1812 *Inorg. Chem.* **1990**, *29*, 1812–1817

Contribution from the Istituto di Chimica Farmaceutica, Università di Milano, I-20129 Milano, Italy, and Laboratorium für Anorganische Chemie, ETH Zürich, CH-8092 Zürich, Switzerland

Weak Pt–H–C Interactions. Extensions to 8-Methylquinoline, Benzoquinoline, and a Tetralone Schiff Base. X-ray Crystal Structure of *trans*-$PtCl_2$(benzoquinoline)(PEt_3)

Alberto Albinati,[1a] Paul S. Pregosin,*[,1b] and Franz Wombacher[1b]

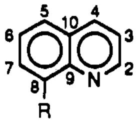
Received August 31, 1989

A series of platinum complexes containing coordinated 8-methylquinoline, benzoquinoline, the cyclohexylamine Schiff base of tetralone, and (among others) quinoline-8-carbaldehyde have been prepared and studied by ^1H and ^{13}C NMR methods. All of these complexes reveal weak Pt←H–C interactions to remote protons to very different extents, with *J*(Pt,H) values ranging from 5 to 21 Hz. There is some correlation to the ^{13}C data in that complexes with small *J*(Pt,H) values show no platinum spin–spin coupling to ^{13}C whereas compounds with ca. 20-Hz couplings show *J*(Pt,C) values of 63 and 66 Hz. Steric boundary conditions for this type of interaction as well as the potential usefulness of chemical shifts in recognizing this interaction are discussed. The molecular structure for *trans*-$PtCl_2$(benzoquinoline)(PEt_3) has been determined by X-ray diffraction. The molecule crystallizes in the space group $P\bar{1}$, with $a = 7.8216$ (8) Å, $b = 7.8607$ (6) Å, $c = 17.0376$ (13) Å, $\alpha = 94.30$ (1)°, $\beta = 98.50$ (2)°, $\gamma = 100.63$ (1)°, and $Z = 2$. The H(10)–Pt separation of ca. 2.5 Å is consistent with the weak bonding interactions described by the NMR experiments.

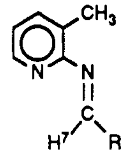
Introduction

There is a continuing interest in the chemistry and molecular structure of molecules demonstrating so-called "agostic" C–H→M interactions.[2-6] These C–H bonds show reduced $^1J(^{13}C,^1H)$ coupling constants, high-field ^1H NMR shifts, and H···M separations (X-ray) of ca. 1.8–2.2 Å.[2]

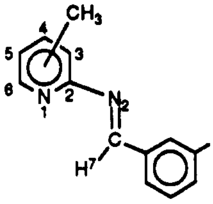
We have recently suggested a much weaker variation of this type of interaction,[7-9] based on the *J*(Pt,H-11) and *J*(Pt,H-7), ca. 8–39 Hz, for two series of molecules *trans*-$PtCl_2L$(**1**) and *trans*-$PtCl_2L$(**2**) (L = PR_3, AsR_3, C_2H_4, PhCH=CH_2). Our molecules show normal $^1J(^{13}C,H)$ values and *low*-field ^1H shifts. Further, we have complemented these NMR data with solid-state[8,9] structural work, which suggested H–Pt separations of ca 2.3–2.5 Å as typical for our interaction. Most recently, we have defined steric boundary conditions[10] for our weak Pt←H–C bonds using, among others, complexes with the ligands



1a, R = CHO
b, R = CH_3
c, R = Pr^i
d, R = $CHBr_2$



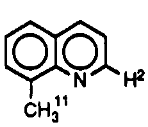
2, R = substituted aryl moiety



3a, 3-CH_3
b, 5-CH_3
c, 6-CH_3

which allow or hinder rotation about the C-2–N-2 bond depending on the position of the pyridine–CH_3 substituent.

We present here an extension of these studies in which we consider the ligands **4**–**8**, L, complexed to platinum in most cases in the form of a *trans*-$PtCl_2$(L)(tertiary phosphine) complex.



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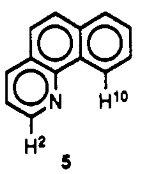

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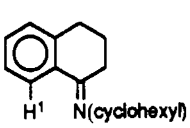

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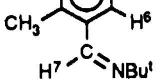

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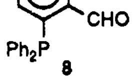

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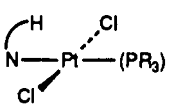
These ligands have been specifically chosen so that, for **4**–**7**, one or more C–H bonds will sit above the coordination plane defined by the Pt and P atoms and the two Cl atoms



and have restricted motional freedom due to built-in rigidity and/or bulky substituents on nitrogen, which increase the energy barrier for rotation about the Pt–N bond.

In the second half of this paper, we discuss (1) a wider range of known molecules that fulfill the above geometric boundary condition, with a view to evaluating the potential significance of relatively large, low-field coordination chemical shifts, and (2) the solid-state structure of *trans*-$PtCl_2$(benzoquinoline)(PEt_3) in connection with the solution studies and previous solid-state structural work.

Results and Discussion

Coupling Constants. Before the individual molecules are presented, it is worth reviewing a few NMR points for these types of complexes:

(1) We take the presence of a significant Pt, H coupling to H-11 of **1**, or H-7 of **2** ..., to signify a weak interaction with the metal since ^5J(Pt,H) values are not known.

(2) Where measured, $^1J(^{13}C,^1H)$ for the carbon concerned decreases very slightly, but there is Pt coupling to this carbon; e.g., $^1J(^{13}C,H)$ = 184.9 Hz in **1a**, 185.4 Hz in *trans*-$PtCl_2$(**1a**)($AsMe_3$)—but *J*(Pt,C-11) = 36.6 Hz. For *trans*-$PtCl_2$(**1a**)($AsTol_3$), $J(^{13}C$,H-11) = 184.8—but *J*(Pt,C-11) = 35.0 Hz.

(3) X-ray studies[8,9] show that the C–H vector is directed toward the metal.

Table I shows new and a few previously reported ^1H NMR data for platinum complexes of **1a**. These latter entries (1–5) were chosen as they (1) show little difference when compared with data

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Table I. NMR Data[a] for Complexes of **1a** and **4**

entry	L	δ(H-11)	*J*(Pt,H-11)	δ(H-2)	*J*(Pt,H-2)	δ(P)	*J*(Pt,P)
			trans-$PtCl_2$(**1a**)L[b]				
1	PEt_3[c]	13.09	13.7	9.50	17.6	1.0	3467
2	PPh_3[d]	13.23	12.4	9.63	20.5	1.1	3719
3	$PTol_3$[e]	13.26	12.4	9.64	20.5	4.1	3955
4	$AsEt_3$	13.27	15.4	9.57	23.2		
5	$AsTol_3$	13.45	14.7	9.69	27.0		
			trans-$PtBr_2$(**1a**)L[f]				
6	PEt_3	13.09	13.7	9.53	17.6	−1.9	3362
7	PPh_3	13.25	13.7	9.67	18.0		
8	$PTol_3$	13.46	13.8	9.74	17.2	2.6	3758
9	PtCl(η^3-methallyl)(**1a**)	12.30	19	9.15	35 (major)		
		11.98	14	9.55	27 (minor)		
			trans-$PtCl_2$(**4**)L[f]				
10	PEt_3[g]	3.96	11.4	9.62	13.7	−0.7	3571
11	PPh_3[h]	4.02	12.2	9.73	14	1.4	3805
12	$PTol_3$[i]	4.03	12.3	9.72	14.5	0.4	3773
13	C_2H_4[j]	3.97	12.7	9.48	29		
14	PhCH=CH_2[k]	3.87	11.2	9.40	24		
	4	2.82		8.97			

[a] Chemical shifts in ppm, *J* values in Hz, δ(H-11) in **1a** = 11.48. [b] Data from ref 7. [c] δ(C-11) 188.1, *J*(C,H) = 183.3, *J*(Pt,C-11) = 31.6, *J*(C,H-11) ligand = 184.9. [d] δ(C-11) = 188.3, *J*(Pt,C-11) = 34.2. [e] Tol = *p*-$CH_3C_6H_4$. [f] $CDCl_3$ solutions. [g] δ(C-11) = 25.1, Δδ = 6.9, *J*(Pt,C-11) = 27; δ(C-2) = 153, Δδ = 4. [h] CD_2Cl_2, δ(C-11) = 25.0, Δδ = 6.8, *J*(Pt,C-11) = 28; δ(C-2) = 154.3, Δδ = 5.0. [i] δ(C-11) = 25.3, Δδ = 7.1, *J*(Pt,C-11) = 29; δ(C-2) = 153.8, Δδ = 4.5. [j] C_2H_4, δ(H) = 4.84, *J*(Pt,H) = 64, δ(C) = 72.3, *J*(Pt,C) = 174, δ(C-11) = 24.5, Δδ = 6.3, *J*(Pt,C) = 22; δ(C-2) = 152.3, Δδ = 3.0, *J*(Pt,C) = 16. [k] PhCH(α)=CH_2, δ(H(α)) = 6.8, δ(H, trans to H(α)) = 5.3, δ(H cis to H(α)) = 4.76.

for the new Br analogues (entries 6–8) and (2) contain the two ligands used most in subsequent discussions, PEt_3 and PPh_3. All the complexes of **1a** show *J*(Pt,H-11) values of ca. 12–19 Hz, with no marked correlation to either the size or donor capacity of L. Note that ^3J(Pt,H-2), the coupling to the proton adjacent to the quinoline nitrogen, varies from 17.6 to 35.0 Hz in accordance with the trans influence of L.[11] The π-allyl complexes (entry 9) are especially interesting with respect to δ(H-11), and we shall return to these in the next section.

Complexes of 8-methylquinoline (**4**) show Pt coupling to the CH_3 protons in the range 11.2–12.7 Hz. Again, proton H-2 shows substantial changes in *J*(Pt,H-2) as a function of the ligand L, whereas the CH_3 coupling to Pt is relatively unaffected by the changes in the coordination sphere (compare entry 13 with entries 10–12).

Table II contains NMR data for three new nitrogen ligands. The benzoquinoline ligand **5** shows Pt coupling to H-10, ca. 14–16 Hz, in the range we have come to expect. This is, after all, another quinoline type, and since we know that our weak interaction is independent of the hybridization at carbon,[7] it is logical that we find a coupling to platinum. Ligand **6**, prepared from α-tetralone and cyclohexylamine, has two bulky components, the cyclohexyl ring and the aromatic moiety, and shows a relatively large coupling to H-1 of ca. 20 Hz. We assume this increase is associated with a somewhat more fixed position of the C–H-1 vector due to hindrance to rotation about the Pt–N bond. Changing the substituent on nitrogen to a benzyl derivative, i.e., smaller than cyclohexyl, results in a reduced, but nevertheless "normal" coupling of Pt to H-1, confirming that the substituent on nitrogen assists in the tuning of this interaction. It is well-known that the plane defined by the H—C=N fragment of sp² nitrogen ligands is twisted away[12] from the coordination plane of Pt(II) and that for bulky pyridine[13] and nitrogen ligands this twist angle is close to 90°. For the benzoquinoline complex[14] [Pd{2-((dimethylamino)methyl)phenyl-*N*}(**5**)(H_2O)]ClO_4, ligand **5** is roughly perpendicular to the coordination plane with the C–H-10 vector facing the metal at a distance of 2.09 (6) Å.

Table II. NMR Data[a] for Complexes of **5–7**

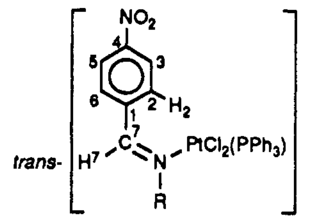
trans-$PtCl_2$(**5**)L	δ(H-10)	*J*(Pt,H-10)	δ(H-2)	*J*(Pt,H-2)	δ(P)	*J*(Pt,P)
L = PEt_3[b]	12.04	14.1	9.64	18.5	0.7	3554
L = PPh_3[c]	12.06	16.2	9.75	17.6	1.8	3813
L = $PTol_3$[d]	12.18	16.1	9.76	16.4	−0.4	3786
5	9.29		8.97			

$PtCl_2$(**6**)L	δ(H-1)	*J*(Pt,H-1)	δ(NCH)	δ(P)	*J*(Pt,P)
L = PEt_3[e]	9.18	21.1	4.11	−4.6	3458
L = PPh_3[f]	9.24	19.0	4.10	1.3	3670
6	8.42		3.70		

$PtCl_2$(**7**)L	δ(H-6)	*J*(Pt,H-6)	δ(H-7)	*J*(Pt,H-7)	δ(P)	*J*(Pt,P)
L = PEt_3[g]	8.53	6	9.05	57	−3.7	3461
L = PPh_3[h]	8.58	5	9.10	64	2.0	3679
7	7.96		8.64			

[a] $CDCl_3$ solutions, δ in ppm, *J* in Hz. [b] δ(C-10) = 127.7, Δδ = 3.4, *J*(Pt,C) = 42; δ(C-2) = 151.6, Δδ = 2.8. [c] CD_2Cl_2. [d] δ(C-10) = 127.8, Δδ = 3.5, *J*(Pt,C) = 41; δ(C-2) = 152.1, Δδ = 3.3. [e] δ(C-1) = 129.8, Δδ = 3.5, *J*(Pt,C) = 66; δ(N*C*H) = 65.6, Δδ = 7.0. [f] δ(C-1) = 129.7, Δδ = 3.4, *J*(Pt,C) = 63; δ(N*C*H) = 65.7, Δδ = 7.1. [g] δ(C-6) = 130.1, Δδ = 2.9, *J*(Pt,C) = 40; δ(C-7) = 167.0, Δδ = 13.3; δ(arom CH_3) = 19.5, Δδ = 0.2; δ(*C*Me_3) = 65.2, Δδ = 7.7, δ(Bu^tCH_3) = 31.9. [h] δ(C-7) = 168.0, Δδ = 14.3, δ(arom CH_3) = 19.7, Δδ = 0.4; δ(*C*Me_3) = 65.5, Δδ = 8.0; δ(Bu^tCH_3) = 32.1, Δδ = 2.3.

Before we start the discussion for **7**, it should be noted that no *J*(Pt,H-2) value was found in complexes **9**,[15] and we believe this to result from relatively free rotation about the C-1–C-7 bond. Given these data and our previous study on **3**,[10] we prepared complexes of **7** containing a 2-CH_3 group in the hope of inducing a conformation in which the C–(H-6) vector spent more time facing the platinum. These molecules (Table II) now reveal a modest *J*(Pt,H-6) value of ca. 5–6 Hz, suggesting that it is indeed possible to tune our weak interaction via the proper choice of the



9, R = Bu^t, CH_2Bu^t, *p*-$CH_3OC_6H_4$, *p*-$Me_2NC_6H_4$

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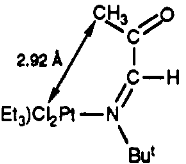
interacting fragment. The Schiff base complex **10**[16] is interesting in that it reveals a 6-Hz coupling from Pt to the acyl CH_3 protons and contains an (average) Pt–H (acyl CH_3) separation[16] of 2.92 Å. In **11** there is no reported Pt coupling to the hydrazone imine proton H-2; however, it has also been located at ca. 2.9 Å from the metal.[17]



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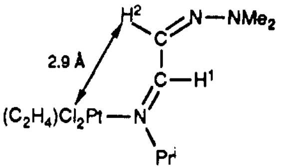

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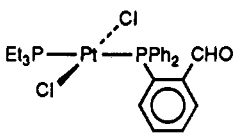
Although we do not emphasize our ^{13}C data, it is worth noting that relatively large J(Pt,C) values are observed for the carbon bearing the proton under discussion: 22–34 Hz for the complexes in **1a** and **4**, ca. 41 Hz for complexes of **5**, and 63 and 66 Hz for molecules with ligand **6** (where we also find the largest J(Pt,H) values), but no coupling to carbon for the complexes of **7** where J(Pt,H-6) is only 5–6 Hz. Consequently, the Pt–C coupling constants qualitatively follow the Pt–H values.

The complex *trans*-$PtCl_2$(**8**)(PEt_3) (**12**) did not show a platinum coupling to the aldehyde proton, presumably due to Pt–P and/or P–C rotation; however, we cannot exclude either electronic reasons for this absence, i.e., lengthening of the Pt–P distance due to the trans influence of the PEt_3, or simple steric considerations. Having taken the Schiff base ligands **9**, which showed no Pt←H–C coupling, and modified them so as to be able to observe this interaction, we note that on going from the complexes *trans*-$PtCl_2$(**2**)L[9] to *trans*-$PtCl(SnCl_3)$(**2**)L[18] via reaction with $SnCl_2$ we reverse matters and no longer observe a J(Pt,H-7) coupling. We do not know which factors are responsible for this change.



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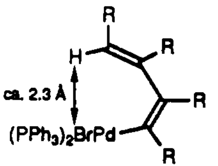
δ(CHO) = 10.72; $\Delta\delta$ = 0.23

δ(P) = 15.7, 13.7 J(Pt,P) = 2442 Hz, J(Pt,P) = 2547 Hz, J(P,P) = 475 Hz

We also give J(Pt,P) values in the tables, since these allow us to compare the nitrogen ligands **1a** and **4**–**7** against each other; e.g., for L = PEt_3 the values fall in the range 3458–3571 Hz, suggesting no major differences in donor capacity for these nitrogen ligands.

Chemical Shifts. It would be valuable to develop an empiricism similar to that for J(Pt,H), but based on chemical shifts, as this would allow us to readily extrapolate to a wider variety of metal complexes.

Inspection of Tables I and II reveals that the ^1H-coordination chemical shifts, $\Delta\delta$, for many of our complexes are surprisingly large, e.g., >2.75 ppm downfield for the complexes of **5**. Before considering the significance of such a change, it is useful to remember that many others have made similar observations. Maitlis and co-workers[18] found a low-field shift for the vinyl proton of **13**. Indeed, this signal appears as a triplet due to ^{31}P coupling, suggesting some form of bonding. Vrieze and co-workers[19] report low-field shifts of ca. 1.2 ppm for the ortho protons of **14**. For complex **11**, $\Delta\delta$ is ca. 0.9 ppm, and van der Poel et al.[20,21] find ca. 2 ppm low-field shifts for H^2 in complexes such as **15**. In addition, there are a number of complexes for which there are informative NMR studies,[22] described in a fine series of papers by Deeming and co-workers,[14,23-25] from which we show only three examples,[23] **16**–**18** (see Chart I), all containing (8-methyl-2-quinolylmethyl)di-*tert*-butylphosphine (mqp). In **16**, mqp coordinates as a monodentate phosphine ligand, thus bringing H-3 into position for a possible interaction, and we note that $\Delta\delta$(H-3) = 1.16. The CH_3 group in **16** is remote from the metal. In **17**, for which there is a crystal structure, mqp functions as an N,P chelate, thereby forcing the CH_3 close to the metal (a halogen is forced out of the coordination plane by ca. 0.6 Å), thereby increasing $\Delta\delta$ to 1.12. Complex **18**, which is a dinuclear compound and contains both four- and five-coordinate rhodium (we show only the latter) has the CH_3 in a pseudoaxial position, with $\Delta\delta$(CH_3) = 0.59 and J(P,H) and J(Rh,H) ≅2.7 Hz. However, not all potential Pt←H–C interactions are accompanied by relatively large $\Delta\delta$ values. Complex **19**, in which the C–H-7 vector faces the metal,[9] shows J(Pt,H) = 11.2 Hz but a modest $\Delta\delta$ of 0.30.



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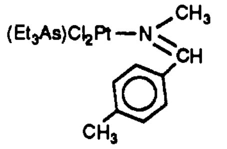

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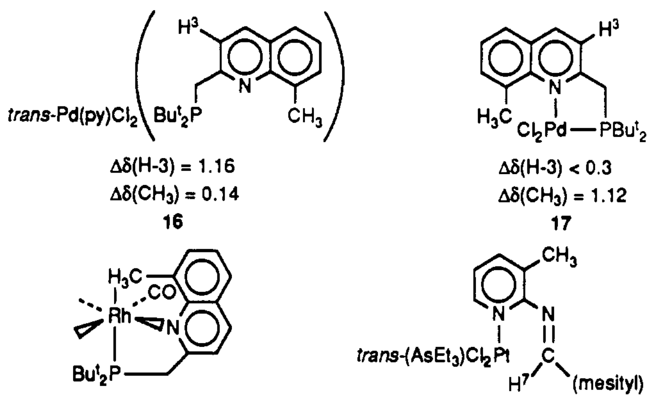
Chart I

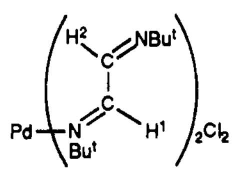


$\Delta\delta$(H-3) = 1.16
$\Delta\delta$(CH_3) = 0.14
16

$\Delta\delta$(H-3) < 0.3
$\Delta\delta$(CH_3) = 1.12
17

$\Delta\delta$(CH_3) = 0.59
$(CO)_2Rh(\mu\text{-}Cl)_2Rh(CO)(mqp)$ = **18**

$\Delta\delta$(H-7) = 0.30
19



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δ(H-1) = 7.60
δ(H-2) = 9.91

The presence of J(P,H) values in **13** and **18** and J(Rh,H) in **18** supports bonding from the appropriate group to the metal; however, the significance of $\Delta\delta$ is unclear. There are at least three major contributors to δ in these molecules: (1) direct bonding, i.e., M←H–C; (2) local anisotropic effects; (3) polarization via the π-system. Point 3, as illustrated by **20**, is unlikely to be a major effect since other protons, e.g., those in para position to a pyridine

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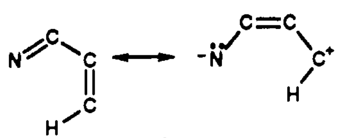
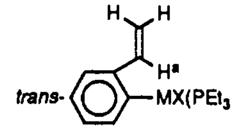


20

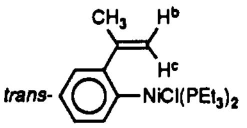
or quinoline nitrogen, do not experience very marked downfield shifts; however, anisotropic effects, associated with electrons in metal orbitals, may be considerable. Anisotropy arising from Pt–Cl bonds and/or a cis-ligand effect in general is not likely to be important since replacement of Cl by Br has little effect (see Table I) and other complexes, e.g., **13**, **18**, or **21**, having tertiary phosphines or CO ligands in the cis positions show similar deshielding. Miller et al.[26] have estimated screening anisotropies for a series of Ni(II) and Pd(II) complexes of the type *trans*-MX(2-vinylphenyl)$(PEt_3)_2$ (**21**) and *trans*-MX(2-allylphenyl)$(PEt_3)_2$ and found that protons in close proximity to the metal in a pseudoaxial position exhibit low-field shifts. Indeed, for **22**, Δδ at 3.31 is exceptional. Since protons occupying pseudoaxial positions clearly will be subject to an anisotropic environment, a clear separation of points 1 and 2 is not readily achieved. Given this difficulty, the π-allyl complexes **23** (entry 9 Table I) provide a useful contrast to complexes **1**–**5**. These isomers arise from the possible orientation of the allyl CH_3 with respect to the CHO function. In both compounds, the aldehyde proton coupling to Pt is in the expected range, *J*(Pt,H-11) = 19 and 14 Hz for **23a** and **23b**, respectively. We attribute this difference in *J* to steric effects since known[27-29] structures of allyl complexes show the 2-allyl substituent bent toward the metal, thereby bringing the CH_3 closer to a pseudoaxial position and presumably interfering with the Pt←H—C=O interaction. Despite the relatively normal Pt couplings, the Δδ values, 0.82 and 0.50 ppm, respectively, are 0.8–1.5 ppm smaller than those for entries 1–5. The markedly different electronic structure for **23**, relative to the other complexes of **1a** leads to a reduced anisotropic contribution to the shielding of H-11; note that δ(H-2) for **23b** is quite normal.



M = Ni, Pd

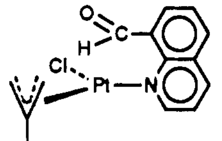
$\Delta\delta(H^a) = 0.96–1.41$

21

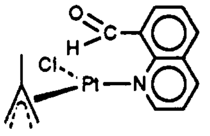


$\Delta\delta(H^c) = 3.31$

22



23a



23b

In summation: assuming the molecule is not subject to nonrelated anisotropic shielding effects (benzene ring currents, lone-pair effects, ...), a substantial low field shift strongly suggests that a C–H bond is correctly positioned; however, the absence of a >1 ppm shift to low field does not rule out a weak M←H–C interaction. Further, a substantial low-field shift, 0.9 ppm in **11**[17] or 0.8–1.2 ppm in **9**,[15] does not guarantee the observation of the *J*(Pt,H) coupling, which we believe is a more reliable indicator. Put slightly differently, the distance and rigidity criteria are more important in determining weak M←H–C interactions than the coincidental placement of the proton in a strongly anisotropic environment.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $PtCl_2$(benzoquinoline)(PEt_3)

Pt–Cl(1)	2.303 (1)	C(4)–C(11)	1.440 (8)
Pt–Cl(2)	2.297 (1)	C(5)–C(11)	1.429 (8)
Pt–P(1)	2.226 (1)	C(5)–C(6)	1.322 (9)
Pt–N	2.142 (4)	C(6)–C(12)	1.412 (8)
Pt–H(10)	2.53 (8)	C(7)–C(12)	1.402 (8)
Pt–C(10)	3.189 (7)	C(7)–C(8)	1.349 (10)
P(1)–C(15)	1.813 (5)	C(8)–C(9)	1.412 (9)
P(1)–C(17)	1.829 (5)	C(9)–C(10)	1.354 (7)
P(1)–C(19)	1.829 (5)	C(10)–C(13)	1.397 (7)
N–C(2)	1.335 (6)	C(11)–C(14)	1.416 (6)
N–C(14)	1.364 (6)	C(12)–C(13)	1.421 (7)
C(2)–C(3)	1.389 (7)	C(13)–C(14)	1.450 (7)
C(3)–C(4)	1.298 (8)	C(10)–H(10)	0.84 (7)
N–Pt–P(1)	175.86 (9)	Pt–N–C(2)	109.15 (31)
Cl(1)–Pt–Cl(2)	172.59 (5)	Pt–N–Cl(14)	130.07 (30)
Cl(1)–Pt–P(1)	94.75 (4)	N–C(14)–C(13)	121.88 (39)
Cl(1)–Pt–N	88.74 (10)	C(10)–C(13)–C(14)	124.47 (43)
Cl(2)–Pt–N	86.86 (10)	C(4)–C(12)–C(7)	121.05 (48)
Cl(2)–Pt–P(1)	89.43 (5)	C(6)–C(12)–C(7)	121.25 (54)

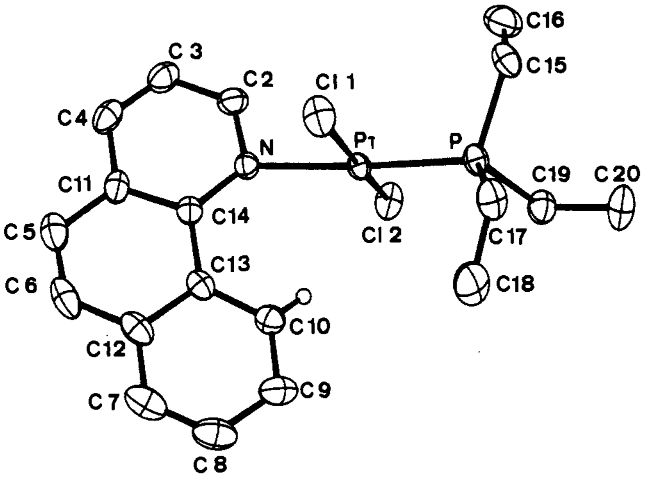


Figure 1. ORTEP view of *trans*-$PtCl_2(5)(PEt_3)$.

Molecular Structure of *trans*-$PtCl_2(5)(PEt_3)$. We have shown[8,9] that complexed **1a** and **2** have molecular structures with the appropriate C–H vector directed toward the platinum and that such Pt–H separations are ca. 2.4 Å. Consequently, the estimation by Deeming et al.[14] of a 2.09-Å separation for the Pt–H-10 distance in [Pd{2-((dimethylamino)methyl)phenyl-*N*}(**5**)$(H_2O)]ClO_4$ was somewhat difficult to rationalize. Our coupling constant data for complexes of **5** (see Table II) are not sufficiently different from those for complexes of **1**, **2**, and **4** to warrant a ca. 0.3-Å change so that we have determined the molecular structure of *trans*-$PtCl_2(5)(PEt_3)$, a **5** analogue of our previous crystallographic efforts. Table III contains selected bond distances and bond angles, and Figure 1 shows an ORTEP plot of the molecule.

The molecular structure reveals a distorted-square-planar geometry with trans disposition of the two halogens. The halogen and nitrogen atoms lie below the least-squares coordination plane defined by the Pt and the four ligand atoms (N, 0.06 Å; Cl(1), 0.11 Å; Cl(2), 0.13 Å). The Pt–Cl separations are normal.[30-32] The Pt–P separation, 2.226 (1) Å, is on the short side,[32-35] and the Pt–N separation, 2.142 (4) Å, is toward the higher end,[8,30,35]

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in keeping with the respective strong and weak structural trans influences[8,9,30-35] for the latter two ligands. The coordination angles within the square plane are not unusual.

As expected the C-10 position of the benzoquinoline occupies a pseudoaxial position above the coordination plane. The Pt–C(10) separation, 3.189 (7) Å, and the Pt–H(10) separation, ca. 2.53 (8) Å, are within the range expected on the basis of both the NMR and our earlier X-ray work.[36] It seems likely that the observed differences in M–H separations between these two benzoquinoline structures are partly related to the ligand trans to the benzoquinoline nitrogen and the consequent change in M–N bond separation: 2.06 (1) Å in the palladium complex (N trans to N) and 2.142 (1) Å in our molecule (N trans to P). A longer M–N separation naturally results in some withdrawal of the attached hydrocarbon. Further, the position of the N atom below the coordination plane leads to markedly different Pt–N–C(2), 109.1 (3)°, and Pt–N–C(14), 130.8 (3)°, angles, thereby indicating that C-10 is somewhat removed from its position above the coordination plane. Our difference here of 21.8° is larger than the 10° difference reported by Deeming et al.[14] for identical angles, again consistent with a larger Pt–C(10) distance in our complex. Although we can now rationalize our NMR data in terms of the crystallography, the fact that H-10 can indeed approach to ca. 2.09 Å has implications for us in terms of future NMR measurements on related platinum complexes. For our current structure there are some few additional facts worth noting:

1. The torsion angles Cl(1)–Pt–N–C(2), -82.0°, and Cl(1)–Pt–N–C(14), 113.8°, as well as the pair Cl(2)–Pt–N–C(2), 92.0°, and Cl(2)–Pt–N–C(14), -72.3°, are consistent with the benzoquinoline rings making an angle of ca. 82° with respect to the coordination plane.

2. The C(14)–C(13) separation is relatively large, 1.450 (7) Å, and the C(5)–C(6) distance relatively short, 1.322 (9) Å, suggesting localized single and double bonds for the middle ring.

Comment

The number of different ligands and complexes showing detectable weak Pt←H–C interactions, via *J*(Pt,H), is now sufficiently numerous as to be convincing. In all cases where crystallographic support is available, the C–H vector faces toward the metal, with Pt–H separations often in the range 2.3–2.9 Å (the 2.09-Å value is the lone exception). These complexes do not resemble the "agostic" type of bond described by Green and Brookhart[2] in that their NMR and X-ray properties are quite different; however, the difference is likely to be one of degree as opposed to type.

Experimental Section

^{1}H, ^{13}C, and ^{31}P NMR spectra were measured by using 90-, 200-, and 250-MHz NMR spectrometers as CDCl$_3$ solutions unless otherwise noted. Due to relative short T_1 ^{195}Pt values at higher B_0 fields, the best quality ^{1}H spectra for signals with ^{195}Pt coupling were obtained at lower magnetic field.[7] In general, ^{1}H spectra were readily interpreted; however, in some few cases 2-D COSY and ^{13}C–H correlations were sufficient to unambiguously assign the spectra.

The ligands were either commercially available or prepared as described in the literature.[37]

Preparation of 6. Three milliliters of α-tetralone (0.018 mol) and 2.2 mL of cyclohexylamine (0.018 mol) were dissolved in 50 mL of benzene and stirred for 1 h. Addition of 0.3 g *p*-toluenesulfonic acid was followed by refluxing using a Dean–Stark trap until 0.35 mL of water was collected (ca. 4 days). Removal of solvent followed by vacuum distillation (110 °C, 0.01 Torr) afforded the product as an oil, which slowly solidifies: yield 3 g (71%); mp = 42 °C. IR: 1623 cm^{-1} (CHCl$_3$ solution), ν(C=N).

Table IV. Experimental Data for the X-ray Diffraction Study of *trans*-PtCl$_2$(benzoquinoline)(PEt$_3$)

chem formula	C$_{19}$H$_{24}$Cl$_2$NPPt	*Z*	2
mol wt	563.37	*V*, Å^3	1012.6 (7)
space group	$P\bar{1}$ (No. 2)	ρ(calcd), g cm^{-3}	1.848
a, Å	7.8216 (8)	μ, cm^{-1}	73.457
b, Å	7.8607 (6)	*T*, °C	23
c, Å	17.0376 (13)	λ, Å	0.71069[a]
α, deg	94.30 (1)	transm coeff	0.6880–0.9963
β, deg	98.50 (2)	$R(F_o)$	0.025
γ, deg	100.63 (1)	$R_w(F_o)$	0.042

[a] Graphite-monochromated Mo K$\bar{\alpha}$ radiation.

Table V. Final Positional and Equivalent Thermal factors for *trans*-PtCl$_2$(**5**)(PEt$_3$) (B_{iso} for the H Atom)

atom	*x/a*	*y/b*	*z/c*	B_{eq},[a] Å^2
Pt(1)	0.16265 (2)	0.44549 (2)	0.29586 (1)	2.693 (4)
Cl(1)	0.3584 (2)	0.6663 (2)	0.3771 (1)	4.24 (3)
Cl(2)	−0.0604 (2)	0.2368 (2)	0.2229 (1)	4.98 (4)
P(1)	0.3043 (2)	0.2371 (2)	0.33418 (9)	3.26 (3)
N	0.0089 (6)	0.6325 (6)	0.2579 (3)	3.01 (9)
C(2)	−0.0939 (8)	0.6589 (8)	0.3118 (4)	4.0 (1)
C(3)	−0.2333 (8)	0.7454 (9)	0.2981 (4)	4.5 (1)
C(4)	−0.2725 (8)	0.7985 (8)	0.2286 (5)	4.5 (2)
C(5)	−0.211 (1)	0.8334 (9)	0.0904 (5)	4.9 (2)
C(6)	−0.111 (1)	0.8094 (9)	0.0361 (5)	5.3 (2)
C(7)	0.147 (1)	0.722 (1)	−0.0089 (5)	5.7 (2)
C(8)	0.296 (1)	0.657 (1)	0.0048 (5)	5.7 (2)
C(9)	0.3471 (9)	0.605 (1)	0.0808 (5)	5.0 (2)
C(10)	0.2463 (8)	0.6161 (8)	0.1383 (4)	3.8 (1)
C(11)	−0.1690 (8)	0.7746 (7)	0.1669 (4)	3.8 (1)
C(12)	0.041 (1)	0.7348 (8)	0.0498 (4)	4.3 (1)
C(13)	0.0884 (8)	0.6767 (7)	0.1255 (4)	3.3 (1)
C(14)	−0.0245 (7)	0.6911 (7)	0.1849 (4)	3.1 (1)
C(15)	0.5299 (9)	0.3107 (9)	0.3846 (4)	4.3 (1)
C(16)	0.630 (1)	0.170 (1)	0.4063 (5)	5.9 (2)
C(17)	0.315 (1)	0.0787 (8)	0.2517 (4)	4.7 (2)
C(18)	0.409 (1)	0.156 (1)	0.1888 (5)	6.5 (2)
C(19)	0.188 (1)	0.1075 (8)	0.4020 (4)	4.3 (1)
C(20)	0.175 (1)	0.209 (1)	0.4763 (5)	6.2 (2)
H(10)	0.28 (1)	0.61 (1)	0.187 (5)	7 (2)

[a] Values for anisotropically refined atoms are given in the form of the isotropic $B_{eq} = {}^1/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VI. Analytical Data PtCl$_2$(X)L Complexes

	anal., %	
L	calcd	found
	X = **1a**	
PEt$_3$	C, 35.56; H, 4.21; N, 2.64; Cl, 13.39	C, 35.49; H, 4.13; N, 2.59; Cl, 13.09
PPh$_3$	C, 48.63; H, 3.22; N, 2.02; Cl, 11.24	C, 48.84; H, 3.23; N, 2.14, Cl, 11.25
	X = **4**	
C$_2$H$_4$	C, 32.97; H, 3.00; N, 3.20; Cl, 16.22	C, 32.94; H, 3.08; N, 3.59; Cl, 16.21
PhCH=CH$_2$	C, 42.11; H, 3.31; N, 2.72	C, 42.17; H, 3.27; N, 2.79
	X = **5**	
PEt$_3$	C, 40.51; H, 4.29; N, 2.49	C, 40.40; H, 4.29; N, 2.56
	X = **6**	
PEt$_3$	C, 43.21; H, 5.89; N, 2.29	C, 43.13; H, 5.85; N, 2.10
	X = **7**	
PEt$_3$	C, 38.65; H, 5.73; N, 2.50; Cl, 12.68	C, 38.53; H, 5.67; N, 2.42; Cl, 12.64
	PtBr$_2$(**1a**)L	
PEt$_3$	C, 30.48; H, 3.49; N, 2.22	C, 30.56; H, 3.52; N, 2.15

Preparation of 7. The condensation of *o*-tolualdehyde (4.5 mL, 0.038 mol) and *tert*-butylamine (4.1 mL, 0.039 mol) was accomplished as for **6**, but without the *p*-toluenesulfonic acid. Vacuum distillation (45 °C, 0.05 Torr) gave 5.6 g (82%) of product as a yellow liquid. IR (CHCl$_3$): 1631 cm^{-1}, ν(C=N). The complexes were prepared as described previously,[8,9] with a typical example as follows.

Preparation of *trans*-PtCl$_2$(6)(PEt$_3$). [Pt(μ-Cl)Cl(PEt$_3$)]$_2$ (76.8 mg, 0.10 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$ and then treated with **6**

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(36) A reviewer has suggested that we place the H(10) at 1.08 Å from C(10). We have done this and find that Pt–H(10) is now reduced to ca. 2.30 Å and Pt–C(10) is now 3.189 (7) Å. Both distances are consistent with our discussion; indeed a separation of 2.30 Å tends to strengthen our arguments.

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Inorg. Chem. **1990**, *29*, 1817–1822

(45.4 mg, 0.20 mmol). Stirring for 0.5 h was followed by concentration to ca. 2 mL and then addition of petroleum ether. The yellow powder that precipitated was collected and recrystallized from $CHCl_3/CH_3OH$ (115 mg, 95%). Microanalytical data for the complexes are shown in Table VI.

Preparation of *trans*-$PtCl_2$(4)(C_2H_4). [Pt(μ-Cl)Cl(C_2H_4)]$_2$ (59 mg, 0.10 mmol) was suspended in 10 mL of CH_2Cl_2 and then treated with **4** (27 μL, 29 mg, 0.20 mmol). Stirring at room temperature was followed by concentration to ca. 2 mL. Addition of petroleum ether induced precipitation of the product, which was recrystallized from CH_2Cl_2/hexane to afford 83 mg (94%) of pure complex.

Crystallography. White air-stable crystals of *trans*-$PtCl_2$(**5**)(PEt_3) suitable for X-ray diffraction were obtained via recrystallization from CH_2Cl_2/hexane. A crystal of prismatic habit was mounted on a glass fiber at a random orientation. The determination of lattice parameters and space group and the data collection were carried out on a Enraf-Nonius CAD4 diffractometer. Cell constants were obtained by a least-squares fit of the 2θ values of 25 high-angle reflections using the CAD4 centering routines. Crystallographic and data collection parameters are listed in Table IV and in Table S1. Data were collected at variable scan speed to obtain constant statistical precision on the recorded intensities.

Three standard reflections ($1\bar{4}\bar{3}$, $03\bar{4}$, $\bar{1}43$) were measured every hour to monitor the stability of the crystal, while the orientation was checked every 300 reflections by measuring three standards (344, $03\bar{6}$, $\bar{3}\bar{4}4$). No significant variations were detected. Data were corrected for Lorentz and polarization factors[38] and an empirical absorption correction was applied using azimuthal (Ψ) scans of three reflections at high χ angles ($85.4 \leq \chi \leq 87.2°$) by using the SDP crystallographic programs.[39] The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o were calculated according to the formula $\sigma(F_o) = [\sigma^2(F_o^2) + f^2(F_o^2)]^{1/2}/2F_o$ with $f = 0.040$. An $F_o = 0.0$ value was given to those reflections having negative net intensities. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques. The function minimized was $\sum w(|F_o| - (1/k)|F_c|)^2$ with $w = [\sigma^2(F_o)]^{-1}$. Anisotropic thermal parameters were used for all atoms. Although peaks (ca. 0.7–0.8 e/Å^3) could be found in the final Fourier difference map corresponding to most of the hydrogen atoms, only their contribution in calculated positions (C–H = 0.95 Å, B_{iso} = 5.0 Å^2) was taken into account but not refined with the exception of the structurally significative H(10), which was located and refined. Final coordinates and equivalent thermal factors are given in Table V. Scattering factors were taken from the literature,[40] and the contribution of the real and imaginary part of the anomalous dispersion was taken into account.[38] No extinction correction was deemed necessary. All calculations were carried out by using the SDP crystallographic package.

Acknowledgment. A.A. thanks MPI and P.S.P. thanks the ETH Zürich and the Swiss National Science Foundation for support and the Johnson Matthey Research Centre, England, for the loan of platinum metals.

Supplementary Material Available: Tables of X-ray experimental data, hydrogen coordinates, anisotropic thermal factors, and extended bond lengths and angles (8 pages); a table of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

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Contribution from the Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (URA 33), Faculté des Sciences, Université de Bourgogne, 6 bd Gabriel, 21000 Dijon, France, and Laboratoire de Chimie des Métaux de Transition associé au CNRS (UA 419), Université P. et M. Curie, 75252 Paris Cédex 05, France

[1]Ferrocenophanes Containing a Group 4 Transition Metal in the Bridge. X-ray Structure of One Representative

Roland Broussier,[1a] Anne Da Rold,[1a] Bernard Gautheron,*[,1a] Yves Dromzee,[1b] and Yves Jeannin[1b]

Received May 31, 1989

New [1]ferrocenophanes (RC_5H_4)$_2$ML_2 (**1**) (R = H, *t*-Bu; L_2 = (C_5H_4)$_2$Fe; M = Ti, Zr, Hf) containing a transition metal in the "phane" bridge have been obtained when the 1,1′-dilithioferrocene–TMEDA complex was reacted with metallocene dichloride at room temperature. Compounds **1** exposed to air led to μ-oxo complexes [(C_5H_5)$_2$ML′]$_2$O (L′ = (C_5H_5)(C_5H_4)Fe). Spectroscopically speaking, the ferrocene part of the molecules is the most affected by structural strains and by the bridging metal electronegativity. The molecular structure of [(H_3C)$_3$CC_5H_4]$_2$Zr(C_5H_4)$_2$Fe has been determined by a single-crystal X-ray diffraction study. The crystal was found to be monoclinic, *C*2/*c*, with *a* = 18.715 (2) Å, *b* = 9.691 (1) Å, *c* = 14.923 (2) Å, β = 122.47 (1)°, *V* = 2283 (1) Å^3, and *Z* = 4. The structure was refined to *R* = 0.026 and R_w = 0.029 with use of 2685 unique reflections with $I \geqslant 3\sigma(I)$ recorded at room temperature. The Zr–Fe distance equal to 2.9621 (5) Å might suggest the occurrence of a weak dative bond between electron-rich and electron-poor metal centers.

Introduction

Many papers dealing with [*n*]ferrocenophanes emphasize the potential ability of the bridging chain to induce steric and electronic perturbations at the iron atom.[2-5] If *n* is small, these effects can result from the bulkiness of the cyclopentadienyl ligands, while greater *n* values allow direct interactions between the iron atom and part of the flexible bridging chain. With the hope of finding both effects in the same molecule, we have now prepared ferrocenophanes incorporating a group 4 transition metal in a short bridge. These new molecules contain one electron-rich and one electron-poor metallic center capable of synergistic interactions. We now report the synthesis and spectroscopic properties of some metalla[1]ferrocenophanes (M = Ti, Zr, Hf), together with the X-ray structure of a representative example, (*t*-BuC_5H_4)$_2$ZrL_2 (L_2 = (C_5H_4)$_2$Fe).

Experimental Section

Materials and Instrumentation. All reactions were conducted under an argon atmosphere with Schlenk tube techniques. Solvents were dried and deoxygenated over sodium/benzophenone ketyl and distilled just before use (transfers were carried out via syringes or cannulas). Melting

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