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Formation, Reactions, and Solution Dynamics of $[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ (M = Pd, Pt)

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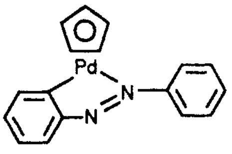
Reactions of $[M(\eta^5\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)]$ (M = Pd, R = H, Me, $SiMe_3$, X = N=NPh or R = H, X = CH=NMe, 2-C_5H_4N; M = Pt, R = H, $SiMe_3$, X = N=NPh) with PEt_3 in toluene solution produce the adducts $[Pd(\eta^5\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)]$ and *trans*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ but none of the ionic $[M(C_6H_4\text{-}2\text{-}X)(PEt_3)_3]^+C_5H_4R^-$ found in halogenated solvents. Instead, the reactive intermediates *cis*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ are detected at -80 °C, but these isomerize as the temperature is raised. The fluxional η^1-C_5H_4R groups of *trans*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ undergo rapid rotation about the M-C bonds at ambient temperature, resulting in apparent magnetic equivalence of the PEt_3 groups. At temperatures around -90 °C bond rotation is slowed sufficiently to allow detection of the nonequivalent P atoms by NMR spectroscopy. The palladium complexes decompose slowly at 25 °C, but the platinum species isomerize readily to sp^2-carbon-bonded vinylic cyclopentadienyl derivatives. At low temperatures the effects of restricted rotation about the Pt-C bonds of the vinylic cyclopentadienyl compounds can be deduced from the detection of syn and anti rotational isomers in solution.

Introduction

We have shown previously that the reactions of (η^5-cyclopentadienyl)[2-(arylazo)phenyl]palladium (**1**) with PEt_3 in $CDCl_3$ or CD_2Cl_2 solution proceed by two competing pathways.[1] One route reversibly produces first $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)]$ (**2**) and then *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ (**3**). The other route, favored by lower temperatures and high PEt_3 concentrations, leads instead to the ionic cyclopentadienyl compound $[Pd(C_6H_4N{=}NPh)(PEt_3)_3]^+C_5H_5^-$ (**4**). Excess PEt_3 does not convert **3** to **4**, leading to the conclusion that **4** is produced via different intermediates, namely $[Pd(\eta^1\text{-}C_5H_5)(C_6H_4\text{-}N{=}NPh)(PEt_3)]$ (η^1-C_5H_5 trans to N) and *cis*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$, neither of which was observed.[1]



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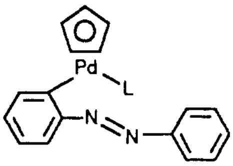

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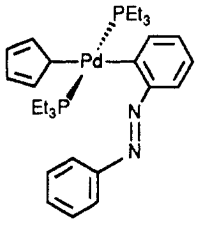

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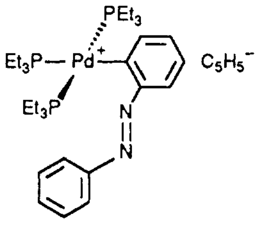

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At temperatures above -40 °C in $CDCl_3$ or CD_2Cl_2, both the η^1-cyclopentadienyl group of **3** and the cyclopentadienyl ion of **4** undergo H-D exchange, deuteriating the C_5H_5 rings. At higher temperatures, further irreversible reactions with both of these chlorinated solvents produce *trans*-$[PdCl(C_6H_4N{=}NPh)(PEt_3)_2]$ (**5**). Because of the reversible nature of the reactions with PEt_3, and the ready chlorination by the solvents used, we were unable to isolate **2**, **3**, or **4**, except when PEt_3 was replaced by the very bulky tricyclohexylphosphine. The reaction of **1** with PCy_3 does not proceed beyond $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)(PCy_3)]$, which was isolated from hydrocarbon solvents and characterized crystallographically. NMR spectroscopic measurements on this and related molecules reveal a considerable barrier to rotation about the palladium-aryl bond in solution.[2]

The platinum analogue of **1**, $[Pt(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)]$, reacts with PEt_3 in $CDCl_3$ or CD_2Cl_2 solution in a way broadly similar to that for the palladium derivative, except that no analogue of **2** could be detected in any reaction sequences.[1] The nickel analogue of **1**, however, does not react at all with PEt_3. X-ray crystal structure analyses of the three molecules $[M(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)]$ (M = Ni, Pd, Pt) reveal no structural differences that could account for these variations.[3]

In this paper we report the reactions of $[M(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)]$ (M = Pd, Pt) and some related molecules with PEt_3 in toluene-d_8 solution. At low temperatures we are able to confirm the presence of previously undetected intermediates en route to compounds **3** and **4**. Also, the platinum complexes produced behave in a way very different from those of palladium in this solvent, the η^1-C_5H_5 ligands converting sequentially to two sp^2-carbon-bonded cyclopentadienyls. The $^{31}P\{^1H\}$ NMR spectra of **3** and the sp^2-bonded derivatives reveal phenomena consistent with restricted rotation about the M-C bonds in each case.

Results and Discussion

1. Palladium Compounds. Mixtures of $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)]$ (**1**) and 2 mol equiv of PEt_3 in toluene-d_8 solution react very slowly at -80 °C. When the reaction is followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, three products can be identified: the known $[Pd(\eta^5\text{-}$

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(1) Anderson, G. K.; Cross, R. J.; Fallis, S.; Rocamora, M. *Organometallics* **1987**, *6*, 1440.

(2) Anderson, G. K.; Cross, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Rocamora, M. *Organometallics* **1988**, *7*, 1520.

(3) Anderson, G. K.; Cross, R. J.; Manojlovic-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1989**, *362*, 225.

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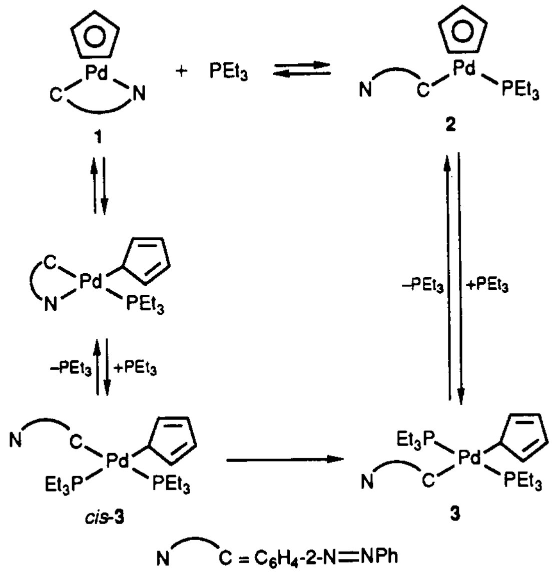
Scheme I



$C_5H_5)(C_6H_4N{=}NPh)(PEt_3)]$ (**2**; $\delta(P)$ 34.2, $\delta(C_5H_5)$ 5.85) and *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ (**3**; $\delta(P)$ 9.2, $\delta(C_5H_5)$ 6.73) and a previously undetected *cis*-bis(phosphine) compound ($\delta(P)$ 11.2 d, 7.6 d, $J_{PP} = 30$ Hz). The last compound exhibits a broad singlet in its ^1H NMR spectrum at 6.38 ppm, characteristic of a fluxional η^1-cyclopentadienyl (the signal is broad due to unresolved couplings to phosphorus). At −40 °C the reaction proceeds more rapidly, and the cis compound converts to **3**, establishing it as the previously undetected species *cis*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ (*cis*-**3**). When the reaction is complete, compounds **2**, **3**, and free PEt_3 equilibrate (eq 1), with lower temperatures favoring **3**. The previously

$$[Pd(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)] + PEt_3 \rightleftharpoons \textit{trans}\text{-}[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2] \quad (1)$$

observed[1] ionic complex $[Pd(C_6H_4N{=}NPh)(PEt_3)_3]^+C_5H_5^-$ (**4**) is not formed in this instance, presumably a consequence of employing a less polar solvent. Under an inert atmosphere this equilibrium persists for several days at room temperature, although cyclopentadiene and zerovalent palladium complexes[4] are gradually produced.

When $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)]$ (**2**) is preformed by allowing 1 equiv of PEt_3 to react with **1** at 25 °C, the addition of a second PEt_3 at −80 °C failed to yield any *cis*-**3**. This supports our previous conclusion[1] that the reaction paths diverge at the addition of the first phosphine (Scheme I). The other mono(phosphine) intermediate has not been observed and must react very rapidly with a second PEt_3.

Analogous low-temperature reactions between PEt_3 and $[Pd(\eta^5\text{-}C_5H_4Me)(C_6H_4N{=}NPh)]$, $[Pd(\eta^5\text{-}C_5H_4SiMe_3)(C_6H_4N{=}NPh)]$, $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}CH{=}NMe)]$, and $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}\{2\text{-}C_5H_4N\})]$ have been examined. $[Pd(\eta^5\text{-}C_5H_4SiMe_3)(C_6H_4N{=}NPh)]$ most closely resembles **1** in its reactions at −80 °C in toluene-d_8 solution, in that the Me_3Si-substituted analogues of **2**, **3**, and *cis*-**3** are all produced slowly. $[Pd(\eta^5\text{-}C_5H_4SiMe_3)(C_6H_4N{=}NPh)(PEt_3)]$ is the dominant species, and *trans*-$[Pd(\eta^1\text{-}C_5H_4SiMe_3)(C_6H_4N{=}NPh)(PEt_3)_2]$ is present in only small relative amounts. The reactions of the methylcyclopentadienyl complex, on the other hand, are striking in that the *trans*-bis(phosphine) complex is not detected in the NMR spectra at −80 °C: $[Pd(\eta^5\text{-}C_5H_4Me)(C_6H_4N{=}NPh)(PEt_3)]$ dominates the spectra, *cis*-$[Pd(\eta^1\text{-}C_5H_4Me)(C_6H_4N{=}NPh)(PEt_3)_2]$ being present also. When these reaction systems are warmed to −40 °C, the NMR signals for the cis compounds diminish to zero intensity within about 15 min. Thereafter the dynamic equilibria involving $[Pd(\eta^5\text{-}C_5H_4R)(C_6H_4N{=}NPh)(PEt_3)]$, *trans*-$[Pd(\eta^1\text{-}C_5H_4R)(C_6H_4N{=}NPh)(PEt_3)_2]$, and free PEt_3 remain the principal features observed.

Table I. NMR Parameters (ppm) for Compounds of the Type *trans*- and *cis*-$[Pd(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ in C_7D_8 Solution

R	X	temp, °C	$\delta(P)$ (J_{PP}, Hz)	$\delta(H)$ (C_5H_4R)	other resonances
		Trans Complexes			
H	N=NPh	−40	9.2	6.62	
Me[a]	N=NPh	−40	10.1	6.03 6.54	2.61 (CH_3)
$SiMe_3$	N=NPh	−40	9.4	6.16 br	0.57 ($SiCH_3$)
H	CH=NMe	−20	10.0	6.48	3.56 (NCH_3)
H	2-C_5H_4N	−40	6.3	6.57	
		Cis Complexes			
H	N=NPh	−80	7.6 d 11.2 d (30)	6.38 br	
Me	N=NPh	−80	8.9 d 10.6 d (29)	6.18 br 6.23 br	2.18 (CH_3)
$SiMe_3$	N=NPh	−80	6.2 d 11.2 d (31)	not resolved	
H	CH=NMe	−80	6.3 d 10.7 d (30)	ca. 6.4 br	

[a] At −90 °C the C_5H_4R signal at 6.1 ppm becomes very broad, whereas the signal at 6.5 ppm is less broad.

Reactions of $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}CH{=}NMe)]$ with 2 mol equiv of PEt_3 at −80 °C similarly produce $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}CH{=}NMe)(PEt_3)]$ and *trans*- and *cis*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}CH{=}NMe)(PEt_3)_2]$. Here *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}CH{=}NMe)(PEt_3)_2]$ is the most abundant product and remains so above −50 °C after the cis isomer has isomerized, presumably reflecting a different equilibrium constant between the mono- and bis(phosphine) complexes with the iminyl ligand. $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}\{2\text{-}C_5H_4N\})]$ reacts with 2 mol equiv of PEt_3 in toluene-d_8 solution to yield a brown precipitate. Although ^{31}P and ^1H NMR parameters assignable to $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}\{2\text{-}C_5H_4N\})(PEt_3)]$ and *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}\{2\text{-}C_5H_4N\})(PEt_3)_2]$ are detected for the remaining solution, no signals due to the cis isomer could be detected, possibly due to its low solubility.

The η^1-cyclopentadienyl groups of *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ (**3**) and related compounds exhibit deceptively simple ^1H NMR spectra characteristic of fluxional rings.[5] Salient ^1H and ^{31}P NMR parameters for these compounds are given in Table I. Parameters for **2** and related compounds have been reported previously.[2]

Since our previous study did not extend to temperatures as low as −80 °C and was more restricted in the range of compounds used, the reactions of the five cyclopentadienyl derivatives above with PEt_3 were also examined in CD_2Cl_2 solution to enable a more direct comparison of the solvent effects to be made. Even at −80 °C, all of the compounds react readily and completely with 2 mol equiv of PEt_3. As well as products of types **2** and **3**, the ionic cyclo-

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[5] (a) Larrabee, R. B. *J. Organomet. Chem.* **1974**, *74*, 313. (b) Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 377. (c) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press, New York, 1982; Vol. 3, p 89. (d) Mann, B. E. *Chem. Soc. Rev.* **1986**, *15*, 167.

Table II. NMR Parameters (ppm) for New Compounds of the Types *trans*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ and $[M(C_6H_4\text{-}2\text{-}X)(PEt_3)_3]^+C_5H_4R^-$ in CD_2Cl_2 Solution

M	R	X	temp, °C	δ(P) (J_{PP}, Hz)	δ(H) (C_5H_4R)	other resonances
			trans-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ Complexes			
Pd	Me	N=NPh[a]	−40	10.0	5.66 br 5.96 br	2.13 (CH_3)
Pd	$SiMe_3$	N=NPh[b]	−70	9.5		
Pd	H	CH=NMe[c]	−40	9.9	6.07	8.93 (CH=) NCH_3 obscured
Pd	H	2-C_5H_4N	−80	6.1	6.01 br	
Pt	$SiMe_3$	N=NPh	−30	9.4 ($^1J_{PtP}$ 2804)		
			$[M(C_6H_4\text{-}2\text{-}X)(PEt_3)_3]^+C_5H_4R^-$ Complexes			
Pd	Me	N=NPh	−40	9.6 d 2.8 t (36)	5.39 t 5.45 t	2.19 (CH_3)
Pd	$SiMe_3$	N=NPh	−70	9.6 d 2.7 t (36)		
Pd	H	CH=NMe	−40	4.6 d 2.1 t (38)	5.64	8.29 (CH=) 3.47 (NCH_3)
Pd	H	2-C_5H_4N	−40	4.5 d 1.6 t (38)	5.65	
Pt	$SiMe_3$	N=NPh	−30	3.9 d ($^1J_{PtP}$ 2550) 0.0 t ($^1J_{PtP}$ 1796) (23)		

[a] $^{13}C\{^1H\}$ NMR: δ(C) 15.7 (CH_3), 97.3 br (C_5H_4Me). [b] $^{13}C\{^1H\}$ NMR: δ(C) −0.7 ($SiCH_3$). [c] $^{13}C\{^1H\}$ NMR (−50 °C): δ(C) 48.1 (NCH_3), 109.6 (C_5H_5), 168.1 (CH=).

pentadienyl derivatives $\{Pd(C_6H_4\text{-}2\text{-}X)(PEt_3)_3]^+C_5H_4R^-$ (X = N=NPh, R = H, Me, $SiMe_3$; X = CH=NMe, 2-C_5H_4N, R = H) are produced, each of which is readily detected by its characteristic ^{31}P NMR doublet and triplet. Only in the reaction of $[Pd(\eta^5\text{-}C_5H_4Me)(C_6H_4N{=}NPh)]$ with PEt_3 is the set of ^{31}P doublets due to the *cis*-bis(phosphine) complex apparent after mixing the reactants at −80 °C, and even at this temperature total conversion of *cis*-$[Pd(\eta^1\text{-}C_5H_4Me)(C_6H_4N{=}NPh)(PEt_3)_2]$ to $[Pd(C_6H_4N{=}NPh)(PEt_3)_3]^+C_5H_4Me^-$ takes place within 4 h.

It thus appears that the ready reaction of the *cis*-bis(phosphine) complexes with PEt_3 in CD_2Cl_2 (or $CDCl_3$) solution generally prevents their detection in these solvents. The electron-donating methyl substituent of the C_5H_4Me compound is likely to render $[Pd(C_6H_4N{=}NPh)(PEt_3)_3]^+C_5H_4Me^-$ less stable and more difficult to generate, hence accounting for the detection of the *cis*-bis(phosphine) complex in that system only. Characteristic NMR parameters for previously unreported derivatives of the types **3** and **4** are given in Table II.

We reported previously the easy exchange of cyclopentadienyl hydrogen atoms of *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ and $[Pd(C_6H_4N{=}NPh)(PEt_3)_3]^+C_5H_5^-$ with deuterium of the $CDCl_3$ solvent.[1,4] Warming the latter to −40 °C in $CDCl_3$ allows observation of H–D exchange by ^1H NMR spectroscopy, while ^{31}P NMR observations confirm the integrity of the cation. Above 0 °C, a further reaction takes place to produce *trans*-$[PdCl(C_6H_4N{=}NPh)(PEt_3)_2]$ (**5**). Similarly *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ undergoes H–D exchange at −20 °C and above 0 °C reacts irreversibly with $CDCl_3$ to produce **5**. We have examined the reactions of the analogous methylcyclopentadienyl and (trimethylsilyl)cyclopentadienyl complexes to explore the nature of substituent effects on these processes.

The ^1H NMR spectrum of $[Pd(C_6H_4N{=}NPh)(PEt_3)_3]^+C_5H_4Me^-$ in $CDCl_3$ solution at −40 °C reveals a steady reduction of both the ring and methyl proton signal intensities with time, while the $^{31}P\{^1H\}$ NMR spectrum shows that the cation remains intact. No increase in the intensity of the $CHCl_3$ signal accompanies this process, however, indicating that H–D exchange with the solvent is not responsible. Moreover, the ^{31}P signals due to the cation slowly decrease, being replaced by that of *trans*-$[PdCl(C_6H_4N{=}NPh)(PEt_3)_2]$ (**5**). We conclude that the $C_5H_4Me^-$ ion reacts irreversibly with $CDCl_3$, probably producing Cl^-, which reacts slowly with the cation. We have shown previously that Cl^- rapidly converts $[Pd(C_6H_4N{=}NPh)(PEt_3)_3]^+$ to **5** and PEt_3 at 25 °C.[1]

The η^1-cyclopentadienyl complex *trans*-$[Pd(\eta^1\text{-}C_5H_4Me)(C_6H_4N{=}NPh)(PEt_3)_2]$ also reacts with $CDCl_3$ to produce **5** at temperatures above 0 °C, and also without an increase in the amount of $CHCl_3$ present. The several H–D exchange mechanisms that operate for the cyclopentadienyls[1,4] are believed to involve acid–base equilibria. It would thus seem that the methyl substituent renders the C_5H_4Me group more reactive toward the halogenated solvent, but too basic to participate in exchange equilibria.

$[Pd(C_6H_4N{=}NPh)(PEt_3)_3]^+C_5H_4SiMe_3^-$ also decomposes to **5** in $CDCl_3$ solution at −50 °C without any H–D exchange, but *trans*-$[Pd(\eta^1\text{-}C_5H_4SiMe_3)(C_6H_4N{=}NPh)(PEt_3)_2]$ decomposes at 0 °C, this time accompanied by $CHCl_3$ production. The acidity of $C_5H_5SiMe_3$ is thus presumably intermediate between C_5H_6 and C_5H_5Me.

All of the analogues of **2**, **3**, and **4** examined here react finally and irreversibly with $CDCl_3$ or CD_2Cl_2 over about 24 h at 25 °C to yield *trans*-$[PdCl(C_6H_4N{=}NPh)(PEt_3)_2]$ (**5**) or an analogue thereof.

2. Platinum Compounds. Reactions of $[Pt(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)]$ with 2 mol equiv of PEt_3 in toluene-d_8 solution at low temperature reveal some intriguing differences compared to those of the palladium compounds. As would be expected, the initial reactions are slower than those involving palladium, barely proceeding at −80 °C and still very slow at −60°C. The main product at these temperaures is *cis*-$[Pt(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$, with smaller amounts of the trans isomer. The $^{31}P\{^1H\}$ NMR spectrum of *cis*-$[Pt(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ reveals Pt–P coupling constants of 1837 and 2518 Hz, characteristic of tertiary phosphines trans to aryl and η^1-cyclopentadienyl, respectively.[6] These data are presented in Table III. As for the related reactions in chlorinated solvents,[1] no trace of any compound of the type $[Pt(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)]$, nor indeed of any mono(phosphine) complex, is detected, and it can be concluded that any such species must react with a second tertiary phosphine faster than they are produced. No ionic

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Table III. NMR Parameters (ppm) for the Compounds [Pt(C_5H_4R)($C_6H_4N{=}NPh$)(PEt_3)$_2$] in C_7D_8 Solution

geom	C_5H_4R bonding	δ(P) ($^1J_{PtP}$, Hz)	δ(H) (C_5H_4R) (J_{PtH}, Hz)	δ(C) (J_{PtC}, Hz)
trans	η^1-C_5H_5[a]	6.6 (2832)	6.48 (23)	91.2 (24) (C_5H_5)
cis	η^1-C_5H_5[a]	4.1 d (2518) 7.4 d (1837) ($^2J_{PP}$ 15)	6.12[b] (32)	ca. 114 br (C_5H_5)
trans	η^1-$C_5H_4SiMe_3$[c]	6.8 br (2818)		
cis	η^1-$C_5H_4SiMe_3$[c]	4.2 d (2538) 7.5 d (1848) ($^2J_{PP}$ 14)		
trans	sp^2-C_5H_5 (A)[d]	8.9 (2833)	3.06[e,f] 6.52 6.95	51.9 (47) 132.1 (28) 134.0 (38) 135.4 (53) 166.3 t (616) ($^2J_{PP}$ 12)
trans	sp^2-C_5H_5 (B)[d]	9.3 (2820)	3.02[e] 6.26 6.62	43.9 (49) 129.3[g] 133.1 br[g] 158.0 br[g]
cis	sp^2-C_5H_5[c]	3.2 d (1870) 5.9 d (1884) ($^2J_{PP}$ 16)	2.98 d (11)[h]	
trans	sp^2-$C_5H_4SiMe_3$[d]	8.8 (2834)	3.18[e] 6.57 7.21	

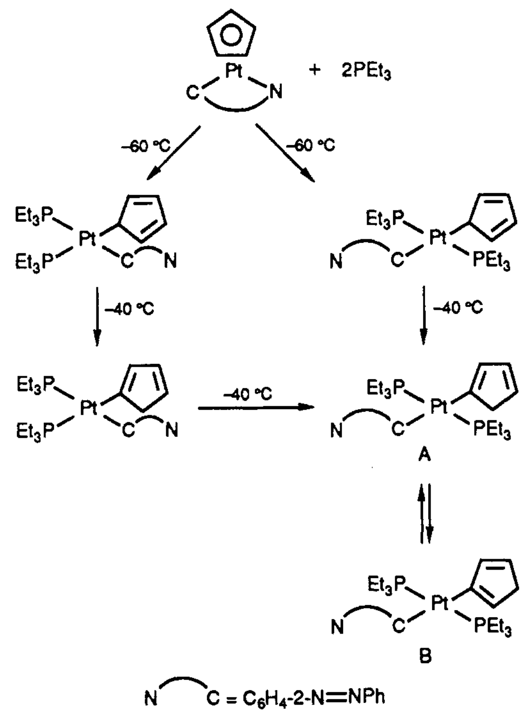
[a] At −25 °C. [b] Apparent triplet with J_{PH} = 3 Hz. [c] At −40 °C. [d] At +25 °C. [e] ^{1}H chemical shifts determined with use of ^{1}H–^{1}H homonuclear correlation experiments. [f] Values in CD_2Cl_2 solution at 25 °C are 2.83, 6.20, and 6.59 ppm. [g] J_{PtC} not observed. The other ^{13}C resonance is not observed. [h] Other signals obscured by the aromatic resonances.

species are produced in toluene solution.

Although *cis*- and *trans*-[Pt(η^1-C_5H_5)($C_6H_4N{=}NPh$)(PEt_3)$_2$] are formed more slowly than their palladium counterparts, they decompose more readily and by a different route. If the compounds are kept at −40 °C, the singlet ^{31}P NMR signal for the trans isomer and the two doublets due to the cis isomer are replaced over 2 or 3 days by a new singlet and pair of doublets, which we assign to trans and cis complexes containing sp^2-carbon-bonded vinylic cyclopentadienyls (Scheme II). The vinylic compound *cis*-[Pt(C_5H_5-sp^2)($C_6H_4N{=}NPh$)(PEt_3)$_2$] is not formed in sufficient quantity to be characterized fully by NMR spectroscopy, but its ^{31}P parameters are given in Table III. The trans vinylic compound A has been characterized fully by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. The C_5H_5 ring exhibits ^{1}H resonances at 3.06, 6.52, and 6.95 ppm, their mutual coupling being revealed by ^{1}H–^{1}H homonuclear correlation (COSY) experiments (there are two overlapping signals at 6.95 ppm). Five resonances are detected in the ^{13}C{^{1}H} NMR spectrum, all of which show coupling to platinum. The methylene carbon appears at 51.9 ppm, the three methine carbons resonate in the region 132.1–135.4 ppm, and the ipso carbon appears as a triplet (due to coupling to the two equivalent P atoms) at 166.3 ppm. The $^1J_{PtC}$ value of 616 Hz is typical of a carbon atom lying trans to a ligand of high trans influence, such as an aryl group[7] (Table III). The vinylic compound *cis*-[Pt(C_5H_5-sp^2)($C_6H_4N{=}NPh$)(PEt_3)$_2$] isomerizes to the trans form A over 1 week at −40 °C or a few hours at 0 °C.

When reactions of [Pt(η^5-C_5H_5)($C_6H_4N{=}NPh$)] and PEt_3 are carried out at room temperature in toluene, benzene, methylene chloride, or chloroform solution, the solution turns green and the vinylic cyclopentadienyl compound *trans*-[Pt(C_5H_5-sp^2)($C_6H_4N{=}NPh$)(PEt_3)$_2$] (A) is formed rapidly. Over about 2 weeks at room temperature, however, this compound isomerizes to and equilibrates with a second *trans*-bis(phosphine) complex, which we assign to the alternative sp^2-carbon-bonded vinylic cyclopentadienyl compound B, in which the CH_2 group is at the 3-position on the cyclopentadienyl ring (Scheme II). Compound B has been characterized spectroscopically and shows features similar to those of A. Three ^{1}H signals are again observed. The methylene carbon appears at 43.9 ppm with a well-resolved coupling to platinum, but the other ^{13}C signals are broad (Table III). Isomerization to B is accompanied by deterioration of the sample. Decomposition takes place relatively slowly in hydrocarbon solvents at room temperaure to produce an intractable mixture of many products, but in halogenated solvents the vinylic cyclopentadienyls react steadily with the solvent to produce *trans*-[PtCl($C_6H_4N{=}NPh$)(PEt_3)$_2$], the platinum analogue of 5.[1]

Scheme II



Isomerizations of η^1-cyclopentadienyl complexes to vinylic species are well-known, particularly among main-group-element species,[8] and this behavior of *cis*- and *trans*-[Pt(η^1-C_5H_5)($C_6H_4N{=}NPh$)(PEt_3)$_2$] closely resem-

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bles that of the boron compound $Me_2BC_5H_5$, in which the fluxional η^1-cyclopentadienyl is converted sequentially by two 1,2-hydrogen shifts to the vinylic-bonded species.[9] As far as we are aware, however, there is only one other report of such a process operating at platinum, and this is in 18-electron species.[10] Many other investigations of 16-electron η^1-C_5H_5 platinum complexes have revealed no counterpart to this isomerization,[6,11] making the facile process described here and its contrast to the palladium analogue all the more striking.

The (trimethylsilyl)cyclopentadienyl complex $[Pt(\eta^5\text{-}C_5H_4SiMe_3)(C_6H_4N{=}NPh)]$ behaves in a similar manner, reacting with PEt_3 at low temperature to produce *cis*- and *trans*-bis(phosphine) complexes with η^1-$C_5H_4SiMe_3$ ligands. At higher temperatures these species, too, are replaced by cis and trans analogues of the vinylic cyclopentadienyls, which at room temperature appear to convert to a single isomer of *trans*-$[Pt(C_5H_4SiMe_3\text{-}sp^2)(C_6H_4N{=}NPh)(PEt_3)_2]$ (Table III). When this species stands for 1 day at ambient temperature, however, a collection of new trans isomers is produced, and this was not examined further. The initial production of a single isomer of the Me_3Si-substituted vinylic cyclopentadienyl complex would seem to indicate that it results from a single preferred orientation of the η^1-$C_5H_4SiMe_3$ species, presumably with the bulky trimethylsilyl substituent as far removed as possible from platinum.

3. Fluxionality. We have shown recently that rotation about the metal–aryl bond in complexes of the type *trans*-$[MCl(C_6H_4\text{-}2\text{-}N{=}NPh)(PMe_2Ph)_2]$ and *trans*-$[M(am)(C_6H_4\text{-}2\text{-}N{=}NPh)L_2]^+$ (M = Pd, Pt; L = PMe_2Ph, PMe_3, PEt_3; am = 2-fluoropyridine, 2,6-dimethylpyridine) is slow at temperatures below 273 K.[12] In the amine complexes, this gives rise to syn and anti isomers in the case of 2-fluoropyridine and to nonequivalent methyls with 2,6-dimethylpyridine. Thus, we may infer that the 2-(phenylazo)phenyl group lies perpendicular to the molecular plane in molecules of the type $[M(C_5H_4R)(C_6H_4N{=}NPh)(PEt_3)_2]$ and cannot readily rotate past the two cis PEt_3 ligands at temperatures below 273 K.

With this in mind, we note that all the compounds of the type *trans*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$, and the sp^2-bonded, vinylic cyclopentadienyl complexes of platinum, reveal variable-temperature ^{31}P NMR spectroscopic phenomena which indicate that rotations about *both* the metal–aryl and metal–cyclopentadienyl bonds must be hindered. The observed effects are manifested in different ways for the two compound types due to the different geometrical properties of the η^1- and sp^2-bonded C_5H_4R groups.

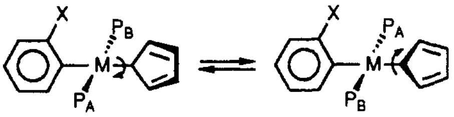
In each of the compounds *trans*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ the singlet ^{31}P NMR resonance broadens and decoalesces at low temperatures (typically ~−90 °C in either C_7D_8 or CD_2Cl_2 solution). Below the coalescence point an AB "quartet" (accompanied by ABX satellites in the platinum case) becomes apparent. In some cases a C_7D_8/CF_2Cl_2 solvent mixture is needed to reach temperatures low enough to resolve the AB pattern. The ^{31}P NMR parameters and coalescence temperatures are listed in Table IV.

Table IV. Low-Temperature ^{31}P NMR Parameters (ppm) and Coalescence Temperatures for Compounds of the Type *trans*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$

M	R	X	solvent (temp, °C)	δ(P) ($^2J_{PP}$, Hz)	T_c, °C[a]
Pd	H	N=NPh[b]	C_7D_8/CF_2Cl_2 (−110)	7.6, 10.2 (398)	−80[c]
			CD_2Cl_2		−98
Pd	Me	N=NPh	C_7D_8 (−95)	8.4, 11.7 (400)	−83
			CD_2Cl_2		−83
Pd	$SiMe_3$	N=NPh	C_7D_8 (−95)	8.9, 10.2 (408)	−75
			CD_2Cl_2		−82
Pd	H	CH=NMe	C_7D_8/CF_2Cl_2 (−120)	8.2, 11.5 (397)	−86[c]
			CD_2Cl_2		−93
Pd	H	2-C_5H_4N	C_7D_8/CF_2Cl_2 (−120)	3.1, 8.8 (392)	−94[c]
Pt	H	N=NPh	C_7D_8/CF_2Cl_2 (−100)	3.3 ($^1J_{PtP}$ 2857) 10.2 ($^1J_{PtP}$ 2741) (410)	−80 (±2)
			CD_2Cl_2		−82 (±2)
Pt	$SiMe_3$	N=NPh	CD_2Cl_2 (−100)	3.9 ($^1J_{PtP}$ 2721) 10.7 ($^1J_{PtP}$ 2859) (405)	−60 (±2)

[a] ±1 °C except where stated otherwise. [b] T_c values (°C) of related compounds in CD_2Cl_2 solution: *trans*-$[Pd(\eta^1\text{-}C_5D_5)(C_6H_4N{=}NPh)(PEt_3)_2$, −97; *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}N\text{-}2\text{-}C_6H_4Me)(PEt_3)_2]$, −96; *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}N\text{-}3\text{-}C_6H_4Me)(PEt_3)_2]$, −96; *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}N\text{-}4\text{-}C_6H_4Me)(PEt_3)_2]$, −98; *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PBu_3)_2]$, −98. [c] T_c measured for C_7D_8 solutions.

Scheme III



This temperature dependence is typical of chemically nonequivalent phosphorus atoms which achieve apparent high-temperature equivalence through rapid fluxionality. Similar observations on the compound *trans*-$[Pt(CPh{=}CHPh)\{CH(SO_2CF_3)_2\}(PPh_3)_2]$ have been ascribed to hindered rotation about the Pt–$CH(SO_2CF_3)_2$ bond.[13] In our compounds we assign the phenomenon to rotations about the metal to η^1-cyclopentadienyl bonds (Scheme III). Most structural information on η^1-cyclopentadienyl complexes indicates the rings to be planar, but with the metal bent out of the plane at the pseudotetrahedral carbon atom.[11e,14] The ring must thus lie perpendicular to the molecular plane and be oriented toward one of the P atoms in *trans*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$ to account for the observed low-temperature inequivalence. Fast rotation about the M–C_5H_4R bond at higher temperatures (Scheme III) will interconvert P_A and P_B.

An additional investigation was made of the trans mixed-phosphine complex $[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)(PBu_3)]$, prepared in toluene-$d_8$ solution by the addition of PBu_3 to $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)]$ at

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Table V. ^{31}P NMR Parameters (ppm) and T_c Values for *trans*-$[Pt(sp^2\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ in C_7D_8 Solution

compd	$\delta(P)$ ($^1J_{PtP}$, Hz)^a	T_c, °C
A	major species 9.4 (2807) minor species 9.2 (2793)	-40
B	major species 10.1 (2792) minor speecies 9.7 (2794)	-2

^{a} At -60 °C.

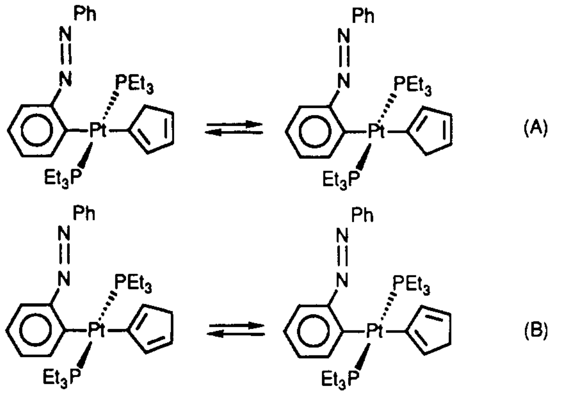
-50 °C. At and below this temperature it remains the major species present, though it is accompanied by small amounts of *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)_2]$ and *trans*-$[Pd(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PBu_3)_2]$ compounds present from its formation. The ^{31}P NMR spectrum of the mixed-phosphine complex reveals the expected AB "quartet" above the coalescence temperature ($\delta(PEt_3)$ 6.28, $\delta(PBu_3)$ 3.97, J_{PP} = 405 Hz; $\delta(C_5H_5)$ 6.66; all at -50 °C). At about -100 °C the lines of the AB pattern broaden and split, and at lower temperatures new resonances consistent with the formation of two AB quartets emerge, behavior consistent with the resolution of two isomers of this compound with the η^1-C_5H_5 ring lying closer to either PEt_3 or PBu_3.

Most η^1-cyclopentadienyls are believed to undergo fluxional "ring whizzing" via 1,2-shifts of the metal around the ring, analogous to 1,5-sigmatropic rearrangements of organic dienes, and such motions are suprafacial.[5a,d,15] On the other hand, 1,3-shifts would be expected to be antarafacial. In all of the cyclopentadienyl compounds studied here, the ring motion remains rapid (as determined by ^{1}H NMR spectroscopy) at temperatures below the decoalescence of the phosphorus signals and, therefore, must involve migration around one face of the ring. There is thus no evidence that the ring whizzing is by other than the conventional 1,2-shifts, P_A and P_B being interconverted by rotations about the M–C bonds.

In contrast to the compounds of the type *trans*-$[M(\eta^1\text{-}C_5H_4R)(C_6H_4\text{-}2\text{-}X)(PEt_3)_2]$, in which the ^{31}P signals decoalesce and resolve to AB systems at low temperatures, the vinylic cyclopentadienylplatinum compounds show ^{31}P signals that simply broaden and then resolve into two sharp signals as the temperature is lowered. The intensities of these signals are unequal, but each has a very similar Pt–P coupling constant (Table V). This behavior is typical of compounds with two asymmetric planar groups perpendicular to the molecular plane, which resolve into syn and anti isomers[16] as rotation about the Pt–C bonds slows (Scheme IV). The higher coalescence temperature of *trans*-$[Pt(C_5H_5\text{-}sp^2)(C_6H_4N{=}NPh)(PEt_3)_2]$ (Scheme IVB), compared with that of its isomer (Scheme IVA), presumably means that ligand rotation about the Pt–C^3 bond is more hindered in the former. Vinyls, like aryls, have been shown to adopt ground-state conformations perpendicular to the molecular planes of square-planar species.[16c,17]

4. Conclusions. Most striking are the ways in which the platinum compounds differ from those of palladium, namely, the apparent inability of Pt to form analogues of $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)]$ (**2**) and the rapid rearrangement of platinum η^1-cyclopentadienyls to produce sp^2-bonded vinyl species. A possible explanation for the former is that the 16-electron η^1-cyclopentadienyl complex $[Pt(\eta^1\text{-}C_5H_5)(C_6H_4N{=}NPh)(PEt_3)]$ (P trans to N) may be thermodynamically preferred to the 18-electron compound, whereas the opposite is the case for palladium.

Scheme IV



The nature of the fluxional behavior of the compounds provides the structural information that in solution the η^1-cyclopentadienyl ligands must adopt ground-state conformations with the rings perpendicular to the molecular planes but bent at C^1 toward one phosphine or the other. The sp^2-bonded vinylic C^2- and C^3-bonded cyclopentadienyls, on the other hand, must adopt perpendicular conformations symmetrically placed between the two phosphines, analogous to the case for ortho-substituted aryl groups.

Experimental Section

NMR spectra were recorded on a Varian XL-300 spectrometer operating in the FT mode. Microanalyses were performed at the University of Glasgow. Preparative details for most of the compounds used have been presented previously, as has the in situ preparation of their PEt_3 derivatives in solution.[1,2] Reactions and NMR operations were carried out under an atmosphere of pure N_2 or Ar.

Preparation of $[Pd(\eta^5\text{-}C_5H_5)(C_6H_4\text{-}2\text{-}\{2\text{-}C_5H_4N\})]$. A suspension of cyclopentadienyllithium was prepared by adding 11.0 mL of a solution of 1.55 M *n*-butyllithium in hexane to cyclopentadiene (3 mL) in ether (100 mL). To this was added $[Pd_2(\mu\text{-}Cl)_2(C_6H_4\text{-}2\text{-}\{2\text{-}C_5H_4N\})_2]$[18] (4.5 g, 7.6 mmol). Stirring for 18 h resulted in formation of a deep red-brown solution and a black solid. After filtration and removal of most of the solvent at reduced pressure, deep purple crystals of the product were deposited (0.54 g, 11%). Anal. Calcd for $C_{16}H_{13}NPd$: C, 59.0; H, 4.0; N, 4.3. Found: C, 59.2; H, 3.9; N, 4.3. ^{1}H NMR data (C_7D_8, -40 °C): δ(H) 5.83 (s, Cp), 5.95 (ddd, 1.3, 5.6, 7.1 Hz), 6.71 (ddd, 1.5, ~7.5, ~7.5 Hz), 7.05 (dd, 1.3, 7.2 Hz), 7.24 (dd, 1.5, 7.8 Hz), 7.73 (dd, 1.3, 7.6 Hz), 7.92 (dd, <1, 5.6 Hz), other signals obscured by solvent.

[(Trimethylsilyl)cyclopentadienyl][2-(phenylazo)phenyl]platinum. To a stirred solution of $Me_3SiC_5H_5$ (1.5 mL) in ether (50 mL) was added 2.0 mL of a solution of *n*-butyllithium in hexane (1.5 M). A white precipitate formed. To this was added $[Pt_2(\mu\text{-}Cl)_2(C_6H_4N{=}NC_6H_5)_2]$ (0.9 g, 1.1 mmol) in ether (40 mL). The solution turned deep red. After 2 h the solution was filtered to remove 0.5 g of a purple solid that contained some starting material. Evaporation of the solution and crystallization from petroleum ether (bp 40–60 °C) yielded 180 mg of the product as deep red crystals. Anal. Calcd for $C_{20}H_{24}PtSi$: C, 46.8; H, 4.3; N, 5.45. Found: C, 47.5; H, 4.5; N, 5.3. NMR data ($CDCl_3$, room temperature): ^{1}H, δ(H) 0.07 ($SiMe_3$), 5.62 (apparent t, 1.9 Hz, J_{PtH} = 11.6 Hz, Cp), 6.02 (apparent t, 1.9 Hz, J_{PtH} = 18.4 Hz, Cp), 6.78 (ddd, 1.4, 6.9, 8.3 Hz), 7.09 (ddd, 1.2, 7.0, 8.2 Hz), 7.30–7.45 (m), 7.70 (dt, 8.0, 1.7 Hz), 8.01 (dd, <1, 8.0 Hz, J_{PtH} = 39.2 Hz),

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8.30 (dd, 1.4, 8.1 Hz, J_{PtH} = 10.0 Hz); $^{13}C\{^1H\}$, δ(C) 0.01 ($SiMe_3$), 93.59 (J_{PtC} = 36.1 Hz, Cp), 94.20 (J_{PtC} = 20.2 Hz, Cp), 106.71 (ipso, Cp), 122.74, 124.48 (int 2), 124.87 (J_{PtC} = 58.0 Hz), 128.42 (int 2), 128.76 (int 2), 137.55 (J_{PtC} = 104.9 Hz), 156.87 (J_{PtC} = 105.8 Hz), 161.08 (J_{PtC} = 95.3 Hz), 165.74 (J_{PtC} = 1351.5 Hz).

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Synthesis and Structural Characterization of $(C_5Me_5)Zr(R)_2(L)_n{}^+$ Complexes

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The reaction of $(C_5Me_5)Zr(CH_3)_3$ with $[(C_5H_4Me)_2Fe][BPh_4]$ in THF yields $[(C_5Me_5)Zr(CH_3)_2(THF)_2][BPh_4]$ (**1**) via oxidative cleavage of a $Zr-CH_3$ bond. X-ray diffraction reveals that the cation of **1** adopts a square-pyramidal/four-legged piano-stool structure with cis CH_3 groups. The orientations of the THF ligands and the Zr–O bond distances suggest that Zr–O π-bonding is important for at least one of the THF ligands. Data for **1**: a = 14.551 (2) Å, b = 15.191 (4) Å, c = 17.852 (19) Å, β = 92.26 (3)°, V = 3943 (6) Å^3, Z = 4 in space group $P2_1/c$. Reaction of **1** with excess dmpe in THF solution yields $[(C_5Me_5)Zr(CH_3)_2(dmpe)(THF)][BPh_4]$ (**2**), which also has been characterized by X-ray diffraction. The cation of **2** has a distorted-octahedral structure with the Cp* ligand in an axial position and equatorial/axial coordination of the dmpe ligand. The two CH_3 groups are equatorial and mutually trans. The THF ligand is equatorial and trans to the dmpe ligand and lies in the square plane in an orientation that precludes Zr–O π-bonding. Data for **2**: a = 10.110 (3) Å, b = 14.701 (8) Å, c = 17.190 (4) Å, α = 70.14 (3)°, β = 78.72 (2)°, γ = 84.68 (4)°, V = 2355.6 (1.9) Å^3, Z = 2 in space group $P\bar{1}$. The reaction of $(C_5Me_5)Zr(CH_2Ph)_3$ with $[(C_5H_4Me)_2Fe][BPh_4]$ in THF at 0 °C yields the thermally sensitive compound $[(C_5Me_5)Zr(CH_2Ph)_2(THF)][BPh_4]$ (**3**). The benzyl ligands of **3** are distorted, most likely as a result of weak donor interactions between the Ph rings and the cationic Zr center.

Cationic Zr(IV) alkyl complexes of general type $Cp^*{}_2Zr(R)^+$ (Cp* = C_5Me_5) and $Cp_2Zr(R)(L)_n{}^+$ contain highly unsaturated Lewis-acidic metal centers, vacant coordination sites and/or labile ligands L, and reactive Zr–R bonds. This combination promotes insertion and σ-bond metathesis chemistry.[1-3] It is currently believed that cationic species of this type play a key role in metallocene-based olefin polymerization catalyst systems.[1-4] Cationic mono-C_5R_5 Zr(IV) alkyl complexes $(C_5R_5)Zr(R)_2(L)_n{}^+$ are of interest because their increased unsaturation may lead to even higher reactivity, particularly with sterically crowded substrates.[5,6] It is also possible that $(C_5R_5)M(R)_2{}^+$ species play a role in some $(C_5R_5)MX_3$-based olefin polymerization catalysts.[7] This paper describes the synthesis and characterization of several $(C_5Me_5)Zr(R)_2(L)_n{}^+$ complexes which are the first examples of this class.

Results and Discussion

Synthesis of $[Cp^*Zr(CH_3)_2(THF)_2][BPh_4]$ (1). The reaction of $Cp^*Zr(CH_3)_3$ with $[Cp'_2Fe][BPh_4]$ (Cp′ =

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