Reversible Formation of η^1- and η^0-Cyclopentadienyl Complexes by Treatment of $[M(C_6H_4N{=}NC_6H_4R)(\eta^5\text{-}C_5H_5)]$ (M = Pd, Pt) with Tertiary Phosphines

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Reactions of [2-(arylazo)phenyl](η^5-cyclopentadienyl)palladium compounds with PEt_3 or P-*n*-Bu_3 in $CDCl_3$ or CD_2Cl_2 solution follow two independent, competing pathways. One route reversibly produces first $[Pd(C_6H_4N{=}NC_6H_4R)(\eta^5\text{-}C_5H_5)(PR'_3)]$ (**2**) and then *trans*-$[Pd(C_6H_4N{=}NC_6H_4R)(\eta^1\text{-}C_5H_5)(PR'_3)_2]$ (**3**). The other route, which is favored by lower temperatures and excess PR'_3, leads instead to the ionic cyclopentadienyl compound $[Pd(C_6H_4N{=}NC_6H_4R)(PR'_3)_3]^+C_5H_5^-$. At temperatures above −40 °C, both the η^1- and η^0-cyclopentadienyl complexes undergo H–D exchange with $CDCl_3$, deuteriating the Cp rings. At higher temperatures, further irreversible reactions with the chlorinated solvents produce *trans*-$[Pd(C_6H_4N{=}NC_6H_4R)Cl(PR'_3)_2]$. Although the platinum complex $[Pt(C_6H_4N{=}NC_6H_5)(\eta^5\text{-}C_5H_5)]$ reacts in a broadly similar way, $[Pt(C_6H_4N{=}NC_6H_5)(\eta^5\text{-}C_5H_5)(PR'_3)]$ could not be detected in any reaction sequences. The mechanisms involved in the H–D exchange reactions are discussed, and complete assignments of the ^1H and $^{13}C\{^1H\}$ NMR spectra of the (arylazo)phenyl compounds have been made.

Introduction

Many cyclopentadienyl complexes of palladium and platinum have been described. Complexes containing η^5-cyclopentadienyl are usually 18-electron molecules, and many have been structurally characterized,[1] whereas η^1-cyclopentadienyl complexes tend to be more reactive and fewer have been reported. Even so, a few structural determinations have been made.[1b,2] In common with η^1-cyclopentadienyl compounds of other elements, all appear to be fluxional, and low-energy barriers to ring rotation lead to deceptively simple ^1H and ^{13}C NMR spectra, often even at low temperatures. Many of the η^1-cyclopentadienyl compounds of palladium and platinum are 16-electron compounds, with approximately square-planar geometry.

The cyclopentadienyl complexes of palladium and platinum undergo a variety of reaction types, sometimes to produce quite complicated products, and not all are understood. Although examples are still not common, conversions between η^5- and η^1-bonding modes are probably the best understood reactions. They are usually promoted by ligand addition or ligand loss,[2b,3,4] although counterbalancing structure changes in other[5] or equivalent[1b] ligands at the same metal can produce the same result. Another reaction pathway is the transfer or exchange of cyclopentadienyl groups (usually η^1-bonded) between metal atoms.[4]

Other reactions of palladium or platinum cyclopentadienyls include eliminations to produce metal–metal bonded compounds[6,7] (though the organic byproducts are usually unidentified) and coupling of C_5H_5, either with itself to form coordinated $C_{10}H_{10}$ groups[1d,6] or with other unsaturated ligands.[8-10] 1,2-Proton shifts around the C_5 ring, resulting in η^1-vinylic bonded C_5H_5 moieties, represents yet another reaction of η^1-cyclopentadienyls of platinum.[6]

A few years ago we reported the reactions of tertiary phosphines with $[Pd(C_6H_4N{=}NC_6H_5)(\eta^5\text{-}C_5H_5)]$ (**1a**).[11] Reversible displacement of the coordinated nitrogen by PR'_3 was observed in several solvents. Subsequent reactions were very dependent on the nature of the phosphine and the solvent and included hydrogen–deuterium exchange between the cyclopentadienyl hydrogens and some deuteriated solvents (CD_3CN, $(CD_3)_2CO$, $CDCl_3$, and CD_2Cl_2) and formation of certain zerovalent palladium complexes. We detected the operation of at least two separate reaction paths and suggested the involvement of $C_5H_5^-$ ions in some of the H–D exchange reactions. We now report a detailed NMR study of the reactions of $[M(C_6H_4N{=}NC_6H_4R)(\eta^5\text{-}C_5H_5)]$ (M = Pd, Pt) with PEt_3 and P-*n*-Bu_3 in $CDCl_3$ or CD_2Cl_2 solution. A preliminary note has appeared.[12]

Results and Discussion

At temperatures above −50 °C, **1a** reacts readily with PEt_3 in $CDCl_3$ or CD_2Cl_2 solution to form $[Pd(C_6H_4N{=}NC_6H_5)(\eta^5\text{-}C_5H_5)(PEt_3)]$ (**2a**) in near quantitative yield. The reaction is accompanied by a dramatic color change from deep blue-black to orange-brown. **1a** reacts similarly with P-*n*-Bu_3 to give $[Pd(C_6H_4N{=}NC_6H_5)(\eta^5\text{-}C_5H_5)(P\text{-}n\text{-}$

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Table I. ^1H and $^{13}C\{^1H\}$ NMR Data (δ) for Complexes of the Type 1 at 20 °C

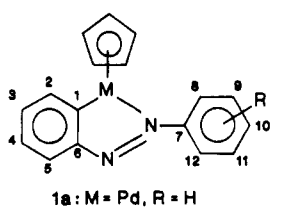
	1a[e]		1c[f]		1d[f]		1f[a,e]
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^{13}C
C_5H_5	5.88	96.60	5.76	96.55	5.89	96.91	91.43 (J_{PtC} = 23.8 Hz)
1		179.37		181.04		179.98	165.28 (J_{PtC} = 1349 Hz)
2	7.94 (dd)[b]	140.75	7.92 (dd)[c]	141.09	7.90 (dd)[d]	141.06	137.39 (J_{PtC} = 104 Hz)
3	6.96 (ddd)[b]	125.69	6.96 (ddd)[c]	125.96	6.92 (ddd)[d]	125.79	125.17 (J_{PtC} = 58.8 Hz)
4	7.22 (ddd)[b]	124.30	7.20 (ddd)[c]	124.23	7.19 (ddd)[d]	124.48	123.02
5	8.28 (dd)[b]	131.51	8.23 (dd)[c]	131.59	8.23 (dd)[d]	131.36 or 131.50	129.09 (J_{PtC} = ca. 12 Hz)
6		161.85		162.02		162.14	161.00 (J_{PtC} = 98.3 Hz)
7		154.53		156.69		154.73	156.70 (J_{PtC} = 106 Hz)
8	7.88 (m)	123.42		129.95	7.66–7.73 (m)	123.94	124.47
9	7.44 (m)	128.66	7.26–7.34 (m)	128.69		139.22	128.49
10	7.42 (t)	130.11	7.26–7.34 (m)	131.08	7.23–7.39 (m)	131.36 or 131.50	128.94
11			7.26–7.34 (m)	126.40	7.23–7.39 (m)	128.82	
12			7.41–7.46 (m)	124.79	7.66–7.73 (m)	121.32	
CH_3			2.32	18.46	2.47	21.47	

[a] $\delta(C_5H_5)$ 5.85 (J_{PtH} = 17.7 Hz). [b] $J_{H_2H_3} = J_{H_4H_5}$ = 7.8 Hz, $J_{H_3H_4}$ = 7.2 Hz, $J_{H_2H_4} = J_{H_3H_5}$ = 1.2 Hz. [c] $J_{H_2H_3} = J_{H_4H_5}$ = 8.1 Hz, $J_{H_3H_4}$ = 7.2 Hz, $J_{H_2H_4}$ = 1.0 Hz, $J_{H_3H_5}$ = 1.6 Hz. [d] $J_{H_2H_3} = J_{H_4H_5}$ = 7.8 Hz, $J_{H_3H_4}$ = 7.2 Hz, $J_{H_2H_4}$ = 1.5 Hz, $J_{H_3H_5}$ = 1.1 Hz. [e] In $CDCl_3$. [f] In CD_2Cl_2.

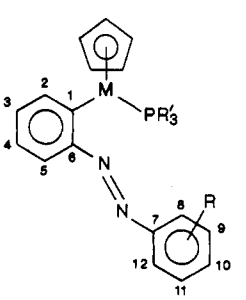
Table II. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR Data (δ) for Complexes of the Type 2

	2a	2b	2c	2d
solv	$CDCl_3$	$CDCl_3$	CD_2Cl_2	$CDCl_3$
temp, °C	20	−60	20	20
^1H				
C_5H_5	5.70 (*d*, J_{PH} = 1.6 Hz)	5.70 (*d*, J_{PH} = 1.3 Hz)	5.70 (*d*, J_{PH} = 1.1 Hz)	5.69 (*d*, J_{PH} = 1.5 Hz)
CH_3			2.77	2.47
^{13}C				
C_5H_5	95.77 (*d*, J_{PC} = 3.8 Hz)		96.08 (J_{PC} unresolved)	95.78 (J_{PC} unresolved)
C_1	147.71 (*d*, J_{PC} = 15.0 Hz)		148.38 (*d*, J_{PC} = 15.1 Hz)	147.73 (*d*, J_{PC} = 15.0 Hz)
C_2	142.46 (*d*, J_{PC} = 5.0 Hz)		142.93 (*d*, J_{PC} = 5.1 Hz)	142.45 (*d*, J_{PC} = 3.2 Hz)
C_3	127.49		127.66	127.45
C_4	123.67		123.82	123.69
C_5	115.26		116.34	115.17
C_6	160.43		161.30	160.35
C_7	153.03		151.37	153.12
C_8	122.86		137.88	123.30
C_9	128.84		130.15	138.62
C_{10}	129.82		131.44	130.60
C_{11}			126.53	128.70
C_{12}			115.78	120.38
CH_3			17.67 (br)	21.46
PCH_2CH_3			19.02 (*d*, J_{PC} = 28.2 Hz)	18.62 (*d*, J_{PC} = 28.4 Hz)
PCH_2CH_3			8.14	7.93
^{31}P				
δ(P)	34.1	25.4	34.2	34.0

Bu_3)] (**2b**), and **1c** and **1d** react likewise with PEt_3 to produce **2c** and **2d**. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR data



1a: M = Pd, R = H
c: M = Pd, R = 8-Me
d: M = Pd, R = 9-Me
f: M = Pt, R = H



2a: M = Pd, R = H, R′ = Et
b: M = Pd, R = H, R′ = *n*-Bu
c: M = Pd, R = 8-Me, R′ = Et
d: M = Pd, R = 9-Me, R′ = Et
f: M = Pt, R = H, R′ = Et

for these compounds are listed in Tables I and II. Comparison of the ^1H and ^{13}C NMR parameters of compounds **1** and **2** reveals very small differences in the chemical shifts of the cyclopentadienyl moiety. These observations support the formulation of **2** as 18-electron molecules with η^5-C_5H_5 and C-bonded (phenylazo)phenyl groups rather than 16-electron species with η^1-C_5H_5 and C,N-bonded (phenylazo)phenyl ligands.

Though indefinitely stable in solution at −50 °C compounds **2** have not been isolated. Above 0 °C they react with the chlorinated solvent to form 1:1 mixtures of **1** and *trans*-$[PdCl(C_6H_4N{=}NC_6H_4R)(PR'_3)_2]$ (**5a–d**). The identities of the latter compounds were confirmed by comparing their NMR spectra (Table V) with those of authentic samples, prepared by adding the appropriate tertiary phosphine to $[Pd(C_6H_4N{=}NC_6H_4R)(\mu\text{-}Cl)]_2$. Compound **5a** was already known;[13] **5b–d** have not been described previously. **5d** was isolated as a representative example, and **5e** was also prepared to aid in the interpretation of the NMR spectra of this family of compounds. The formation of compounds **5** from **2** in $CDCl_3$ solution was accompanied by the generation of significant amounts of $CHCl_3$.

Compounds **2a–d** react rapidly in $CDCl_3$ or CD_2Cl_2 solution with a second mole equivalent of PR'_3 to produce orange-red solutions of *trans*-$[Pd(C_6H_4N{=}NC_6H_4R)(\eta^1\text{-}C_5H_5)(PR'_3)_2]$ (**3**). Each of the complexes **3a–d** remains in equilibrium with its precursor **2a–d**, but addition of excess phosphine or lowering the solution temperature to −50 °C displaces the equilibrium toward the bis(phosphine) complex almost quantitatively. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$

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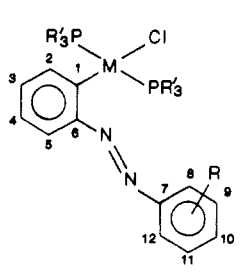
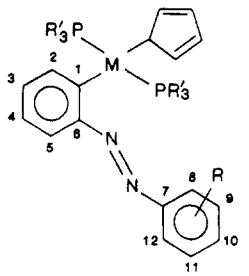


5a: M = Pd, R = H, R′ = Et
b: M = Pd, R = H, R′ = *n*-Bu
c: M = Pd, R = 8-Me, R′ = Et
d: M = Pd, R = 9-Me, R′ = Et
e: M = Pd, R = 10-Me, R′ = Et
f: M = Pt, R = H, R′ = Et

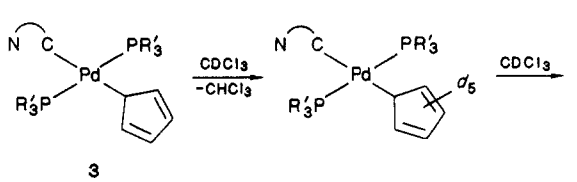


3a: M = Pd, R = H, R′ = Et
b: M = Pd, R = H, R′ = *n*-Bu
c: M = Pd, R = 8-Me, R′ = Et
d: M = Pd, R = 9-Me, R′ = Et
f: M = Pt, R = H, R′ = Et

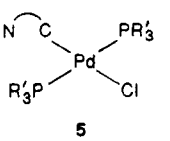
NMR data for the compounds **3** are given in Table III. The ^{31}P NMR spectra indicate the two phosphines are equivalent, and the triplet structure of the ^{13}C resonances of the α-carbons of the phosphines in **3a**, **3c**, and **3d** indicate trans square-planar arrangements.[14] Thus **3** are the expected 16-electron molecules with fluxional η^1-cyclopentadienyl ligands, and not 18-electron species with fluxional η^3-C_5H_5 groups.

Compounds **3** are stable in solution at −50 °C, but they react with $CDCl_3$ at room temperature to produce **5** and $CHCl_3$. It therefore seems likely that the formation of $CHCl_3$, **5**, and **1** from compounds **2** proceeds via the intermediacy of **3** (**1** does not react with $CDCl_3$ in the absence of PR'_3) rather than from a separate reaction of **2** with $CDCl_3$.

Allowing a $CDCl_3$ solution of **3a** to warm in stages from −50 °C permitted the operation of two distinct processes to be observed. At −20 °C, the ^1H cyclopentadienyl resonances of **3a** (and those of the small amount of **2a** which equilibrates with it at this temperature) diminished to zero over 5 h, while the $CHCl_3$ signal increased by a comparable amount. During this period, however, the ^{31}P NMR signals of **3a** (and **2a**) remained practically unaltered, the amount of **5a** produced being very small. When the temperature is raised to room temperature, **5a** is produced almost quantitatively over a similar time span. It thus appears that the reactions producing **5** and chloroform are distinct (eq 1). Compounds **3c** and **3d** behave in a similar way,



3

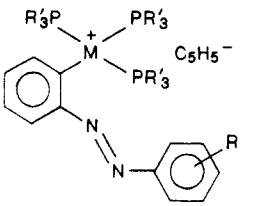


5 (1)

but in CD_2Cl_2 solution both reactions are much slower and little H–D exchange proceeds[11] before formation of **5c** or **5d** is complete (ca. 24 h at ambient temperatures).

Reactions of η^1-cyclopentadienyls of nickel, palladium, and platinum with halogenated solvents are well-known,[3,15] but the mechanism is not understood, and in only one case, that being the reaction of nickelocene with PPh_3 in CCl_4 solution,[15] has a major organic byproduct been identified. The H–D exchange that precedes or accompanies most of the reactions in the present work makes NMR identification of the organic products virtually impossible, though formation of C_5H_6 can be distinguished in some cases. We have detected C_5H_6 among the decomposition products of other η^1-cyclopentadienyls[4] in the past, and it does not appear that the sixth proton originates from the solvent. Further work on the present system in other solvents is planned to elucidate this part of the reaction sequence.

When a $CDCl_3$ or CD_2Cl_2 solution of **1a** is treated with PEt_3 at −50 °C, the compound $[Pd(C_6H_4N{=}NC_6H_5)(PEt_3)_3]C_5H_5$ (**4a**), which contains ionic $C_5H_5^-$, is produced in addition to **2a** and **3a**. Similarly, use of P-*n*-Bu_3 leads to **4b**, and the reaction of **1d** with PEt_3 gives **4d**. NMR data for these compounds are given in Table IV.



4a: M = Pd, R = H, R′ = Et
b: M = Pd, R = H, R′ = *n*-Bu
d: M = Pd, R = 9-Me, R′ = Et
f: M = Pt, R = H, R′ = Et

The ionic character of cyclopentadienyl compounds of early main-group metals is well-understood, and a large degree of ionic character in the bonding of $Mn(C_5H_5)_2$ is generally accepted.[16] The generation of $C_5H_5^-$ from covalent compounds, however, is little documented. Solutions of $V(C_5H_5)_2$ or $Cr(C_5H_5)_2$ in liquid ammonia display conductivity in keeping with $C_5H_5^-$ elimination,[16] and the 20-electron $Ni(C_5H_5)_2$ is reported to eliminate $C_5H_5^-$ on treatment with pyridine[17a] or with cyanide in liquid NH_3.[17b] Elimination of $C_5H_5^-$ also occurs when $Ni(C_5H_5)_2$ is treated with CH_2PPh_3 in benzene or toluene solution.[18] Similarly, loss of ^{117}Sn and ^{119}Sn coupling to the fluxional η^1-cyclopentadienyl in $(CH_3)_3SnC_5H_5$ on treatment with donor solvents L indicates partial conversion to the ion-paired species $[(CH_3)_3SnL]C_5H_5$.[19] More recently, Casey et al. have described the displacement of $C_5H_5^-$ from rhenium by PMe_3,[20] and $[Ir(dppe)_2]C_5H_5$ has been prepared by the reaction of $[Ir(dppe)_2]Cl$ with LiC_5H_5.[21]

The formation of $C_5H_5^-$ in our reactions, which involve neither electropositive transition metals nor 20-electron species, suggests that cyclopentadienyl ion elimination should be kept in mind as a possible general reaction pathway of cyclopentadienyl compounds of these and other metals. In particular, it adds to the already complex list of reaction types for palladium and platinum cyclopentadienyls described in the Introduction.

Raising the temperature of a $CDCl_3$ solution of **4a** to −40 °C causes a reduction in the intensity of the ^1H NMR

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Table III. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR Data (δ) for Complexes of the Type 3

	3a	3b	3c	3d	3f
solv	$CDCl_3$	$CDCl_3$	CD_2Cl_2	$CDCl_3$	$CDCl_3$
temp, °C	−50	−60	−50	−50	−30
^1H					
C_5H_5	6.23	6.23	6.15	6.21	6.12 (J_{PtH} = 21.4 Hz)
CH_3			2.76	2.46	
^{13}C					
C_5H_5	109.46		109.37	109.49	112.72 (J_{PtC} = 37.6 Hz)
C_1	166.81 (t, J_{PC} = 9.0 Hz)		168.28 (t, J_{PC} = ca. 6 Hz)	166.92 (t, J_{PC} = 4.9 Hz)	
C_2	138.56		138.05	138.58	
C_3	128.14		127.93	128.07	
C_4	123.13		122.75	123.10	
C_5	116.37		115.35 or 115.48	116.27	
C_6	157.73		158.08	157.57	
C_7	151.72		149.59	151.78	
C_8	122.86		138.77	122.20	
C_9	128.78		130.13	138.52	
C_{10}	130.21		131.08	130.94	
C_{11}			125.93	128.57	
C_{12}			115.35 or 115.48	121.32	
CH_3			17.68 (br)	21.42	
PCH_2CH_3	12.74 (t, J_{PC} = 12.0 Hz)		12.73 (t, J_{PC} = 12.6 Hz)	12.70 (t, J_{PC} = 12.6 Hz)	
PCH_2CH_3	8.09		7.96	8.08	
^{31}P					
δ(P)	9.24	−0.08	9.51	9.45	7.08 (J_{PtP} = 2810 Hz)

Table IV. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR Data (δ) for Complexes of the Type 4

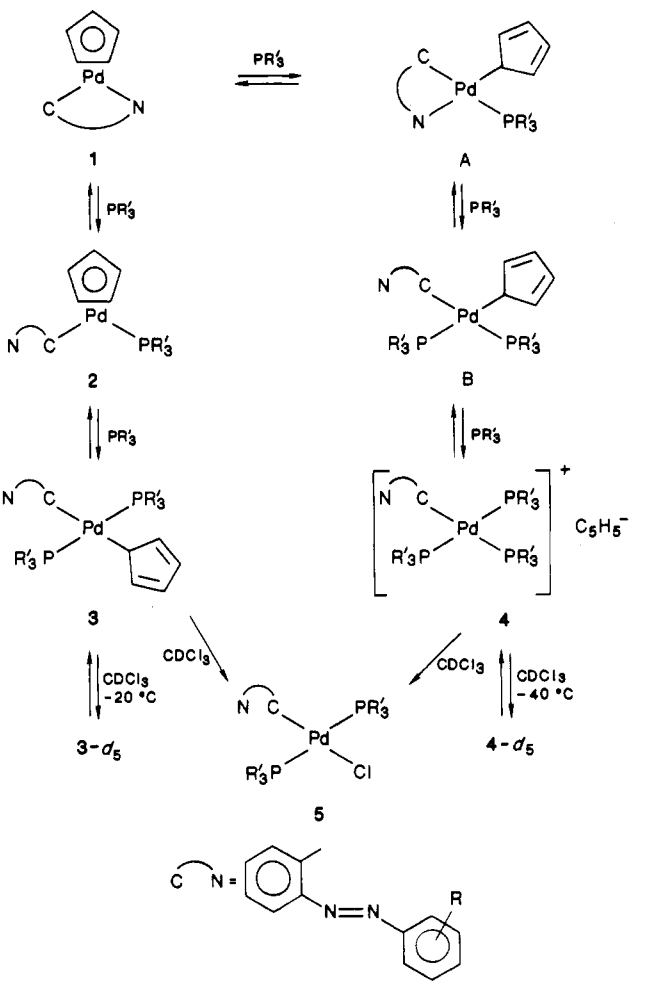
	4a	4b	4d	4f
solv	$CDCl_3$	$CDCl_3$	$CDCl_3$	CD_2Cl_2
temp, °C	−50	−60	−50	−50
^1H				
$C_5H_5^-$	6.07	6.13	6.10	5.63
CH_3			2.42	
^{13}C				
$C_5H_5^-$	103.25		103.46	103.01
^{31}P				
$\delta(P)_{trans\ to\ C}$	2.08 (t)	3.90 (t)	2.24 (t)	−0.14 (t, J_{PtP} = 1786 Hz)
$\delta(P)_{trans\ to\ P}$	9.66 (d)	2.04 (d)	9.13 (d)	3.81 (d, J_{PtP} = 2535 Hz)
$^2J_{PP}$, Hz	36.3	35.0	35.8	22.0

signal due to the $C_5H_5^-$ anion, with a corresponding increase in the intensity of the $CHCl_3$ resonance, whereas the ^{31}P NMR signals of the $[Pd(C_6H_4N{=}NC_6H_5)(PEt_3)_3]^+$ cation remain unchanged. This indicates that H–D exchange has occurred between $C_5H_5^-$ and $CDCl_3$. Reaction with the solvent to liberate Cl^- does not occur at this temperature, since independent experiments have shown that Cl^- reacts with the tris(phosphine) cation to produce **5a**. As the temperature is raised further to −20 °C, however, reaction to produce **5a** does occur.

Similar reactions of $C_5H_5^-$ involving H–D exchange with acidic solvents,[20,22] and decomposition in chlorinated hydrocarbons,[21] have been reported. The slow rate of H–D exchange reported in CD_3CN[20] is unexpected in view of the solvent dependence previously found by us.[11] It is probable, however, that this reaction is critically affected by traces of moisture in the solvent.[11] Though the present reactions were performed under an argon atmosphere, no special precautions were taken to dry the $CDCl_3$ or CD_2Cl_2 solvents.

We have been unable to convert $[Pd(C_6H_4N{=}NC_6H_5)(\eta^5\text{-}C_5H_5)(PEt_3)]$ (**2a**) to the tris(phosphine) compound **4a**, even on treatment with an 11-fold excess of PEt_3 at low temperature. It is apparent, therefore, that a divergent pathway must operate from **1**. The routes involved

Scheme I



are summarized in Scheme I. Intermediates A and B must be involved between **1** and **4**, but we have identified neither with certainty, so they must react very rapidly. The amount of **4** produced from **1** increases when the reaction is performed at lower temperatures and when excess PR'_3 is used. This suggests the establishment of an initial rapid equilibrium between **1** and A, with the equilibrium position favoring **1**. Reaction with more PR'_3 then produces **2**

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Table V. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR Data (δ) for Complexes of the Type 5 at 20 °C

	5a[d] ^{13}C	**5b**[d] ^{13}C	**5c**[e] ^{13}C	**5d**[d] ^1H	**5d**[d] ^{13}C	**5e**[d] ^{13}C	**5f**[d] ^{13}C
1	156.60 (t, J_{PC} = 6.0 Hz)	157.00 br	159.24 (t, J_{PC} = 6.0 Hz)		156.77 (t, J_{PC} = 6.0 Hz)	156.23 (t, J_{PC} = 6.0 Hz)	143.52 (t, J_{PC} = 9.0 Hz, J_{PtC} = 979 Hz)
2	137.77 (J_{PC} unresolved)	137.68 (t, J_{PC} = 3.2 Hz)	138.08 (t, J_{PC} = 7.0 Hz)	7.56 (br d)[a]	137.70 (t, J_{PC} = 3.5 Hz)	137.69 (t, J_{PC} = 4.5 Hz)	138.76 (J_{PtC} = 25.5 Hz)
3	128.93	128.85	128.89	7.02 (dd)[a]	128.74	128.74	129.02
4	123.33	123.20	123.43	7.00 (dd)[a]	123.26	123.28	122.83
5	120.37	120.54	116.93	7.51 (d)[a]	119.71	120.14	116.44 (J_{PtC} = 42.3 Hz)
6	156.86 (t, J_{PC} = 2.0 Hz)	157.09 (br)	157.87 (J_{PC} unresolved)		156.83 (J_{PC} unresolved)	156.76 (J_{PC} unresolved)	157.04 (J_{PC}, J_{PtC} unresolved)
7	152.48	152.56	150.86		152.57	150.61	152.76
8	123.01	123.03	138.11	7.82	122.57	122.96	122.83
9	128.93	128.93	130.56		138.70	129.58	128.86
10	130.33	130.20	131.44	7.86 (d)[a]	131.09	140.72	129.97
11			126.49	7.34 (dd)[a]	128.74		
12			115.97	7.21 (d)[a]	121.13		
CH_3			17.74 (br)[b]	2.41	21.31	21.44[c]	
PCH_2CH_3	br		14.75 (t, J_{PC} = 13.0 Hz)		14.41 (t, J_{PC} = 12.6 Hz)	14.38 (t, J_{PC} = 13.6 Hz)	13.78 (t, J_{PC} = 16.6 Hz)
PCH_2CH_3	br		8.19		7.98	7.93	7.72
^{31}P δ(P)	12.51	3.87	13.58	12.67		12.37	13.48 (J_{PtP} = 2756 Hz)

[a] $J_{H_2H_3}$ = 7.5 Hz, $J_{H_3H_4} \approx$ 8 Hz, $J_{H_4H_5}$ = 7.2 Hz, $J_{H_{10}H_{11}}$ = 6.9 Hz, $J_{H_{11}H_{12}}$ = 7.5 Hz. [b] $\delta(CH_3)$ 2.76. [c] $\delta(CH_3)$ 2.39. [d] In $CDCl_3$. [e] In CD_2Cl_2.

(which is relatively stable) from **1**, or B (which must react further very rapidly) from A. The additional PR'_3 or lower temperature would displace the first equilibrium toward A, producing the observed effect.

The inability to convert **2** or **3** to **4** means that the H–D exchange observed between **3** and the solvent cannot proceed via reversible formation of **4** and thus presumably does not involve $C_5H_5^-$ formation. A second H–D exchange route applicable to these systems proceeds via formation of the zerovalent complexes $Pd(PR'_3)_4$,[11] but we have found no evidence for its operation in the $CDCl_3$ or CD_2Cl_2 solvents used here. Clearly a third route must also apply to these systems operating via compound **3**. One possibility could involve reversible H migration between C_5H_5 and Pd, previously suggested by us.[11]

A number of experiments was performed on [Pd(C$_6$H$_4$N=NC$_6$H$_5$)(η^5-C$_5$D$_5$)][22] (**1a**-d_5). Addition of P-*n*-Bu_3 to a $CHCl_3$ solution of **1a**-d_5 at room temperature resulted in formation of **2b**-d_5 (in reality it was observed by ^1H NMR spectroscopy as the 20% d_4 material resulting from the preparation[22]), but as the reaction proceeded, the ^1H cyclopentadienyl signal of regenerated **1a** grew progressively, in keeping with the discovered reversibility of all the reaction steps until production of **5a** (Scheme I). Samples of **1a**-d_5 stirred with TlC_5H_5 in $CDCl_3$, CD_2Cl_2, or toluene-d_8 showed no evidence of reaction when examined by NMR spectroscopy. Addition of 1 mol equiv of P-*n*-Bu_3 to the mixtures resulted in exchange of C_5D_5 for C_5H_5, however. In toluene-d_8 and CD_2Cl_2, the signal from **2b** increased rapidly over 30 min, converting to **1a** after 3 days, as expected from our previous studies.[11] Although in $CDCl_3$ no increase in the cyclopentadienyl proton signals was observed, the signal due to $CHCl_3$ grew dramatically, so presumably in this solvent also exchange of C_5D_5 for C_5H_5 has proceeded, but equally rapid H–D exchange reconverted the protonated material to its deuteriated analogue.

The dark red platinum complex [Pt(C$_6$H$_4$N=NC$_6$H$_5$)(η^5-C$_5$H$_5$)] (**1f**) displays some curious differences in its reactions with PEt_3. At room temperature, it reacts readily with either 1 or 2 mol equiv of PEt_3 in $CDCl_3$ solution to produce *trans*-[Pt(C$_6$H$_4$N=NC$_6$H$_5$)Cl(PEt_3)$_2$] (**5f**) along with significant quantities of $CHCl_3$. At −50 °C, the reaction with PEt_3 is extremely slow, but warming to −30 °C allows steady formation of *trans*-[Pt(C$_6$H$_4$N=NC$_6$H$_5$)(η^1-C$_5$H$_5$)(PEt_3)$_2$] (**3f**) and [Pt(C$_6$H$_4$N=NC$_6$H$_5$)(PEt_3)$_3$]C$_5$H$_5$ (**4f**). When a CD_2Cl_2 solution of **1f** to which 2 mol equiv of PEt_3 had been added was maintained at −30 °C for 18 h, the major species in solution was **4f**. The ^1H NMR signal assigned to $C_5H_5^-$ in **4f** is shifted upfield, relative to those of the ionic palladium compounds, whereas the ^{13}C shift is very similar to those for **4a** and **4d**. No coupling to ^{195}Pt or ^{31}P is detected in either case, supporting the formulation of **4f** as an ionic species. We have not observed a platinum compound of type **2** under any conditions, nor any of the likely intermediates between **1f** and **3f** or **4f**. We conclude that either a platinum compound of type **2** is not formed or it is extremely reactive toward PEt_3.

Even at the lowest temperatures at which they are formed, **3f** and **4f** react slowly with CD_2Cl_2 or $CDCl_3$. Above −30 °C the reactions proceed more rapidly, forming **3f**-d_5 and **4f**-d_5 by H–D exchange with the solvent, whereas above 0 °C both complexes are converted largely to **5f**.

In order to gain more information about the formation of **2** and to attempt to synthesize a platinum analogue, we have examined the reactions of cyclopentadienylthallium with [Pd(C$_6$H$_4$N=NC$_6$H$_5$)Cl(PEt_3)] (**6a**) and [Pt(C$_6$H$_4$N=NC$_6$H$_5$)Cl(PEt_3)] (**6f**) (Table VI). These were prepared by the sequences shown in eq 2 and 3, since reactions of [M(C$_6$H$_4$N=NC$_6$H$_5$)(μ-Cl)]$_2$ with PEt_3 result only in **5a** or **5f**.[23] The CO cleavage used for the platinum complex[24] is inappropriate for palladium because insertion is likely.[23b,25]

The reaction of **6a** with TlC_5H_5 in diethyl ether solution does not produce **2a**, but an equimolar mixture of **1a** and

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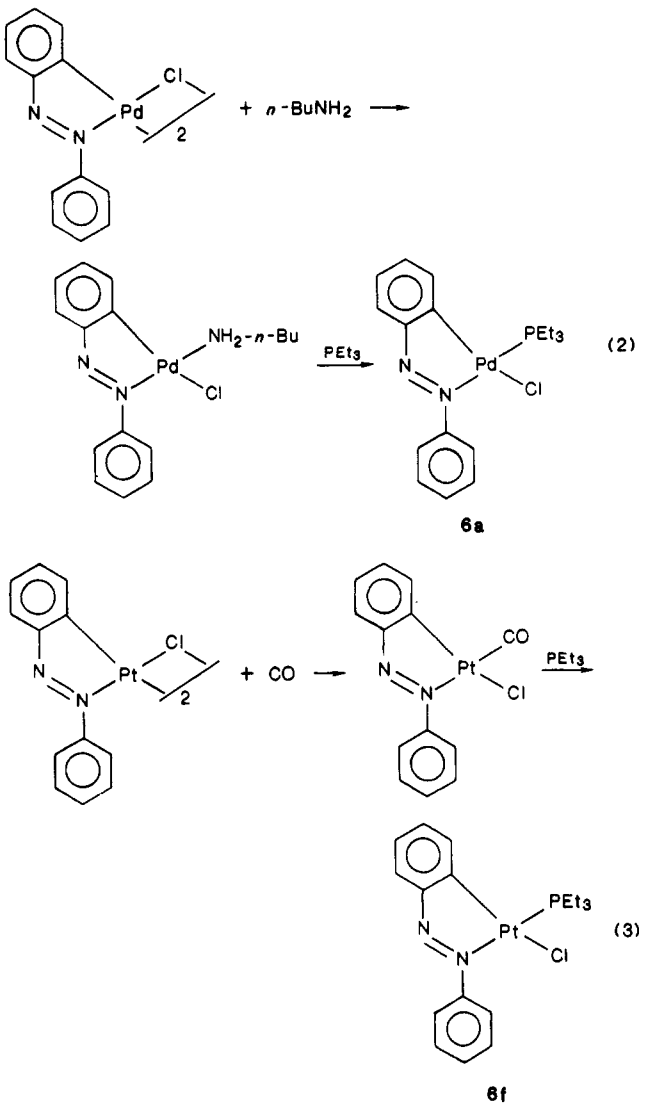


5a. Although in principle these products could result from disproportionation of **6a** to give $[\overline{Pd(C_6H_4N{=}NC_6H_5)}(\mu\text{-}Cl)]_2$ (which reacts with TlC_5H_5 to form **1a**) and **5a** (which we have established does not react readily with TlC_5H_5), this is not the case because disproportionation does not proceed in any solvent we have tried. Since the reverse reaction does not proceed,[23] any disproportionation would be evident. We therefore propose Scheme II to account for the products; **2a** is formed slowly, but it equilibrates with **1a** and free PEt_3. The latter reacts readily with **6a** to give **5a**.

The reaction of **6f** with TlC_5H_5 is more difficult to interpret. In ether, $CDCl_3$, or toluene-d_8 solution the reaction is slow, and the only phosphorus-containing product is *trans*-$[Pt(C_6H_4N{=}NC_6H_5)Cl(PEt_3)_2]$ (**5f**). The ^1H NMR spectra of the soluble residues revealed no singlet C_5H_5 resonances but complicated signals in the vinyl region (5.5–7.0 ppm). Again we find no evidence for disproportionation of **6f**, and neither TlC_5H_5 nor TlCl catalyzes such a process.

NMR Spectra. All of the compounds have been characterized by NMR spectroscopy, and the progress of the reactions of compounds of the type **1** with tertiary phosphines was monitored spectroscopically. It was not possible to obtain complete $^{13}C\{^1H\}$ NMR spectra for compounds of the type **4**, because they were always produced as minor components of mixtures with **2** and **3**.

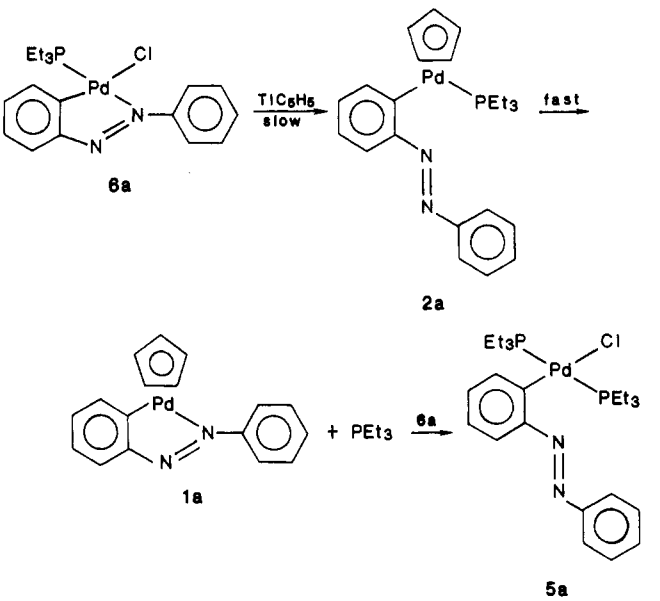
The ^1H and ^{13}C chemical shifts are quite indicative of the mode of bonding of the cyclopentadienyl moiety.

Table VI. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR Data (δ) for Complexes of the Type 6 at 20 °C in $CDCl_3$

	6a[b]		6f[c]
	^1H	^{13}C	^{13}C
1		156.22 (d, J_{PC} = 4.0 Hz)	143.41 (d, J_{PC} = 7.8 Hz, J_{PtC} = 1111 Hz)
2	7.27 (dd)[a]	135.06 (d, J_{PC} = 6.0 Hz)	133.65 (d, J_{PC} = 1.7 Hz, J_{PtC} = 109 Hz)
3	7.21 (dd)[a]	132.11 (d, J_{PC} = 5.0 Hz)	134.04 (J_{PtC} = 60.4 Hz)
4	7.27 (dd)[a]	125.65	124.40
5	8.03 (br d)[a]	131.56	131.38 (J_{PtC} = 16.8 Hz)
6		165.65	164.70 (d, J_{PC} = 3.4 Hz, J_{PtC} = 28.2 Hz)
7		151.74 (d, J_{PC} = 4.5 Hz)	151.17 (d, J_{PC} = 5.0 Hz, J_{PtC} = 55.0 Hz)
8	7.89 (br d)[a]	124.31	124.40
9	7.45 (dd)	127.88	127.60
10	7.42 (t)	130.30	129.60

[a] $J_{PH_2} = J_{H_2H_3} = J_{H_3H_4} = J_{H_4H_5} \approx 7$ Hz; H_5 and H_8 resonances broadened due to coupling to phosphorus. [b] ^{31}P NMR δ 31.5. [c] ^{31}P NMR δ 8.2 (J_{PtP} = 3858 Hz).

Scheme II



Conversion of **1** to **2** causes a small upfield shift of both the ^1H and ^{13}C resonances, and the doublet structures reveal that coordination of one phosphine occurs. The addition of a second phosphine, and $\eta^5 \rightarrow \eta^1$ rearrangement of the ring, results in a significant downfield shift of both resonances, and the larger J_{PtH} and J_{PtC} values in **3f** (relative to **1f**) are typical of a (η^1-cyclopentadienyl)platinum complex.[3,9] Neither the ^1H nor ^{13}C resonance shows coupling to ^{31}P, but the resonances due to C_1 and the methylene carbons of the PEt_3 ligands in **3a**, **3c**, and **3d** appear as triplets, indicating the presence of two phosphines in a trans square-planar configuration.[14] The ^1H and ^{13}C shifts due to $C_5H_5^-$ are intermediate between those of the η^5- and η^1-bonded rings.

The ^1H resonances due to the ring methyl in **1d**, **2d**, **3d**, and **5d** shift little, whereas the 8-methyl group exhibits considerable deshielding when the nitrogen is not coordinated to palladium. On the other hand, the methyl carbon resonances in **2c**, **3c**, and **5c** appear at higher field than that in **1c**.

The ^1H and ^{13}C resonances due to the substituted azobenzene moieties have been assigned by using ^1H–^1H shift-correlated (COSY) and ^{13}C–^1H shift-correlated

(HETCOR) two-dimensional NMR spectra in certain cases, by comparison with published data,[13,26,27] and by extrapolation between compounds in this study. For the platinum compounds, assignments are aided by the observation of coupling to platinum in certain cases; particularly instrumental in this regard is the large magnitude of $^1J_{PtC}$ for the metalated carbon.

The metalated carbon C_1 exhibits a particularly large downfield shift, especially in the case of palladium. The two nitrogen-bearing carbons C_6 and C_7 also appear at low field. The former is deshielded by 4–13 ppm compared with the quaternary carbon in azobenzene,[26] and C_2, which is also adjacent to the metalated carbon, exhibits a significant downfield shift as well. Somewhat surprisingly, significant changes in the ^{13}C chemical shifts for the non-metalated ring do not occur between complexes containing coordinated and uncoordinated nitrogen, the largest effects being seen for the 8-methyl compounds for which steric factors will be important. For the unsubstituted compounds **1a–6a**, the chemical shifts of C_7, which might be expected to show the largest effect of N-coordination, varies by only 3 ppm and is very close to that in azobenzene. Thus ^{13}C chemical shifts of the azobenzenyl moiety do not provide a satisfactory means of determining whether the substituted azobenzene acts as a mono- or bidentate ligand.

In the square-planar complexes **3**, **5**, and **6** the chemical shift of C_1 is indicative of the nature of the trans ligand; when trans to η^1-C_5H_5 the chemical shift is 10 ppm greater than when C_1 lies trans to Cl. The non-square-planar compounds **1** and **2** exhibit the largest and smallest C_1 chemical shifts, respectively, of the compounds we have studied, so magnitudes of $\delta(C_1)$ do not provide an indication of compound geometry.

Experimental Section

NMR spectra were recorded on Varian XL-100 and XL-300 and Bruker WP200SY spectrometers operating in the Fourier transform mode. ^1H and ^{13}C chemical shifts are relative to tetramethylsilane, and ^{31}P shifts are relative to external H_3PO_4, positive shifts representing deshielding. In some cases ^1H and ^{13}C NMR peak assignments were made by using ^1H–^1H shift-correlated (COSY) and ^{13}C–^1H shift-correlated (HETCOR) 2D spectra. Samples were maintained under atmospheres of dry nitrogen or argon. Microanalyses were performed at the University of Glasgow.

The preparations of $[Pt(C_6H_4N{=}NC_6H_5)(\eta^5\text{-}C_5H_5)]$ (**1f**)[24] and $[Pd(C_6H_4N{=}NC_6H_5)(\eta^5\text{-}C_5D_5)]$ (**1a**-d_5)[22] have been described previously. Compound **1a**[28] was prepared from $[Pd(C_6H_4N{=}NC_6H_5)(\mu\text{-}Cl)]_2$ and TlC_5H_5 in a manner similar to its deuteriated analogue.[22] Compound **1d** was prepared in similar fashion from $[Pd(C_6H_4N{=}NC_6H_4Me)(\mu\text{-}Cl)]_2$ and TlC_5H_5; this material has been prepared previously,[27] but not isolated. Anal. Calcd for $C_{18}H_{16}N_2Pd$: C, 58.95; H, 4.4; N, 7.6. Found: C, 58.8; H, 4.4; N, 7.9.

Preparation of $[Pd(C_6H_4N{=}NC_6H_5)Cl(PEt_3)]$ (6a). To a suspension of $[Pd(C_6H_4N{=}NC_6H_5)(\mu\text{-}Cl)]_2$ (0.50 g, 0.77 mmol) in toluene (60 mL) was added *n*-butylamine (0.113 g, 1.55 mmol) under nitrogen. After the solution was stirred for 1 h, all the material dissolved, and PEt_3 (0.182 g, 1.54 mmol) in toluene (12 mL) was added dropwise. Removal of the solvent under vacuum, and recrystallization from ether/pentane gave the product as orange crystals (0.461 g, 63%). Anal. Calcd for $C_{18}H_{24}ClN_2PPd$: C, 49.0; H, 5.5; N, 6.35. Found: C, 49.0; H, 5.5; N, 6.3.

Preparation of $[Pt(C_6H_4N{=}NC_6H_5)Cl(PEt_3)]$ (6f). Carbon monoxide was bubbled through a suspension of $[Pt(C_6H_4N{=}NC_6H_5)(\mu\text{-}Cl)]$ (0.213 g, 0.259 mmol) in toluene (400 mL) for 1 h, during which time the material dissolved to produce an orange solution.[24] A solution of PEt_3 (0.061 g, 0.52 mmol) in toluene (2 mL) was added dropwise, and the color changed to maroon. Removal of the solvent under vacuum, and recrystallization from ether/pentane gave the product as dark red crystals (0.208 g, 76%). Anal. Calcd for $C_{18}H_{24}ClN_2PPt$: C, 40.8; H, 4.6; N, 5.3. Found: C, 40.1; H, 4.4; N, 5.1.

Preparation of *trans*-$[Pd(C_6H_4N{=}NC_6H_4Me\text{-}9)Cl(PEt_3)_2]$ (5d). To a toluene suspension of $[Pd(C_6H_4N{=}NC_6H_4Me\text{-}9)(\mu\text{-}Cl)]_2$ was added 4 mol equiv of PEt_3. After solvent removal and recrystallization from hexane, the product was obtained as brick-red crystals. Anal. Calcd for $C_{25}H_{41}ClN_2P_2Pd$: C, 52.4; H, 7.2; N, 4.9. Found: C, 52.2; H, 7.4; N, 4.8. *trans*-$[Pd(C_6H_4N{=}NC_6H_4Me\text{-}10)Cl(PEt_3)_2]$ (**5d**) was prepared similarly. Found: C, 52.1; H, 7.3; N, 4.8.

NMR Studies. In a typical experiment, complex **1** (ca. 20 mg) was loaded into a 5-mm NMR tube fitted with a rubber septum. The tube was evacuated and then filled with argon, and the solvent (ca. 0.3 mL) was introduced by syringe. After dissolution of the complex, the appropriate tertiary phosphine was added by syringe. Low-temperature reactions were performed by immersing the tube in a slush bath maintained at −50 °C for several minutes prior to addition of the phosphine.

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