most popular substrates involve nitrogen donors, but oxygen, sulfur, and phosphorus ligands have also been cyclometallated by use of various metal complexes [1,2]. Cyclopalladation has attracted the most interest, and in respect of preparative procedures this reaction seems to proceed in good yield starting from $Pd(OAc)_2$, unless the acetate ion poses a special problem [3], in which case various chloride containing starting materials are frequently suitable. Cycloplatination, on the other hand, is neither as widely studied nor as readily accomplished; although there are a number of examples [4–6]. It has been noted that "... reactions require longer reaction times and the yields are poorer" [6], and there are reported cycloplatinations, which took two weeks [4] or required relatively forcing conditions, e.g., refluxing DMF [5]. In recent studies [7] we have emphasized the advantage of choosing as the starting material a complex which (1) can increase its extent of coordinative unsaturation and (2) has electrophilic character. For quinoline 8-carboxyaldehyde, cycloplatination can be facilitated by using $SnCl_2$ or Ag^+

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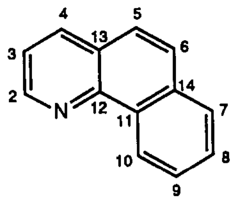

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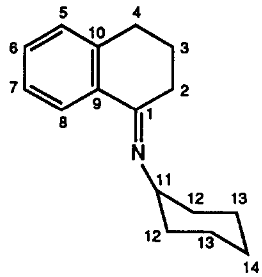

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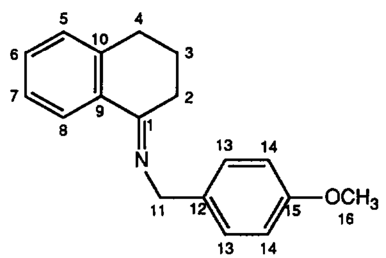

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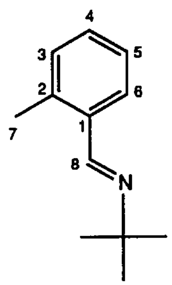

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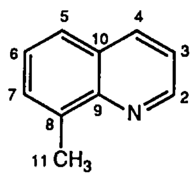

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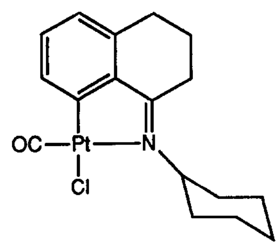
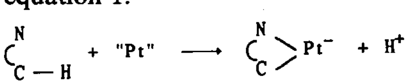


2d, CO *cis* to C

as halogen extracting reagents when the complex has a Pt–Cl bond, thereby achieving (1) and (2) simultaneously [7]. Nevertheless, it would be useful to have alternative methods for preparing cycloplatinated complexes in good-to-excellent yield under mild conditions which are not dependent on the use of such reagents.

In a parallel series of studies [8] we have shown that ligands such as **1–5** give rise to weak Pt←H–C interactions between the platinum and H(10), H(8) (in both **2** and **3**), H(6) and the CH_3, respectively. Since these are the positions at which one expects cycloplatination to take place it was of interest to find a single reagent with which to carry out this transformation, i.e., to bring about the reaction shown in equation 1.



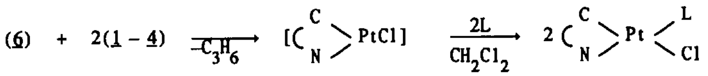
(1)

Having achieved this goal one could then consider whether this Pt←H–C bond, which we detect through J(Pt,H) coupling [8,9], is in any way relevant to the cyclometallation chemistry. We report here (1) the use of $[Pt(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)]_2$, **6**, as reagent of choice for this reaction with ligands **1–4**, (2) the cycloplatination of **5** starting from $[Pt(\mu\text{-Cl})ClL]_2$, L = PEt_3, PPh_3 and P(*p*-Tol)$_3$ in conjunction with Tl^+, (3) the crystal structure of **2d**, the thermodynamically favored isomer with CO *trans* to N, and (4) some related cycloplatination and cyclopalladation chemistry.

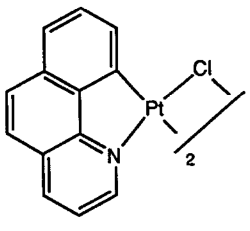
Results and discussion

1. Chemistry of 1–4

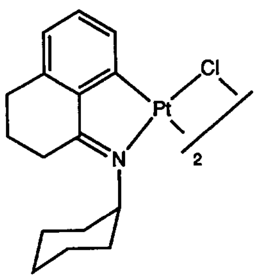
The dinuclear cycloplatinated chloride-bridged complexes **1a–4a** were prepared in 62–87% yield by treating one equivalent of **6** with two equivalents of the appropriate ligand in refluxing acetone for 3 h. The reaction time, conditions and resulting yields all compare favorably with those in earlier studies on cycloplatination of aromatic substrates [4–6]. The chloride-bridged complexes **1a**, **2a**, **3a** and **4a** are all only sparingly soluble (although in some cases ^{1}H-NMR spectra were



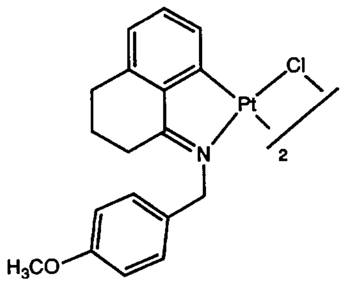
1a – 4a



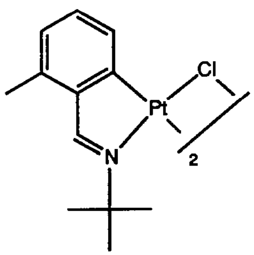
1a



2a



3a



4a

Scheme 1. Cycloplatination for **1–4**. The numbers refer to the ligands **1–4**, and the letters refer to: **a**, μ-Cl dinuclear; **b**, PPh_3; **c**, PEt_3; **d**, CO, derivatives respectively (**2d**: ^{13}CO).

recorded), and were best identified by using the monomeric more soluble tertiary phosphine complexes **1b–4b**, L = PPh_3, see Scheme 1. Analytical and spectroscopic data for these compounds are given in Tables 1–3. The phosphine complexes were characterized primarily from their NMR data. The two possible geometric isomers (P *trans* to N vs P *trans* to C) are readily distinguished by their ^1J(Pt,P) values, which are relatively large, indicating that the PR_3 ligand is *trans* to N [10a]. The ^{13}C spectra, see Fig. 1 for **1c**, show an aromatic resonance flanked by ^{195}Pt satellites whose separation is typical [11,12] for ^1J(Pt,C) in which the carbon is *trans* to a ligand of weak-to-moderate *trans* influence. Furthermore the relatively low field ^1H resonance for H(10) in coordinated **1** [8] (or H(8) in coordinated **2** ...) is now absent, which is very suggestive of cyclometallation at this position.

The dependence of ^1J(Pt,*C*O) on the strength of the *trans* influence was helpful in the case of **2d**, for which there are two geometric isomers in solution (see Fig. 2). The isomer with CO *trans* to carbon, with ^1J(Pt,CO) = 987 Hz, is readily distinguished from that with CO *cis* to carbon, with ^1J(Pt,CO) = 1680 Hz, in keeping with the literature [13–17]. The former isomer slowly disappears when a CH_2Cl_2

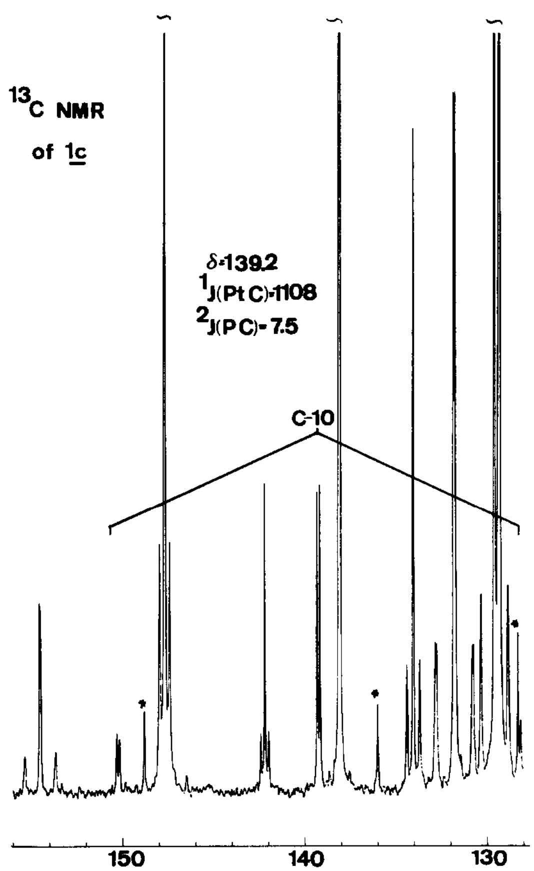


Fig. 1. Part of the aromatic section of the ^{13}C NMR spectrum of **1c**. The ^{195}Pt satellites for the metallated carbon, C(10), are indicated. This resonance is shifted to relatively low field [3]. The asterisks mark signals from an impurity. One of these covers half of one satellite.

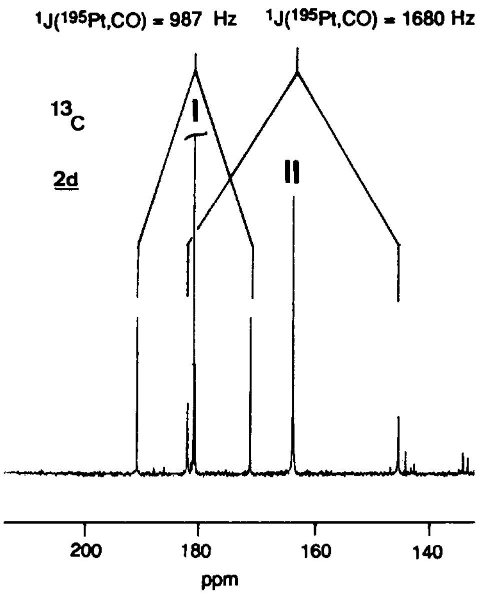


Fig. 2. CO (90 atom % ^{13}C enriched) region of the carbon spectrum of **2d** showing the two ^{13}CO signals with their markedly different $^1J(Pt,C)$ values. The major isomer has ^{13}CO *trans* to carbon (kinetic product).

solution containing both isomers is kept for 3 h at ca. 40 °C. We assume that the bridge splitting reaction places CO initially *trans* to carbon (kinetic product) [18], in keeping with the expected larger *trans* effect of an aryl carbon ligand relative to a pyridine nitrogen, but that this complex isomerizes to the thermodynamically-favored isomer with CO *cis* to carbon.

2. Molecular structure of ***2d***

Not surprisingly, the molecular structure determined with a crystal grown from a methylene chloride/hexane solution shows ligand **2** to be cycloplatinated at C(8) with the CO ligand *cis* to the metallated carbon. Although there are two independent molecules in the unit cell, they are not significantly different, and the values noted below refer to the means. Figure 3 shows an ORTEP plot for the thermodynamically favored isomer of **2d**, and Tables 4–6 give bond lengths and angles, positional parameters, and experimental details for the complex. The compound has a distorted square planar coordination sphere. The chelate bite angle N–Pt–C(8) is ca. 80 °, and the Cl–Pt–C(8) angle, 100 °, reflects this small bite angle. The Cl ligand lies 0.16 Å away from the plane defined by Pt, N and C(8). The Pt–CO separation, 1.86(1) Å, is comparable to that of 1.85(1) Å found in *cis*-$PtCl_2(CO)PPh_3$ [19a] as well as that in the $PtCl_3(CO)^-$-anion, 1.82(1) Å [19b]. The long Pt–Cl distance, 2.403(3) Å, is expected for chloride *trans* to carbon [20], and the Pt–C(8) and Pt–N separations, 2.00(1) and 2.073(8) Å, respectively, are also as expected [21]. The C(11)–O carbonyl bond, with a length of 1.12(1) Å, is a triple bond, and the N–C(12) bond occupies an equatorial position with respect to the cyclohexane ring (which adopts the chair conformation).

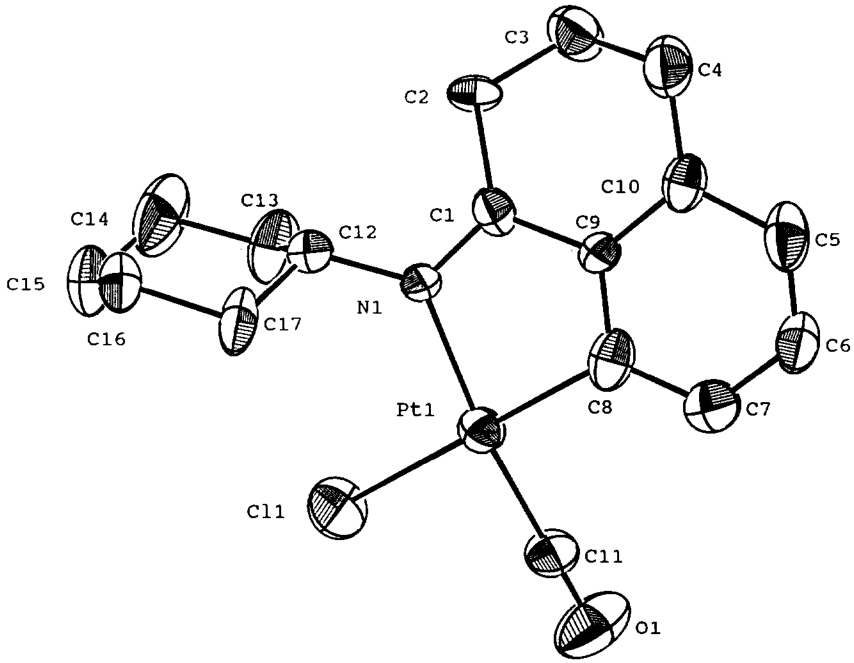
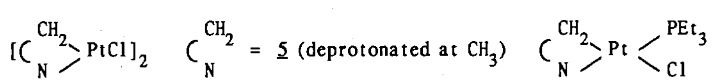


Fig. 3. ORTEP plot of the more stable isomer of **2d**. Only one of the two independent molecules in the unit cell is shown.

The structure of **2d** is to our knowledge the first to be determined for a cyclometallated tetralone derivative. We also note that whereas crystal structures are known for platinum complexes containing a $Pt(\widehat{N\ C})_2$ coordination sphere [22,23], relatively few are available for those with a $Pt(\widehat{N\ C})XY$ structure in marked contrast to the situation for palladium [1,2,24].

3. Cycloplatination of 8-methylquinoline, 5

Cyclometallation of **5** with Pd^{II} is well known [25,26], but a similar approach using Pt^{II} is not as satisfactory. Hartwell et al. [25] reported a preparation of **5a**, but gave no details. Our modification of his approach (K_2PtCl_4, 2 equiv. **5**, $MeOH/H_2O$, 3 h, at 20 °C) gave a 44% yield of impure **5a**, which was converted into **5c** as generally described for the PR_3 complexes (see Experimental section).



5a 5c

The bromo-analog of **5b** (with PPh_3) was prepared by the reaction of $Pt(PPh_3)_4$ with 8-bromomethylquinoline [27], but reaction of the allyl complex **6** with **5** did not lead to cyclometallated products *. Whatever mechanism is involved in the cycloplatination of **1–4** **, it is not sufficient in itself to platinate the methyl group.

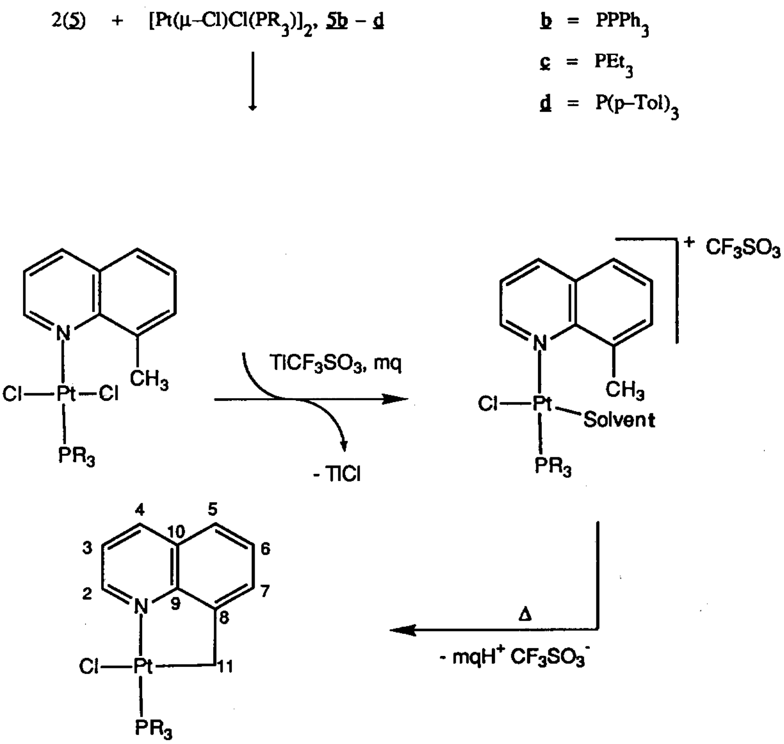
* Ligand **5** reacts with **6** to give $[PtCl(\eta^3\text{-}C_3H_5)(5)]$, and so lack of complexation is not the cause of the slow cycloplatination.

** An η^3-η^1 rearrangement would open a coordination position but we have no direct evidence for such a process. An open coordination site might allow electrophilic attack on an aryl double bond.

Similarly, Crabtree and co-workers [28] observed cyclometallation in the reaction of $Ir(COD)(PPh_3)_2^+$ and H_2 with **1**, but no cyclometallation occurred under the same conditions with **5** (although an agostic interaction between the Ir and the CH_3 did develop).

To increase the electrophilicity of the metal we returned to the halogen extraction approach, and our procedure for use with ligand **5** is shown in Scheme 2. The use of a soluble Tl^+ salt, an additional equivalent ligand of **5** as a base, and reaction for 3 h in refluxing CH_2Cl_2/acetone afforded ca. 75% isolated yields of **5b–5d** (based on platinum) starting from the three phosphine complexes **7**. Complexes **5b–5d** are also readily characterized by ^{31}P, ^{13}C and (since the cyclometallation affords a Pt–CH_2 fragment) ^1H NMR spectroscopy (see Tables 1 and 7). The protons of Pt–CH_2 normally give rise to an AB sub-spin system (see Fig. 4) with additional spin–spin couplings to ^{195}Pt, ^{31}P and H-7. This AB ^1H spin-system suggests these protons are now part of a ring.

During the characterization of **5b** and **5c** the values $^1J(Pt,CH_2)$ were obtained (745 and 751 Hz, respectively). Interestingly, these values are comparable to that found for C(8) in **2d**, 766 Hz, but smaller than that for C(8) in **2b**, 1087 Hz. The ratios $^1J(Pt,C)$, **2b**/$^1J(Pt,C)$, **5b** and $^1J(Pt,C)$, **2c**/$^1J(Pt,C)$, **5c** are ca. 1.43. This is only somewhat larger than might be expected on the basis of crude *s*-hybridization arguments [11], i.e., $sp^2 = 33.3\%$ *s*, $sp^3 = 25\%$ *s*, $33.3/25 = 1.33$, Why, then, is the value for **2d**, 766 Hz, relatively small? We believe there are two reasons for this low



Scheme 2. Cycloplatination chemistry of **5**.

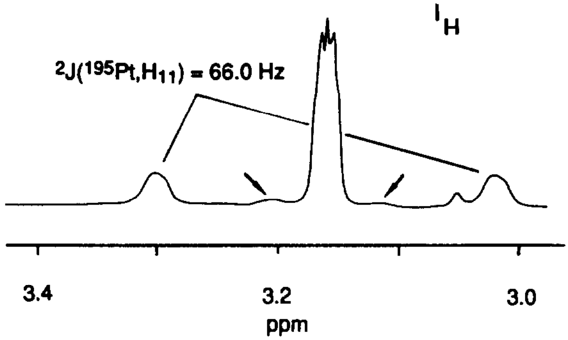


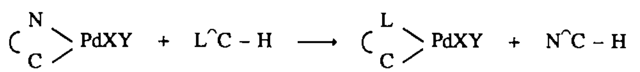
Fig. 4. ^{1}H NMR for **5c** showing the Pt–CH_2 resonance. The ^{195}Pt satellites are broad due to relatively fast ^{195}Pt relaxation. The main-band shows fine structure arising from ^{3}J(P,H) and ^{4}J(H,H). The outer lines of the AB are shown with arrows.

value: (1) the *trans* influence of Cl^- is greater than that for NO_3^-, thereby reducing ^{1}J in **2d** somewhat; and (2) the *cis* influence of CO (and other π-acceptors) causes a reduction of ^{1}J in **2d** [10b], whereas the *cis* influence of a phosphine (or a strong σ-donor) cause an increase in ^{1}J([10b].

The combined results of (1) and (2) outweigh the expected hybridization (*s*-character) effect. There are now a number of examples of significant *cis*-effects on ^{1}J(Pt,X), and perhaps this parameter deserves more consideration.

4. Transmetallation chemistry

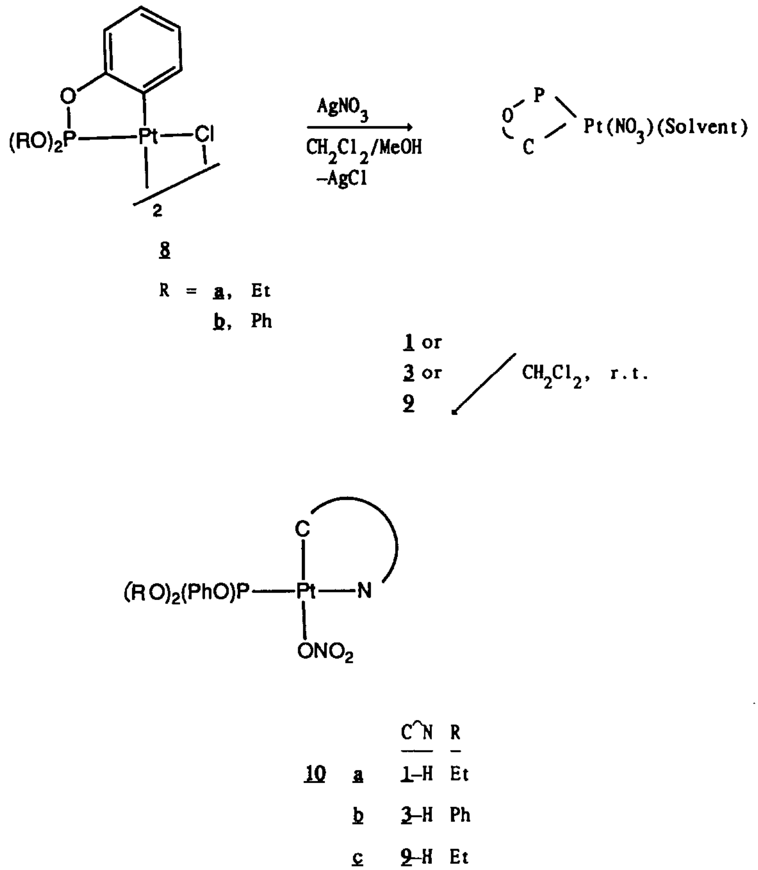
Ryabov and co-workers [29] and other groups [30] have described Pd^{II} chemistry in which one cyclometallated ligand is exchanged for another, as in eq. 2:



(2)

In the case studied L was a nitrogen-ligating group. We are interested in the possible consequence for reaction 2 of starting from a cyclometallated complex in which both coordinating ligand atoms were good-to-strong donors. We previously described [3] the synthesis of several cyclometallated phosphite complexes, e.g., **8**, Scheme 3, and considered this to be an interesting starting material for a transmetallation. The reaction was studied for **1**, **3** and quinoline-8-carboxyaldehyde, **9**, and was carried out at room temperature for 0.5–2 h with $AgNO_3$ present to promote cyclometallation. In all three cases the cyclometallated product $Pt(NO_3)$(phosphite)($\widehat{N\,C}$) was obtained in good yield. Clearly, the presence of the carbon and phosphorus donors does not inhibit the cyclometallation of the phosphite **8**. It would seem that Cl^- extraction and the subsequent introduction of a weakly coordinating NO_3^- (or solvent) produces the necessary conditions for smooth cycloplatination. The products **10** were characterized by microanalytical and NMR data. It is noteworthy that the relatively high field ^{31}P chemical shift of the phosphite [3] and the disappearance of the low field shifted H(10), H(8) and C*HO* protons [8,9] provide important clues to the structure of the product. The large value of ^{1}J(Pt,P) is consistent with P *trans* to NO_3^-.

For the sake of completeness we give details of the preparation of the new chloro-bridged palladium analogs of **2a** and **3a**, complexes **11** and **12**, respectively, in the Experimental section.



Scheme 3. (i) The solvent complex is prepared before addition of the ligand to be cycloplatinated. (ii) For **10a–c** cyclometallation occurs at C(1), C(8) and the aldehyde carbon, respectively.

Comments and conclusions

We have shown that the cycloplatination of various aromatic substrates can proceed smoothly under mild conditions with $[Pt(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$, **6**, as starting material. This complex may function well because of possible $\eta^3 \to \eta^1$ isomerisation or simply because the η^3-allyl is a π-acceptor. In any case **6** is not sufficiently active to cycloplatinate 8 -methylquinoline under similar conditions but such a reaction is readily brought about by use of $[Pt(\mu\text{-}Cl)Cl(PR_3)]_2$ and $Tl(CF_3SO_3)$.

Is there a connection between these observations on preparative aspects of cyclometallation and our $J(Pt \leftarrow H\text{–}C)$ values? For comparable complexes [8a] this coupling constant is ca. 14–16 Hz for complexed **1**, ca. 20 Hz for complexed **2**, only 5–6 Hz for complexed **4**, and ca. 12 Hz for complexed **5**. Although the values for **1** and **2** are larger than those for **5**, the ability to cycloplatinate **4** (with its small J value) but not **5** under similar conditions suggests that $J(Pt \leftarrow H\text{–}C)$ alone is not a quantitative indicator. It remains, however, a suggestive indicator for cyclometallation chemistry.

Experimental

The NMR spectra were recorded with Bruker WM-250 and AM-200 NMR spectrometers as $CDCl_3$ solutions, unless otherwise indicated. ^1H and ^{13}C chemical shifts are to TMS and ^{31}P shifts to external H_3PO_4. IR spectra were measured on a

Table 1

Microanalytical, IR and ^{31}P NMR data [a] for the complexes

Compound	Microanalyses Found (calcd.) (%)			IR	^{31}P
	C	H	N		
1a	38.01	2.23	3.30		
	(38.09)	(2.19)	(3.41)		
1b					23.4
					[4331]
1c	43.27	4.54	2.88		9.2
	(43.31)	(4.40)	(2.66)		[3988]
2a	39.78	4.25	2.67	ν(C=N) 1562	
	(39.69)	(4.24)	(2.81)	ν(Pt–Cl) 330	
2b	56.30	5.12	1.99	ν(C=N) 1595	24.4
	(56.78)	(4.91)	(1.95)		[4214]
2c	45.95	6.31	2.37	ν(C=N) 1597	6.3
	(45.95)	(6.13)	(2.44)		[3930]
2d	42.25	4.16	2.59	ν(C=N) 1561, 1582	
	(42.19)	(4.12)	(2.88)	ν(C≡O) 2100	
3a	43.34	3.62	3.25	ν(C=N) 1588	
	(43.69)	(3.67)	(2.83)	ν(Pt–Cl) 327	
3b	41.12	4.65	2.25	ν(C=N) 1584	24.2
	(40.75)	(4.40)	(2.26)		[4170]
3d	44.01	3.40	2.56	ν(C=N) 1593	
	(43.64)	(3.47)	(2.68)	ν(Pt–Cl) 298	
				ν (C≡O) 2084	
4a				ν(C=N) 1589	
4c				ν(C=N) 1586	23.8
					[4370]
5b	52.48	3.39	3.11		15.3
	(52.96)	(3.65)	(2.21)		[4268]
5c					6.9
					[3975]
5d					12.8
					[4253]
10a					79.4
					[6827]
10b	51.56	4.16	3.48	ν(C=N) 1596	76.5
	(51.99)	(4.00)	(3.37)		[6848]
10c					76.7
					[7611]
11	56.18	6.30	3.43	ν(C=N) 1588	
	(55.18)	(5.92)	(3.57)	ν(Pd–Cl) 329	
12	52.20	4.51	3.50	ν(C=N) 1595	
	(53.22)	(4.47)	(3.45)	ν(Pd–Cl) 332	

[a] IR data in cm^{-1} for Pt–Cl or Pd–Cl measured as CsCl or CsI pellets, ^{31}P chemical shifts relative to ext. H_3PO_4, $^1J(Pt,P)$ values in square brackets.

Table 2
^{1}H-NMR data [a] for selected cycloplatinated complexes of **1–4**

	1b	**1c**	**2b**	**2c**	**2d**	**4b**
H_2	10.08	9.92	2.92	2.80	2.89	–
$^4J(^{31}P,H_2)$	(3.9)	(4.1)	–	–	–	–
$^3J(^{195}Pt,H_2)$	[29.1]	[31.0]	–	–	–	
H_3	7.58	7.59	1.97	1.94	2.00	6.60
H_4	8.33	8.21	2.73	2.73	2.77	6.35
H_5	7.6	7.6	6.38	6.78	6.92	6.40
$^3J(^{195}Pt,H_5)$	–	–	–	–	–	[48.0]
H_6	7.6	7.6	6.63	6.94	7.04	
H_7	7.73	7.71	6.39	7.12	7.18	2.52
$^3J(^{195}Pt,H_7)$	–	–	[49.0]	[56.0]	[72.0]	–
H_8	7.41	7.43	–	–	–	8.75
$^4J(^{31}P,H_8)$	–	–	–	–	–	(5.5)
$^3J(^{195}Pt,H_8)$	–	–	–	–	–	[97.0]
H_9	7.59	7.60	–	–	–	–
H_{10}	–	–	–	–	–	1.73
H_{11}	–	–	4.62	4.60	4.29	–
H_{12}	–	–	2.55/1.7	2.6/1.7	2.66/1.68	–
H_{13}	–	–	1.8/1.3	1.8/1.3	1.92/1.3	–
H_{14}	–	–	1.53	1.54	1.47	–

[a] 250.13 Hz, RT, $CDCl_3$; coupling constants to ^{31}P ( ), resp. ^{195}Pt [ ].

Beckmann 883 instrument. Microanalytical measurements were performed in the analytical laboratory of the ETH, Zürich.

The ligands were either commercially available or prepared as described previously [8,9]. Complex **6** was prepared as described by Maitlis and co-workers [31].

Preparation of 1a–3a

To a solution of **6** in 5 ml acetone was added two equivalents of the ligand. The color of the solution changed immediately from red to yellow. Refluxing for several hours (see below) was followed by filtration of the crude product, washing with methylene chloride, acetone and ether, and drying under vacuum.

Complex	reaction time, h	**6**, mg	ligand, mg	yield, mg (%)
1a	2	286	179	335 (82)
2a	1	286	227	361 (79)
3a	3	200	186	298 (87)
4a	8	114	70	105 (62)

The mononuclear phosphine derivatives were prepared as follows:

A suspension of one equivalent of the chloro-bridged dinuclear complex in CH_2Cl_2 was treated with two equivalents of the tertiary phosphine. After 30 min stirring the solvent was removed under vacuum and the residual solid recrystallized

Table 3

^{13}C-NMR data [a] for selected cycloplatinated complexes of **1–4**

	1b	**1c**	**2**	**2c**	**2d**	**4b**
C_1	–	–	183.1	181.7	187.9	137.7
	–	–	(6.2)	(3.0)	–	–
	–	–	[96.0]	[91.0]	[100.0]	[32.2]
C_2	148.6	147.6	31.5	31.1	30.8	145.4
	–	–	(4.8)	(5.0)	–	–
	[27.8]	[28.1]	[42.0]	[36.0]	[47.0]	[25.0]
C_3	121.3	121.1	23.5	23.3	23.7	124.9
	(4.0)	(4.1)	–	–	–	–
	[23.2]	[23.0]	–	–	–	–
C_4	138.3	138.0	29.5	29.6	29.2	131.1
C_5	123.3	123.5	122.6	123.1	125.2	135.6
	–	–	–	–	–	[97.2]
C_6	122.0	122.4	130.3	131.1	133.3	145.5
	–	–	–	–	–	(5.0)
	–	–	[58.0]	[60.0]	[47.0]	[1030.0]
C_7	129.5	129.3	131.5	135.2	134.2	20.4
	–	–	(3.9)	(4.0)	–	–
	–	–	[100.8]	[102.0]	[60.0]	–
C_8	129.8	129.6	145.2	144.3	143.4	169.8
	–	–	(7.0)	(6.2)	–	(4.0)
	[73.5]	[75.0]	[1059.0]	[1087.0]	[766.0]	[47.1]
C_9	131.0	131.7	141.6	142.2	144.0	64.7
	(4.1)	(4.2)	–	–	–	–
	[99.8]	[101.0]	[41.1]	[41.0]	[39.0]	[32.0]
C_{10}	140.0	139.2	145.9	146.1	144.6	30.2
	(6.5)	(7.5)	–	–	–	–
	[1097.0]	[1108.0]	–	–	–	–
C_{11}	155.1	154.5	63.2	62.7	63.4	–
	(2.1)	(2.0)	–	–	–	–
	[85.5]	[86.1]	[28.0]	[26.0]	[29.0]	–
C_{12}	142.4	142.2	30.5	30.2	30.2	–
	[22.1]	[22.0]	–	–	–	–
C_{13}	126.8	126.6	25.8	25.8	25.7	–
	(1.9)	(1.8)	–	–	–	–
	[23.5]	[24.0]	–	–	–	–
C_{14}	134.1	134.0	25.3	25.2	24.9	–
	[34.6]	[35.0]	–	–	–	–
CO	–	–	–	–	163.8	–
	–	–	–	–	[1680.0]	–

[a] Coupling constants to ^{31}P ( ) resp. ^{195}Pt [ ]. 50.32 MHz, RT, $CDCl_3$.

from methylene chloride/hexane.

Complex	dimer, mg	PR_3, mg or μl	yield, mg (%)
1b	81.9	PPh_3, 52.4	131 (98)
1c	81.9	PEt_3, 24 μl	101 (96)
2b	91.3	PPh_3, 52.4	135 (94)
2c	91.3	PEt_3, 24 μl	105 (92)
4b	80.9	PPh_3, 52.4	127 (95)

Table 4

Selected bond lengths (Å), bond angles (°) and torsion angles (°) for compound **2d**

Pt-Cl	2.397(4)		2.407(4) [a]
Pt-N(1)	2.07(1)		2.07(1)
Pt-C(8)	2.00(1)		2.00(2)
Pt-C(11)	1.86(1)		1.86(2)
O(1)-C(11)	1.11(2)		1.12(2)
N(1)-C(1)	1.32(2)		1.30(2)
N(1)-C(12)	1.47(2)		1.47(2)
C(1)-C(2)	1.51(2)		1.52(2)
C(1)-C(9)	1.44(2)		1.46(2)
C(2)-C(3)	1.53(2)		1.55(2)
C(3)-C(4)	1.53(2)		1.56(2)
C(4)-C(10)	1.46(2)		1.49(2)
C(5)-C(6)	1.34(2)		1.39(3)
C(5)-C(10)	1.44(2)		1.36(2)
C(6)-C(7)	1.35(2)		1.42(3)
C(7)-C(8)	1.41(2)		1.40(2)
C(8)-C(9)	1.37(2)		1.40(2)
C(9)-C(10)	1.42(2)		1.40(2)
$\overline{C-C}$ [b]		1.53(3)	
Cl(1)-Pt(1)-N(1)	100.6(2)		99.6(3)
Cl(1)-Pt(1)-C(8)	175.6(4)		176.4(4)
Cl(1)-Pt(1)-C(11)	86.1(5)		86.4(5)
N(1)-Pt(1)-C(8)	80.0(5)		79.8(6)
N(1)-Pt(1)-C(11)	172.7(6)		173.9(6)
C(8)-Pt(1)-Cl(1)	93.1(7)		94.4(6)
Pt(1)-N(1)-C(1)	113.2(8)		113.7(9)
Pt(1)-N(1)-C(12)	126.9(7)		127.7(8)
C(1)-N(1)-C(12)	120(1)		119(1)
Pt(1)-C(8)-C(7)	129(1)		129(1)
Pt(1)-C(8)-C(9)	113(1)		113(1)
Pt(1)-C(11)-O(1)	177(1)		177(2)
Pt(1)-N(1)-C(1)-C(2)	171(1)		171(1)
Pt(1)-N(1)-C(12)-C(17)	52(19)		49(2)

[a] The two sets of values refer to the two independent molecules in the unit cell. [b] Average value of the C–C distance in the cyclohexal moiety.

The carbonyl complex **2d**, containing ^{13}CO, was prepared as follows:

A suspension of the dinuclear complex **2a** (137 mg, 0.15 mmol) in 5 ml of CH_2Cl_2 contained in a 10 ml Schlenk tube was cooled until the liquid froze and the air was then extracted. ^{13}CO (Stohler Isotopes) was introduced via a vacuum line and the solids slowly brought to room temperature. Vigorous stirring for 2 h was followed by removal of the solvent. Recrystallization from methylene chloride/ether gave 197 mg (88%) of the product. Crystals suitable for the X-ray study were obtained from chloroform/hexane solution at −20 °C.

Preparation of ***5b–d***

Complex **5** (0.3 mmol) was added to a suspension of the dinuclear phosphine complex (0.1 mmol) in 20 ml of methylene chloride/acetone (4:1) and the mixture was stirred for 30 min. To the resulting clear solution was added $Tl(CF_3SO_3)$ (70

Table 5

Final positional parameters and equivalent thermal parameters for **2d** (esd's in parentheses)

Atom	x	y	z	$B(Å^2)$ [a]
Pt(1′)	0.49435(4)	0.11352(4)	0.68567(2)	3.16(1)
Pt(1)	−0.11917(3)	−0.04451(4)	0.58377(2)	2.86(1)
Cl(1)	0.0211(3)	−0.0118(3)	0.6240(2)	5.2(1)
Cl(1′)	0.6159(2)	0.0102(3)	0.6840(2)	4.9(1)
O(1)	−0.1893(8)	0.0850(8)	0.6484(5)	6.5(3)
O(1′)	0.6266(8)	0.2636(8)	0.6(19(5)	7.0(3)
N(1)	−0.0830(6)	−0.1294(7)	0.5329(4)	2.2(2)
N(1′)	0.3921(7)	0.0206(7)	0.6783(4)	3.3(2)
C(1)	−0.1437(8)	−0.1368(9)	0.4980(5)	2.7(3)
C(1′)	0.3194(9)	0.0518(9)	0.6914(5)	3.0(3)
C(2)	−0.1312(9)	−0.183(1)	0.4532(4)	3.4(3)
C(2′)	0.2380(9)	−0.004(1)	0.6966(6)	3.8(3)
C(3)	−0.199(1)	−0.149(1)	0.4152(6)	4.2(4)
C(3′)	0.181(1)	0.042(1)	0.7305(6)	4.7(4)
C(4)	−0.2911(9)	−0.161(1)	0.4295(6)	4.2(4)
C(4′)	0.158(1)	0.140(1)	0.7126(6)	4.7(4)
C(5)	−0.3838(9)	−0.087(1)	0.4873(6)	4.2(4)
C(5′)	0.238(1)	0.288(1)	0.7058(6)	5.3(4)
C(6)	−0.3900(9)	−0.048(1)	0.5278(6)	3.7(3)
C(6′)	0.313(1)	0.338(1)	0.6994(6)	5.7(5)
C(7)	−0.319(1)	−0.036(1)	0.5586(5)	3.9(3)
C(7′)	0.391(1)	0.292(1)	0.6914(6)	5.0(4)
C(8′)	0.393(1)	0.1969(9)	0.6912(5)	3.7(3)
C(8)	−0.2358(9)	−0.0627(9)	0.5476(5)	3.3(3)
C(9)	−0.2288(8)	−0.1028(9)	0.5061(5)	2.4(3)
C(9′)	0.3158(9)	0.1507(9)	0.6983(5)	3.3(3)
C(10)	−0.3014(8)	−0.1174(9)	0.4732(5)	3.0(3)
C(10′)	0.2383(9)	0.195(1)	0.7062(5)	3.8(3)
C(11)	−0.1644(9)	0.0349(9)	0.6244(5)	3.6(3)
C(11′)	0.577(1)	0.207(1)	0.6910(7)	5.6(5)
C(12)	0.0021(8)	−0.174(1)	0.5313(5)	3.2(3)
C(12′)	0.3939(9)	−0.0735(9)	0.6610(5)	3.2(3)
C(13)	0.438(1)	−0.139(1)	0.6969(5)	3.6(3)
C(14′)	0.442(1)	−0.237(1)	0.6795(7)	5.1(4)
C(14)	0.161(1)	−0.159(1)	0.5197(8)	6.9(6)
C(15′)	0.483(1)	−0.237(1)	0.6333(6)	4.7(4)
C(15)	0.185(1)	−0.214(1)	0.5622(7)	6.1(5)
C(16′)	0.439(1)	−0.174(1)	0.5977(6)	4.8(4)
C(16)	0.114(1)	−0.280(1)	0.5710(6)	4.7(4)
C(17′)	0.434(1)	−0.076(1)	0.6168(5)	3.3(3)
C(17)	0.0280(9)	−0.227(1)	0.5743(6)	4.1(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

mg, 0.2 mmol), and stirring continued for an additional 1 h. The resulting suspension was filtered through Celite to remove TlCl and the yellow filtrate refluxed for 3 h. Removal of the solvents was followed by addition of benzene; the quinolinium salt is insoluble in this solvent and was removed by filtration. The benzene was removed under vacuum and the residue recrystallized from methylene chloride/petroleum ether; **5b**, 95 mg, 75%; **5c**, 75 mg, 76%; **5d**, 97 mg, 72%.

Table 6

Experimental details for the X-ray diffraction study of **2d**

Formula	$C_{17}H_{21}ClONPt$
Molecular weight	485.89
Crystal dimensions, mm	0.20 × 0.40 × 0.45
Data collection T, °C	22
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	15.359(5)
b, Å	14.644(2)
c, Å	29.491(8)
β, deg	96.00(3)
V, Å^3	6596.7(5)
z	16
ρ(calcd), g cm^{-3}	1.956
μ, cm^{-1}	87.54
Radiation	Mo-$K_{\bar{\alpha}}$, graphite monchromated $\lambda = 0.71069$
Measured reflections	$\pm h, +k, +l$
θ range, deg	$2.20 < \theta < 25.0$
Scan type	$\omega/2\theta$
Scan width, deg	$1.1 + 0.35 \tan\theta$
Max counting time, s	65
Background time, s	0.5 × scan-time
Max scan speed, deg min^{-1}	10.5
Prescan rejection limit	0.500 (2.00 σ)
Prescan acceptance limit	0.025 (40.00σ)
Horizontal receiving slit, mm	$1.80 + \tan\theta$
vert receiving slit, mm	4.0
No. of independent data	5805
No. of observed reflections (n_o) ($\lvert F_o\rvert^2 > 2.0\sigma(\lvert F\rvert^2)$)	3738
No. of parameters refined (n_v)	383
R	0.046
R_w	0.056
GOF	1.976

$R = \Sigma \| F_o| - (1/k)|F_c\| / \Sigma|F_o|$. $R_w = [> sw(|F_o| - (1/k)|F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o^2) + f^2(F_o^4)]^{1/2}/2F_o$ with $f = 0.050$. GOF $= [\Sigma w(F_o - (1/k)|F_c|)^2/(n_o - n_v)]^{1/2}$.

*Preparation of **10a–c***

A solution of one equivalent of the phosphite complex [3] in 20 ml of methylene chloride/methanol (1 : 3) was treated with 2.05 equivalents of $AgNO_3$. After 3 min stirring the resulting suspension was filtered through Celite into a methylene chloride solution containing two equivalents of either **1**, **3** or **9**, resulting in a color change from orange-red to yellow. The solvents were removed and the residue dissolved in methylene chloride. The solution was stirred for 30 min, and the resulting suspension (residual $AgNO_3$) was filtered into ether causing the crude product to separate. Recrystallization (see yield, below) gave the pure product.

	dimer, mg (mmol)	ligand, mg (mmol)	yield, mg (%)
10a	89 (0.10)	36 (0.20)	100 (80) (CH_2Cl_2/ether)
10b	61 (0.056)	30 (0.113)	72 (80) (CH_2Cl_2/hexane)
10c	44 (0.05)	16 (0.10)	41 (70) (CH_2Cl_2/ether)

Table 7

Combined ^1H [a] and ^{13}C [b] NMR data [c] for the complexes **5b–d**

	5b [d]	**5c**	**5d**
H_2	10.12	9.89	10.12
	(3.9)	(4.1)	(3.8)
	[32.2]	[28.1]	[31.0]
H_3	[e]	7.43	7.42
H_4	8.33	8.29	8.31
H_5	[e]	7.71	[e]
H_6	[e]	7.51	7.48
H_7	[e]	7.68	[e]
H_{11}	2.75	3.17	2.77
	(2.8)	(2.7)	(2.8)
	[65.0]	[66.0]	[67.2]
C_2	149.1	148.4	–
	[27.0]	[26.0]	–
C_3	121.3	121.5	–
	(4.0)	(3.5)	–
	[12.0]	[12.0]	–
C_4	138.4	138.0	–
C_5	130.1	130.7	–
C_6	123.6	123.8	–
C_7	131.3	131.5	–
C_8	148.4	148.4	–
	(4.0)	(4.1)	–
	[29.0]	[28.7]	–
C_9	152.3	152.6	–
C_{10}	129.4	129.3	–
C_{11}	16.9	17.1	–
	(4.9)	(4.8)	–
	[745.0]	[751.0]	–

[a] 200.13 MHz. [b] 50.32 MHz. [c] Coupling constants to ^{31}P ( ) and ^{195}Pt [ ]. [d] 200.13 MHz. [e] Hidden by phosphine protons.

*Cyclopalladation of **2** to afford **11***

A mixture of $Li_2[PdCl_4]$ (200 mg, 0.76 mmol) in 1 ml of methanol, **2** (173 mg, 0.76 mmol), and NaOAc (62 mg, 0.76 mmol) in 4 ml of methanol was stirred for 2 h at room temperature. The solid was filtered off and extracted with warm methylene chloride. The extract was filtered through Celite and then concentrated to remove the solvent. The crude product was washed with hexane and filtered off to give the product, 287 mg (87%). This material was analysed both as its PPh_3 derivative **11b**, and in its μ-Cl dinuclear form **11a**. For **11a**: IR, ν, Pd–Cl = 329 cm^{-1}; for **11b**: ^{31}P NMR: 43.4.

*Cyclopalladation of **3** to afford **12***

A solution of Na_2PdCl_4 (98 mg, 0.33 mmol) in 5 ml of methanol was then added dropwise during 2 h to a solution of **3** (100 mg, 0.38 mmol) and NaOAc (24 mg, 0.33 mmol) in 3ml of methanol. The resulting suspension was filtered and the solid dissolved in methylene chloride. This solution was then treated with active charcoal, filtered through Celite, and concentrated to give the crude product. Recyrstallization from methylene chloride/hexane gave the pure product, 67 mg (53%). This

Table 8

^1H NMR data [a] for **10a–10c**

	10a	**10b** [c,d]	**10c**
H_2	8.89 (2.5) [28.5]	2.64 [b]	9.30 (2.5) [28.0]
H_3	7.55	1.85	7.75
H_4	8.30	2.64 [b]	8.57
H_5	7.60	6.74	8.12
H_6	7.73	6.93	7.66
H_7	7.72	7.54 [54]	8.11
H_8	7.41		
H_9	7.52		
$H_{2'}$,$H_{3'}$	7.2–7.4		7.2–7.4
$H_{4'}$	7.10		7.09
	4.45 (7.6) (OCH_2)	3.79 (OCH_3)	4.40 (7.6) (OCH_2)
	1.34 (CH_3)	4.81 (NCH_2)	1.39 (CH_3)
		(7.7) [18]	

[a] Coupling constants to ^{31}P ( ) resp. ^{195}Pt [ ], 250.13 MHz, RT, $CDCl_3$. [b] Overlapping multiplets. [c] H(13), 7.18, H(14), 6.78. [d] Phosphite protons relative to oxygen atom; *ortho*, 7.35, *meta*, 7.28, *para*, 7.13 (500 MHz).

Table 9

^{13}C NMR data [a] for **10a–10c**

	10a	**10b** [b]	**10c**
C_2	146.7 [27.5]	28.7, 29.2	149.1 [22.2]
C_3	121.4 (6.2) [22.4]	22.8	122.9 (5.6) [26.2]
C_4	139.3	28.7, 29.2 [c]	139.5
C_5	123.7	124.6	129.3
C_6	123.3	134.2	125.9 [11.2]
C_7	129.6		130.7
C_8	129.8 [72.4]	134.5 (7.2)	144.2 [211.0]
C_9	134.6 (5.9) [101.3]	142.4	150.5 [24.5]
C_{10}	129.1 (11.2) [1073.0]	143.0	128.7 (3.7)
C_{11}	153.6 (2.2) [84.9]	52.5 (NCH_2)	187.6 (9.7) [1221.5]
C_{12}	140.8 [22.2]	128.6	
C_{13}	126.7 (1.9) [26.6]	128.6	
C_{14}	133.8 [33.4]	113.9	

[a] Coupling constants to ^{31}P ( ) resp. ^{195}Pt [1 1]. 50.32 MHz, RT $CDCl_3$. [b] C=N, 187.2(3), C(2), C(4) not assigned, OCH_3 55.2; C(15), 158.7. $P(OPh)_3$ relative to O: 150.5 (5.7), 120.4 (5.9), 129.8, 125.1.

material was analysed both as its $P(OCH_3)_3$ derivative, **12b**, and as its μ-Cl dinuclear complex, **12a**. For **12a**: IR: ν(Pd–Cl) = 332 cm^{-1}. ^1H NMR: 3.73 (OCH_3). For **12b**: IR: ν(Pd–Cl) = 307 cm^{-1}. ^1H NMR: 3.87 (OCH_3); 3.79 ($P(OCH_3)_3$. ^{31}P NMR: 124.4. ^{13}C NMR: 185.2 (C=N).

Crystallography

Crystals suitable for X-ray diffraction of compound **2d** were obtained by crystallization from methylene chloride/hexane solution. They are air stable.

A prismatic crystal was mounted on a glass fiber at a random orientation on an Enraf–Nonius CAD4 diffractometer for the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by least squares fit of the 2θ values of 25 high order reflections ($9.6 < \theta < 15.6$) using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table 6.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections (-5 5 1; 5 -5 -1; -2 6 -7) were used to check the stability of the crystal and of the experimental conditions, and measured every hour; no significant variation was detected. The orientation of the crystal was checked by measuring three standard reflections every 300 measurements. Data were corrected for Lorentz and polarization factors using the data reduction programs of the CAD4. An empirical adsorption correction was applied by use of the aximuthal (ψ) scans of three "high-" χ angle reflections ($\chi > 87.7°$; $10.53 < \theta < 18.92°$). Transmission factors were in the range 0.4941–0.9941. The standard deviations in intensities were calculated in terms of statistics alone, while those on F_o were calculated indicated in Table 6. Intensities were considered as observed if $F_o^2 > 2.0\sigma(F^2)$, and used for the solution and refinement of the structure. A value of F_o of 0.0 was given to those reflections having negative net intensities.

The structure was solved by a combination of Patterson and Fourier methods and refined by full-matrix least-squares [32] (the function minimized was $[\Sigma w(|F_o| - (1/k)|F_c|)^2]$ with $w = [\sigma^2(F_o)]^{-1}$). No extinction correction was applied. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature [33]. Anisotropic temperature factors were used for all but the hydrogen atoms.

The hydrogen atoms were kept fixed in their calculated positions (C–H = 0.95 Å, B(Å^2) set equal to $1.5 \times B$ of the atom to which they are bound) but not refined.

Upon convergence (no parameter shift $> 0.02\sigma\ (p)$) the Fourier difference map showed no significant feature. All calculations were carried out by using the SDP crystallographic package [32]. Final atomic coordinates and equivalent thermal factors are given in Table 5. Tables of anisotropic displacements, hydrogen coordinates, observed and calculated structure factors and a complete list of bond lengths and angles are available from the authors.

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