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Pentamethylcyclopentadienyl Platinum Chemistry: Synthesis, X-ray Structure, Two-Dimensional NMR Spectroscopy, and Reactivity of $[Pt(\eta\text{-}C_5Me_5)\{\sigma{:}\eta^2\text{-}C_8H_{12}(C_5Me_5)\}]$

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Treatment of $[Pt(\eta\text{-}C_8H_{12})Cl_2]$ with NaCp* (Cp* = C_5Me_5) gives $[Pt(\eta\text{-}C_5Me_5)\{\sigma{:}\eta^2\text{-}C_8H_{12}(Cp^*)\}]$, which has been characterized by two-dimensional NMR spectroscopy and a single-crystal X-ray structure determination. Reaction of $[Pt(\eta\text{-}C_5Me_5)\{\sigma{:}\eta^2\text{-}C_8H_{12}(Cp^*)\}]$ with HBF_4 causes elimination of Cp*H to give $[Pt(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_{12})]BF_4$. $[Pt(PMe_3)_2\{\sigma^2\text{-}C_8H_{12}(Cp^*)_2\}]$ is formed by reaction of $[Pt(\eta\text{-}C_5Me_5)\{\sigma{:}\eta^2\text{-}C_8H_{12}(Cp^*)\}]$ with trimethylphosphine. Double quantum filtered phase sensitive (DQPH), two-dimensional correlated NMR spectroscopy (COSY) allows the characterization of $[Pt(PMe_3)_2\{\sigma^2\text{-}C_8H_{12}(Cp^*)_2\}]$. Reaction of $[Pt(\eta\text{-}C_8H_{12})Cl_2]$ with either 1 or 2 equiv of NaInd (Ind = C_9H_7) gives the compounds $[Pt(\eta\text{-}C_8H_{12})(\eta^1\text{-}Ind)Cl]$ and $[Pt(\eta\text{-}C_8H_{12})(\eta^1\text{-}Ind)_2]$, respectively. $[Pt(\eta\text{-}C_8H_{12})(\eta^1\text{-}Ind)_2]$ exists as a mixture of diasterioisomers.

Introduction

Pentamethylcyclopentadienyl transition-metal complexes are ubiquitous in organometallic chemistry, and these compounds have exhibited examples of fundamental processes in organometallic chemistry such as olefin polymerization,[1] β-elimination,[2] C–H bond activation,[3] and agostic interactions.[4] However, the chemistry of η-Cp* complexes of the platinum group metals has been relatively unexplored in comparison to the remaining transition metals. For example, only one η-Cp* complex of platinum has been reported, i.e., $[Pt_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br)_3]Br_3$.[5] The proposed structure of the compound was only tentative, due to insolubility and instability.

We were interested to prepare new η-Cp* platinum complexes, with view to ascertaining whether the high stability of the η-Cp*–[M] bond commonly found for the other transition metals also occurs for platinum.

Results and Discussion

Treatment of $[Pt(\eta\text{-}C_8H_{12})Cl_2]$ with 2 equiv of either NaCp* or LiCp* (Cp* = C_5Me_5) in tetrahydrofuran gives good yields (60–70%) of bright yellow crystals of $[Pt(\eta\text{-}C_5Me_5)\{\sigma{:}\eta^2\text{-}C_8H_{12}(Cp^*)\}]$ (1). Compound 1 exhibits complex ^1H and ^{13}C NMR spectra, and 18 ^1H and 20 ^{13}C environments are resolvable. However, it is possible to assign the NMR spectra of 1 and the remaining compounds by using the two-dimensional NMR techniques described below. The ^{13}C NMR spectrum of 1 contains a resonance which exhibits a characteristically large $^1J(^{195}Pt\text{-}^{13}C)$ of 798 Hz which may be assigned as C_c, the σ-bonded carbon resonance. A combination of two-dimensional $^1H\text{-}^1H$ COSY[6] and $^{13}C\text{-}^1H$ heteronuclear shift correlation[6] experiments establishes the remaining connectivities.

The available spectroscopic data did not allow us to unambiguously assign 1 as the endo or exo isomer; however, the exo structure was confirmed by a single-crystal X-ray analysis.

Table I. Crystallographic Details for $[Pt(\eta\text{-}C_5Me_5)\{\sigma{:}\eta^2C_8H_{12}(Cp^*)\}]$ (1)

formula	$PtC_{28}H_{42}$
formula mass	573.73
space group	$P2_12_12_1$
a, Å	8.8743 (8)
b, Å	12.957 (2)
c, Å	21.762 (6)
V, Å^3	2502.3
Z	4
ρ(calcd), g cm^{-3}	1.52
cryst dimens, mm	1.2 × 0.8 × 0.4
μ(Mo Kα), cm^{-1}	56.76
F(000)	1152
temp, °C	20
scan mode	ω–2θ
2θ limits, deg	2.0–32.0
max h,k,l	10,16,26
unique data	7023
unique data with $I > 3\sigma(I)$	2361
final no. of variables	264
no. of restraints	15
weighting scheme	3-term Chebyshev
weighting coeff	144.2, 185.7, 56.2
extinctn parameter	19 (7)
R^a	0.0252
$R_w{}^b$	0.0417
largest residual, e Å^{-3}	0.9

$^a R = \sum(|F_o| - |F_c|)/\sum(|F_o|)$. $^b R_w = \sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2$.

Crystal Structure Determination. Crystals of 1 were grown from pentane solution at −30 °C. Compound 1 crystallizes in the orthrombic system with space group $P2_12_12_1$ (Table I). The molecular structure of 1 is shown in Figure 1, and the bond distances and angles are given in Table II. The results of the X-ray analysis confirm the molecular structure proposed on the basis of the ^1H and ^{13}C NMR data. One Cp* ligand is bonded to the platinum in an η^5-fashion $\{Pt\text{-}(Cp^*)_{centroid} = 1.971\ (9)\ \text{Å}\}$. The distance being similar to that observed in $[Pt(\eta\text{-}C_5H_5)(Me)_3]$ $\{Pt\text{-}(Cp)_{centroid} = 1.91\ (6)\ \text{Å}\}$.[7] The other Cp* ligand in 1 appears as an exo substituent on the cycloocta-1,5-dienyl ligand. The structural features of this unusal $\{\sigma{:}\eta^2\text{-}C_8H_{12}(Cp^*)\}$ ligand may be compared to those of the 2-methoxycycloocta-1,5-dienyl ligand in $[Pt(\sigma{:}\eta^2\text{-}$

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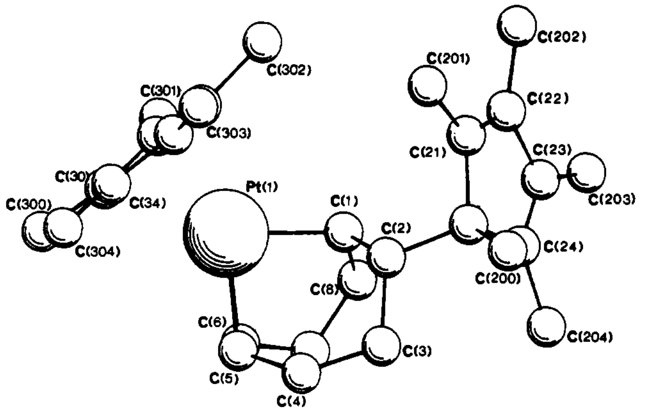

Figure 1. Molecular structure of 1 with labeling scheme.

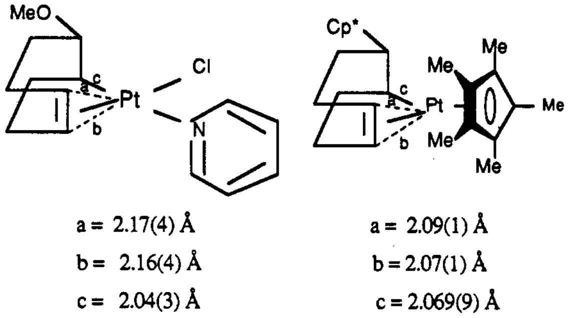

Figure 2. Comparison of the bond distances for the $\{\sigma:\eta^2\text{-}C_8H_{12}(R)\}$ ligand.

$C_8H_{12}OMe)(py)Cl]$,[8] in this example the distances *a* and *b* (Figure 2) are significantly longer than the σ-bond (*c*). This trend is not observed for 1 presumably since there is no trans influence.[9]

The Pt–C σ-bond length is 2.096 (9) Å, which is equivalent to the sum of the atomic radii[10] and falls midway in the range 2.0–2.2 Å observed for the Pt–C(sp^3) distances in many structurally characterized Pt–Me complexes.[11] The Pt–C(sp^2)$_{\text{centroid}}$ bond length of 1.96 (9) Å is short; typically Pt–olefin distances fall in the range 2.0–2.16 Å.[12]

Many years ago the related $\sigma:\eta^2$-cyclooctenyl nickel complex $[Ni(\eta\text{-}C_5H_5)(\sigma:\eta^2\text{-}C_8H_{13})]$ has been synthesized by the reaction of $[Ni(\eta\text{-}C_8H_{12})_2]$ with cyclopentadiene.[13]

When $[Pt(\eta\text{-}C_8H_{12})Cl_2]$ is treated with only 1 equiv of LiCp*, we are able to isolate 1 and unreacted $[Pt(\eta\text{-}C_8H_{12})Cl_2]$. It is probable that the first formed product is $[Pt(\eta^1\text{-}C_5Me_5)(\eta\text{-}C_8H_{12})Cl]$ which isomerizes to $[Pt(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_8H_{12})]^+Cl^-$ faster than attack by a second Cp* which would give a bis η^1-Cp* product. The proposed intermediate $[Pt(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_8H_{12})]^+$ could react further with LiCp* to yield 1 (vide infra). In fact, we have synthesized the mono $\eta^1\text{-}C_5H_5$ analogue $[Pt(\eta^1\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})Cl]$[14] by treatment of $[Pt(\eta\text{-}C_8H_{12})Cl_2]$ with 1 equiv of $n\text{-}Bu_3SnCp$, and this compound rapidly isomerizes at room temperature in CH_3CN solution to $[Pt(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_8H_{12})]^+Cl^-$.

Table II. Bond Distances and Angles for 1[a]

a. Bond Distances (Å)

Pt(1)–C(1)	2.096 (9)	C(20)–C(21)	1.53 (2)
Pt(1)–C(5)	2.09 (1)	C(20)–C(24)	1.53 (1)
Pt(1)–C(6)	2.07 (1)	C(20)–C(200)	1.56 (1)
Pt(1)–C(30)	2.327 (9)	C(21)–C(22)	1.34 (2)
Pt(1)–C(31)	2.32 (1)	C(21)–C(201)	1.48 (2)
Pt(1)–C(32)	2.24 (1)	C(22)–C(23)	1.50 (2)
Pt(1)–C(33)	2.28 (1)	C(22)–C(202)	1.52 (2)
Pt(1)–C(34)	2.38 (1)	C(23)–C(24)	1.36 (2)
		C(23)–C(203)	1.51 (2)
C(1)–C(2)	1.53 (1)	C(24)–C(204)	1.49 (2)
C(1)–C(8)	1.57 (1)	C(30)–C(31)	1.423 (7)
C(2)–C(3)	1.53 (2)	C(30)–C(34)	1.399 (7)
C(2)–C(20)	1.58 (1)	C(30)–C(300)	1.535 (8)
C(3)–C(4)	1.52 (2)	C(31)–C(32)	1.407 (7)
C(4)–C(5)	1.52 (2)	C(31)–C(301)	1.535 (8)
C(5)–C(6)	1.37 (2)	C(32)–C(33)	1.413 (7)
C(6)–C(7)	1.50 (2)	C(32)–C(302)	1.524 (9)
C(7)–C(8)	1.48 (2)	C(33)–C(34)	1.422 (7)
		C(33)–C(303)	1.518 (9)
		C(34)–C(304)	1.526 (9)

b. Bond Angles (deg)

C(5)–Pt(1)–C(1)	86.9 (5)	C(23)–C(22)–C(21)	110.0 (13)
C(6)–Pt(1)–C(1)	81.2 (5)	C(202)–C(22)–C(21)	127.0 (15)
C(6)–Pt(1)–C(5)	38.5 (5)	C(202)–C(22)–C(23)	123.0 (14)
		C(24)–C(23)–C(22)	108.8 (12)
C(8)–C(1)–C(2)	117.9 (10)	C(203)–C(23)–C(22)	123.3 (17)
C(3)–C(2)–C(1)	111.3 (9)	C(203)–C(23)–C(24)	127.9 (15)
C(20)–C(2)–C(1)	113.2 (8)	C(23)–C(24)–C(20)	108.8 (11)
C(20)–C(2)–C(3)	114.1 (9)	C(204)–C(24)–C(20)	124.6 (11)
C(4)–C(3)–C(2)	112.6 (10)	C(204)–C(24)–C(23)	126.6 (11)
C(5)–C(4)–C(3)	119.1 (10)	C(34)–C(30)–C(31)	107.94 (9)
C(6)–C(5)–C(4)	128.7 (12)	C(300)–C(30)–C(31)	124.9 (9)
C(7)–C(6)–C(5)	125.0 (12)	C(300)–C(30)–C(34)	126.3 (9)
C(8)–C(7)–C(6)	111.5 (11)	C(32)–C(31)–C(30)	107.92 (9)
C(7)–C(8)–C(1)	113.2 (10)	C(301)–C(31)–C(30)	122.0 (9)
		C(301)–C(31)–C(32)	130.1 (9)
C(21)–C(20)–C(2)	109.9 (9)	C(33)–C(32)–C(31)	107.89 (9)
C(24)–C(20)–C(2)	115.9 (8)	C(302)–C(32)–C(31)	123.8 (12)
C(24)–C(20)–C(21)	103.4 (10)	C(302)–C(32)–C(33)	127.9 (12)
C(200)–C(20)–C(2)	110.1 (9)	C(34)–C(33)–C(32)	107.88 (9)
C(200)–C(20)–C(21)	108.9 (10)	C(303)–C(33)–C(32)	124.3 (14)
C(200)–C(20)–C(24)	108.2 (9)	C(303)–C(33)–C(34)	127.2 (13)
C(22)–C(21)–C(20)	108.8 (11)	C(33)–C(34)–C(30)	107.94 (9)
C(201)–C(21)–C(20)	123.6 (12)	C(304)–C(34)–C(30)	125.5 (13)
C(201)–C(21)–C(22)	127.6 (13)	C(304)–C(34)–C(33)	126.4 (13)

[a] Estimated standard deviations are given in parentheses.

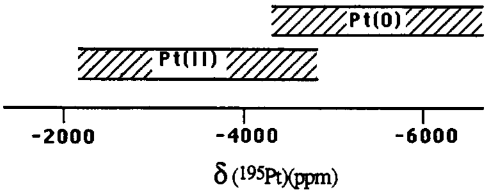

Figure 3. ^{195}Pt chemical shift range observed for Pt(0) and Pt(II) complexes.

Attempts were made to displace the $\{\sigma:\eta^2\text{-}C_8H_{12}(Cp^*)_2\}$ ligand by using protic acids or donor ligands. Treatment of 1 with HBF_4 in diethyl ether results in elimination of Cp*H to give $[Pt(\eta\text{-}C_5Me_5)(\eta\text{-}C_8H_{12})]BF_4$ (2). Compound 2 reacts instantaneously with LiCp* giving 1. Reaction of 1 with HCl(g) gives quantitative formation of $[Pt(\eta\text{-}C_8H_{12})Cl_2]$. While treatment of 1 with benzoic acid gave no reaction even at elevated temperatures. Compound 1 reacts with iodine to give $[Pt(\eta\text{-}C_8H_{12})I_2]$.

As for many other metal nuclei, a relationship exists between the oxidation state of the platinum and the δ-(^{195}Pt).[15] Both 1 and 2 exhibit highly shielded ^{195}Pt res-

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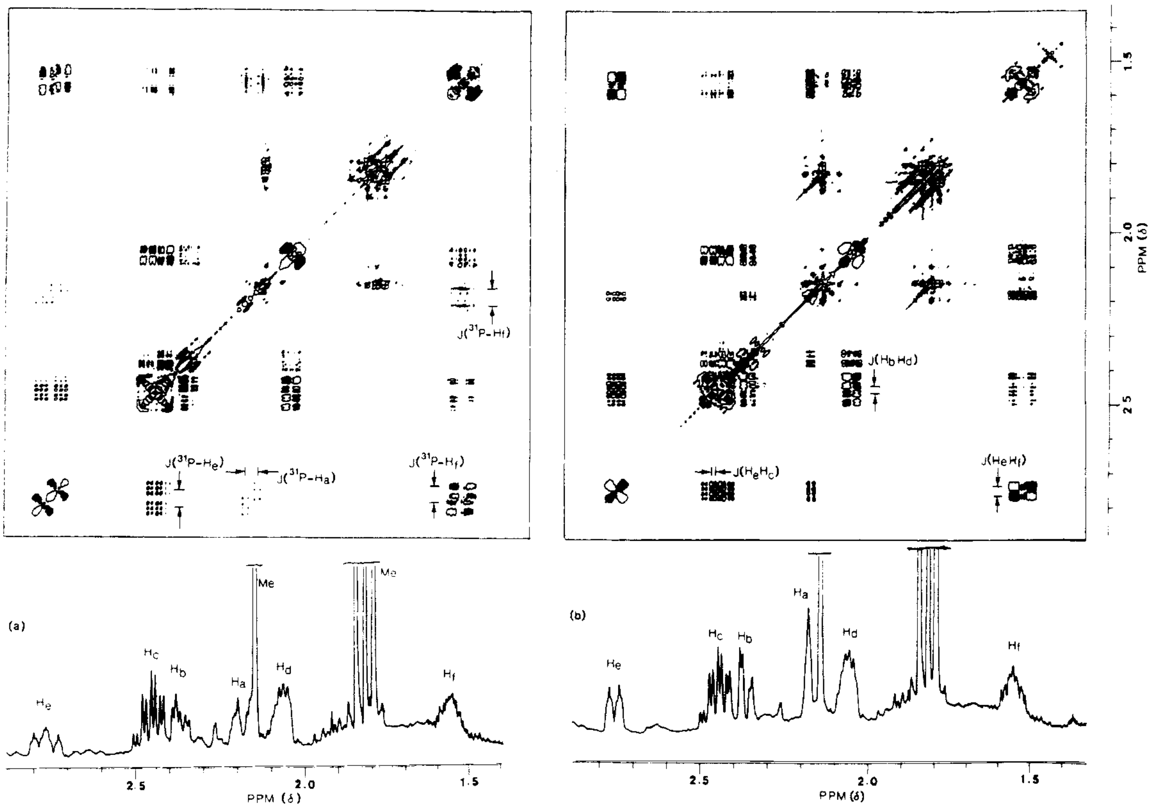

Figure 4. (a) Expanded region of the 500-MHz two-dimensional (^1H–^1H) DQPH-COSY NMR spectrum of **3** (contour plot), run on a Bruker AM 500. (Negative peaks are given as filled in contours.) (b) Spectrum as in (a) with simultaneous ^{31}P-decoupling. *Note*: 1-D spectra are not projections of the COSY matrix but are normal resolution enhanced 1-D spectra.

onances at δ–5516 and −5750, respectively (Table V). These values fall outside the range normally expected for Pt(II) complexes (Figure 3). This is presumably due to the donating ability of the η^5-C_5Me_5 ligand.

Compound **1** reacts with an excess of trimethylphosphine to give a white crystalline compound, [Pt$(PMe_3)_2\{\sigma^2$-$C_8H_{12}(Cp^*)_2\}$] (**3**). The overall reaction involves addition of two phosphine ligands with concomitant migration of the η^5-C_5Me_5 ligand to the octadienyl ligand. It is interesting to note that the migration of the η-Cp* ligand to the $\{\sigma{:}\eta^2$-$C_8H_{12}(Cp^*)\}$ ligand has occurred regiospecifically giving only the isomer which possesses a C_2 symmetry axis bisecting the P–Pt–P angle as demonstrated by the observation of a 1:4:1 triplet resonance in the $^{31}P\{^1H\}$ NMR spectrum and a binomial triplet in the $^{195}Pt\{^1H\}$ NMR spectrum. The value of $^1J(^{195}Pt$–$^{31}P)$ = 1550 Hz is at the low end of the range expected for Pt(II) complexes.[16]

In contrast to the chemistry described above with η-Cp* derivatives, treatment of [Pt(η-$C_8H_{12})Cl_2$] with 1 equiv of NaInd (Ind = C_9H_7) in tetrahydrofuran yields the mono(η^1-indenyl) derivative [Pt(η-C_8H_{12})(η-C_9H_7)Cl] (**4**). The values of $^1J(Pt$–$C_{CH})$ and the $^2J(Pt$–$H_{CH})$ coupling constants for the η^4-C_8H_{12} ligand in **4** show the effects of the strong NMR trans influence for the Ind ligand. The relevant coupling constants are given in Table VI; the data place the Ind ligand higher in the trans influence series than Cp.

Unlike the η^1-C_5H_5 or η^1-C_5Me_5 analogues compound **4** appears to be thermally stable in polar solvents and shows no evidence for isomerization to the η^5-indenyl compound. However, abstraction of Cl^- from **4** by $AgBF_4$ results in isomerization to [Pt(η-C_9H_7)(η-C_8H_{12})]BF_4 (**6**).

Reaction of [Pt(η-$C_8H_{12})Cl_2$] with excess NaInd gives the thermally unstable bis(η^1-indenyl) complex [Pt(η-C_8H_{12})(η^1-$C_9H_7)_2$] (**5**). NMR samples show significant decomposition after 12 h at room temperature. We were able to assign the ^1H and ^{13}C NMR spectra of **5** assuming there exists in solution a 1:1 mixture of diastereoisomers as shown in Scheme I.

[Pt(η-C_9H_7)(η-C_8H_{12})]BF_4 (**6**) can also be synthesized from **5** by protonation with HBF_4 in diethyl ether at −78 °C.

Two-Dimensional NMR Analysis. Two-dimensional correlated spectroscopy (COSY) has in recent years been employed as an important NMR method for the elucidation of spin–spin coupling networks in complex systems such as proteins.[17] While the early investigations used absolute value presentations of the data, more recent work has shown that phase-sensitive COSY experiments can provide important additional information, particularly with additional double quantum filtration[18] to overcome problems in line shape.[19]

The double quantum filtered phase sensitive (DQPH)-COSY experiment allows identification of the coupling network analogous to the basic COSY experiment, in addition quantitative measurements of the active spin–spin coupling constants can be obtained, in the limit of the line widths being much less than the scaler couplings.[20]

An expansion of the DQPH-COSY spectrum of **3** is shown in Figure 3a. The improved resolution and line shape offered by this experiment compared to normal COSY method with the same digital resolution has enabled

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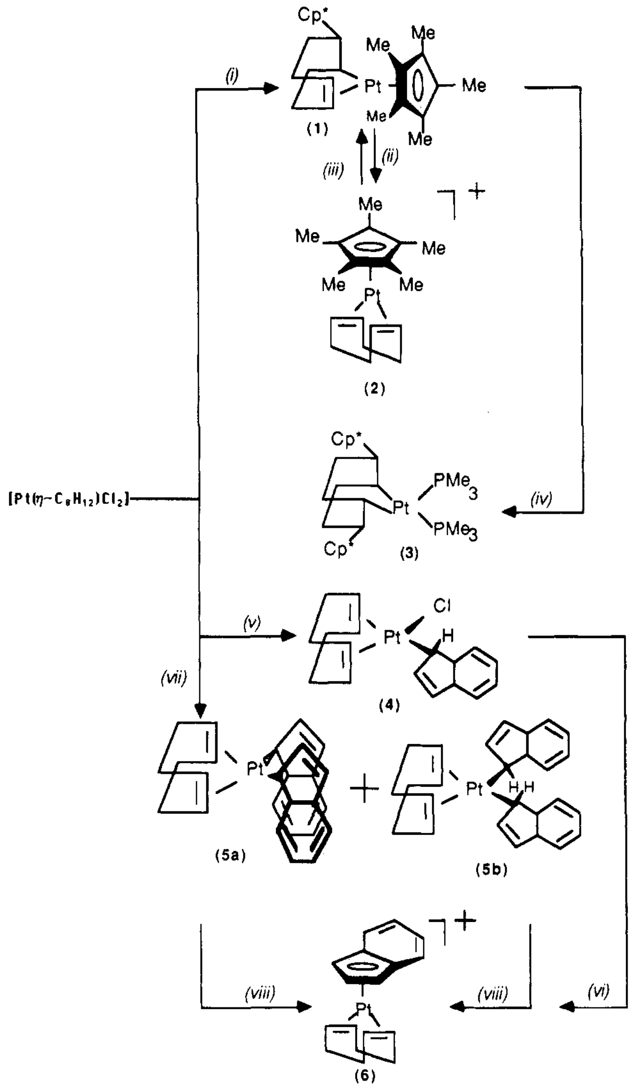
Scheme I[a]



[a] (i) NaCp* or LiCp* (2 equiv) in THF at room temperature (71%). (ii) $HBF_4 \cdot Et_2O$ (2–3 drops) in pentane at −78 °C (70%). (iii) LiCp* in THF at room temperature (80%). (iv) PMe_3(excess) in THF at room temperature for 12 h (80%). (v) NaInd (1 equiv) in THF at room temperature for 12 h (70%). (vi) $AgBF_4$ (1 equiv) in CH_2Cl_2 at room temperature (90%). (vii) NaInd (2.5 equiv) in THF at room-temperature for 12 h (71%). (viii) $HBF_4 \cdot Et_2O$ (2–3 drops) in Et_2O at −78 °C (90%).

cross peaks close to the diagonal to be clearly identified. The reversal in phase exhibited in the off-diagonal elements enables us to identify the coupling constants linking any of the connected multiplets. In cases where the couplings are quite large quantiative measurements of the active coupling constants can be obtained. It has also proved possible in this example to distinguish the homonuclear ^1H–^1H coupling from the heteronuclear ^{31}P–^1H coupling as shown in Figure 4a. This assignment was confirmed by recording the above experiment with simultaneous ^{31}P decoupling as shown in Figure 4b.

In Figure 4a,b the geminal pairs of protons can be clearly identified by their characteristically large value of ^1J(H–H). C_a was again assigned from the ^{13}C NMR spectrum where it exhibited values of $^1J(^{13}C–^{195}Pt)$ = 702 Hz, $^2J(^{13}C–^{31}P_{cis})$ = 5 Hz, and $^2J(^{13}C–^{31}P_{trans})$ = 125 Hz. The attached proton was identified by a two-dimensional ^{13}C–^1H heteronuclear shift correlation experiment. Surprisingly, this proton did not exhibit the largest $J(^{31}P–H)$.

In conclusion, we note that the two-dimensional DQPH-COSY method will prove invaluable in the future for characterization of organometallic transition-metal compounds with complex hydrocarbon ligand systems. The experiment is straightforward to implement, and the additional processing and display software required is available for most modern high-field spectrometers.

Table III. Fractional Atomic Coordinates (×10^4) for 1[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)/ *U*(equiv),[b] Å^2
Pt(1)	1197.1 (4)	196.8 (3)	−4334.0 (2)	340
C(1)	1307 (14)	−1248 (7)	−3902 (4)	357
C(2)	872 (12)	−1205 (8)	−3225 (4)	344
C(3)	−834 (13)	−1082 (10)	−3145 (5)	466
C(4)	−1410 (13)	−51 (9)	−3383 (5)	498
C(5)	−1044 (13)	268 (10)	−4038 (5)	488
C(6)	−939 (13)	−339 (10)	−4553 (5)	466
C(7)	−1042 (18)	−1492 (10)	−4557 (6)	517
C(8)	365 (15)	−1972 (9)	−4336 (6)	480
C(20)	1577 (12)	−2110 (8)	−2834 (4)	344
C(21)	3302 (13)	−2083 (10)	−2884 (5)	407
C(22)	3780 (17)	−2983 (10)	−3121 (6)	550
C(23)	2462 (16)	−3691 (12)	−3223 (7)	543
C(24)	1177 (15)	−3201 (8)	−3041 (5)	407
C(30)	1958 (11)	1395 (7)	−5068 (4)	437
C(31)	3012 (11)	567 (7)	−5069 (4)	466
C(32)	3651 (10)	504 (8)	−4478 (5)	523
C(33)	3092 (14)	1338 (9)	−4128 (4)	566
C(34)	2081 (12)	1907 (7)	−4504 (5)	509
C(200)	1122 (21)	−1994 (10)	−2144 (5)	534
C(201)	4235 (17)	−1195 (13)	−2683 (7)	649
C(202)	5395 (19)	−3283 (17)	−3274 (9)	769
C(203)	2609 (23)	−4754 (13)	−3506 (8)	776
C(204)	−371 (16)	−3648 (11)	−3025 (7)	526
C(300)	1068 (17)	1765 (14)	−5631 (6)	704
C(301)	3305 (20)	−88 (12)	−5644 (6)	705
C(302)	4886 (13)	−259 (13)	−4303 (11)	786
C(303)	3686 (29)	1642 (17)	−3499 (5)	811
C(304)	1199 (24)	2869 (10)	−4317 (13)	910

[a] Estimated standard deviations are given in parentheses. [b] *U*(equiv) = $^1/_3\{U(11) + U(22) + U(33)\}$.

Summary

It is clear from the reactivity described above that for η-cyclopentadienyl platinum complexes, the chemistry is dominated by the facility with which the $\eta^5 \rightleftharpoons \eta^1$ interconversion occurs. It appears that the order for this interconversion is Cp* ≫ Cp > Ind.

Experimental Section

General Experimental Data. Dichloro(cycloocta-1,5-diene)platinum was synthesized by the published method.[21] All manipulations were carried out under an atmosphere of dinitrogen, using standard Schlenk or vacuum line techniques. Nitrogen was purified by passage through a gas drying column containing BASF catalyst and 5-Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated pumping followed by admission of nitrogen. Solvents were predried over molecular sieves and then distilled from potassium (toluene, benzene, tetrahydrofuran) or Na–K alloy (pentane, diethyl ether) under an inert atmosphere of dinitrogen. Deuteriated solvents for NMR experiments were stored in glass ampules equipped with greaseless stopcocks over a potassium film and transferred by vacuum distillation.

Elemental analyses were performed by the analytical department of this laboratory. Low-resolution mass spectra were recorded on an AEI M.S 902 mass spectrometer, updated by a data handling system supplied by Mass Spectroscopy Services Plc, U.K.

NMR Details. All multiple pulse and two-dimensional experiments were performed on a Bruker AM500 instrument equipped with a process controller and array processor. The experiments were acquired by using standard Bruker software and processed by using an ASPECT 3000 computer. Some "in

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[21] Drew, D.; Doyle, J. R. *Inorg. Synth.* 1972, *13*, 47.

Table IV. ^{1}H and ^{13}C NMR Data for Compounds 1–6

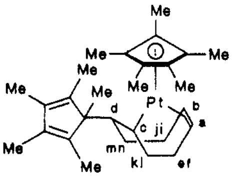
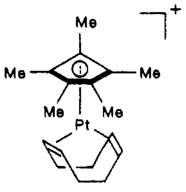
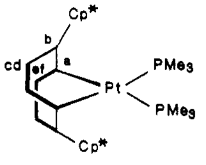
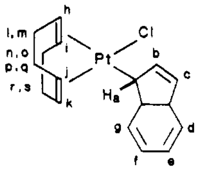
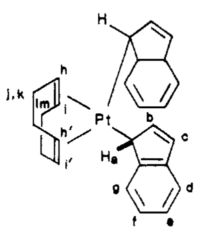
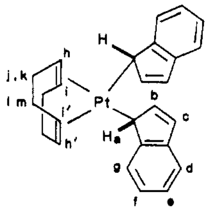
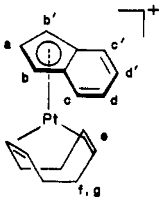
compd	NMR data[a]	
	^{1}H	^{13}C
 1	3.28 [2 H, m (7 lines), J(Pt–H$_{a/b}$) = 88, H$_a$ + H$_b$], 2.88 [1 H, ddt, J(Pt–H$_{e/f}$) = 111, J(H$_e$–H$_f$) = 15, J(H$_{e/f}$–H$_k$) = J(H$_{e/f}$–H$_c$) = 1, H$_e$ or H$_f$], 2.18 [1 H, m (20 lines), H$_f$ or H$_e$], 2.04 [1 H, m (10 lines), H$_d$], 1.89 [3 H, s, Me(Cp*)], 1.86 (2 H, m br, H$_i$ + H$_j$), 1.83 [15 H, d, J(Pt–H) = 13, η^5-C$_5$Me$_5$], 1.80 [3 H, s, *Me*(Cp*)], 1.77 (2 H, m br, H$_k$ + H$_l$), 1.76 [3 H, s, *Me*(Cp*)], 1.75 (2 H, m br, H$_m$ + H$_n$), 1.74 [3 H, s, *Me*(Cp*)], 1.01 [3 H, s, *Me*(Cp*)][b]	142.7 [s, *C*Me(Cp*)], 141.5 [s, *C*Me(Cp*)], 134.3 [s, *C*Me(Cp*)], 133.3 [s, *C*Me(Cp*)], 100.8 [d, J(Pt–C) = 10, *C*Me(η^5-C$_5$Me$_5$)], 61.2 [dd, J(Pt–C$_{a/b}$) = 291, J(C–H) = 151, C$_a$ or C$_b$], 60.2 [s, *C*Me(Cp*)], 51.5 [dd, J(Pt–C$_d$) = 34, J(C–H) = 121, C$_d$], 49.9 [d, J(Pt–C$_{b/a}$) = 319, J(C–H) = 151, C$_b$ or C$_a$], 43.4 [t, J(C–H) = 122, C$_{i,j}$], 31.5 [t, J(C–H) = 124, C$_{k,l}$], 30.4 [t, J(C–H) = 124, C$_{e,f}$], 28.0 [t, J(C–H) = 123, C$_{m,n}$], 25.8 [dt, J(Pt–C$_c$) = 798, J(C–H) = 125, C$_c$], 21.5 [q, J(C–H) = 125, *Me*(Cp*)], 13.3 [q, J(C–H) = 125, *Me*-(Cp*)], 11.8 [q, J(C–H) = 125, *Me*(Cp*)], 11.1 [q, J(C–H) = 125, *Me*(Cp*)], 11.0 [q, J(C–H) = 125, *Me*-(Cp*)], 9.4 [q, *Me*(η^5-C$_5$Me$_5$)][b]
 2	4.81 [4 H, s br, J(Pt–H) = 78, *CH*(η-C$_8$H$_{12}$)], 2.58 [8 H, br, *CH*$_2$(η-C$_8$H$_{12}$)], 2.18 [15 H, d, J(Pt–H) = 15, (η-C$_5$Me$_5$)][c]	98.14 [d, J(Pt–C) = 28, C(η-C$_5$Me$_5$)], 74.3 [dd, J(Pt–C) = 198, J(C–H) = 159, (η-C$_8$H$_{12}$)], 22.51 [t, J(C–H) = 129, (η-C$_8$H$_{12}$)], –1.09 [q, J(C–H) = 128, (η-C$_5$Me$_5$)][c]
 3	2.83 [2 H, m br, J(Pt–H$_e$) = 124, J(P–H$_e$) = 18.5, J(H$_e$–H$_f$) = 23, H$_{ee'}$], 2.51 [2 H, m (8 lines), H$_{cc'}$], 2.45 [2 H, m (5 lines), H$_{bb'}$], 2.28 [2 H, m br, J(Pt–H$_a$) = 111, J(P–H$_a$) = 18, H$_{aa'}$], 2.20 (6 H, s, 2 × Me), 2.13 [2 H, m br, H$_{dd'}$], 1.91 (6 H, s, 2 × Me), 1.88 (6 H, s, 2 × Me), 1.63 [2 H, m br, J(H$_f$–H$_e$) = 23, H$_{ff'}$], 1.12 (6 H, s, 2 × Me), 1.05 [18 H, dd, J(Pt–H) = 24, J(P–H) = 7, 2 × PMe$_3$][b]	143.6 [s, *C*Me(Cp*)], 143.1 [s, *C*Me(Cp*)], 133.5 [s, *C*Me(Cp*)], 132.1 [s, *C*Me(Cp*)], 61.2 [s, *C*Me(Cp*)], 49.5 [d, J(C–H) = 122, C$_b$], 35.6 [t, J(C–H) = 121, C$_{e,f}$], 28.1 [t, J(C–H) = 121, C$_{c,d}$], 21.3 [ddd, J(Pt–C$_a$) = 702, J(P–C$_a$) = 89, J(P–C$_a$) = 5, J(C–H) = 125, C$_a$], 21.25 [q, J(C–H) = 127, *Me*(Cp*)], 16.4 (m, PMe$_3$), 13.0 [q, J(C–H) = 125, *Me*(Cp*)], 11.4 [q, J(C–H) = 125, *Me*(Cp*)], 11.3 [q, J(C–H) = 125, *Me*(Cp*)], 11.1 [q, J(C–H) = 125, *Me*(Cp*)][b]
 4	7.68 [1 H, m (6 lines), H$_d$], 7.32 [1 H, m (5 lines), H$_g$], 7.12 [2 H, m (7 lines), H$_e$ + H$_f$], 6.82 [1 H, dd, J(H$_b$–H$_c$) = 5, J(H$_b$–H$_a$) = 2, H$_b$], 6.71 [1 H, dt, J(H$_c$–H$_b$) = 5, J(H$_c$–H$_a$) = J(H$_c$–H$_d$) = 1, H$_c$], 5.82 [1 H, s br, J(Pt–H$_a$) = 159, H$_a$], 5.35 [1 H, m (6 lines), J(Pt–H) = 39, H$_j$ or H$_k$], 5.27 [1 H, m (8 lines), J(Pt–H) = 40, H$_j$ or H$_k$], 3.28 [1 H, m (6 lines), J(Pt–H) = 79, H$_h$ or H$_i$], 3.13 [1 H, m (8 lines), J(Pt–H) = 80, H$_h$ or H$_i$], 1.53 [2 H, m (9 lines), two of H$_l$–H$_s$], 1.43 [2 H, m (15 lines), two of H$_l$–H$_s$], 1.23 [1 H, m (8 lines), one of H$_l$–H$_s$], 1.15 [1 H, m (8 lines), one of H$_l$–H$_s$], 1.05 [1 H, m (10 lines), one of H$_l$–H$_s$], 0.91 [1 H, m (10 lines), one of H$_l$–H$_s$][b]	149.2 [s, C(η^1-C$_9$H$_7$)], 144.1 [s, C(η^1-C$_9$H$_7$)], 140.1 [dd, J(Pt–C$_b$) = 41, J(C–H) = 166, C$_b$], 125.5 [dd, J(Pt–C$_c$) = 30, J(C–H) = 165, C$_c$], 125.0 [d, J(C–H) = 158, C$_e$ or C$_f$], 123.4 [d, J(C–H) = 158, C$_f$ or C$_e$], 121.2 [d, J(C–H) = 157, C$_g$], 111.5 [dd, J(Pt–C) = 46, J(C–H) = 162, C$_j$ or C$_k$], 110.4 [dd, J(Pt–C) = 46, J(C–H) = 162, C$_j$ or C$_k$], 90.8 [dd, J(Pt–C) = 215, J(C–H) = 164, H$_h$ or H$_i$], 90.2 [dd, J(Pt–C) = 210, J(C–H) = 167, H$_h$ or H$_i$], 50.1 [dd, J(Pt–C) = 511, J(C–H) = 145, C$_a$], 31.6 [dt, J(Pt–C) = 18, J(C–H) = 131, one of C$_{l,m}$–C$_{r,s}$], 30.3 [dt, J(Pt–C) = 18, J(C–H) = 131, one of C$_{l,m}$–C$_{r,s}$], 28.2 [dt, J(Pt–C) = 18, J(C–H) = 131, one of C$_{l,m}$–C$_{r,s}$], 27.5 [dt, J(Pt–C) = 18, J(C–H) = 131, one of C$_{l,m}$–C$_{r,s}$][b]
 5a or 5b[d]	7.71 [1 H, d, J(H$_d$–H$_e$) = 9.5, H$_d$], 7.55 [1 H, m (6 lines), H$_f$], 7.28 [1 H, m (4 lines), H$_e$], 7.23 [1 H, m (8 lines), H$_g$], 6.81 [1 H, dd, J(Pt–H$_b$) = 31, J(H$_b$–H$_c$) = 6, H$_b$], 6.64 [1 H, d, J(H$_c$–H$_b$) = 6, H$_c$], 4.61 [1 H, br, J(Pt–H$_a$) = 164, H$_a$], 4.02 [2 H, m br (10 lines), J(Pt–H$_{h/i}$) = 50, H$_{hh'}$ or H$_{ii'}$], 3.41 [2 H, m br (5 lines), J(Pt–H$_{i/h}$) = 43, H$_{ii'}$ or H$_{hh'}$], 1.72 [2 H, m (10 lines), H$_{jj'}$ or H$_{kk'}$], 1.45 [2 H, m br, H$_{kk'}$ or H$_{jj'}$], 1.33 [2 H, m (10 lines), H$_{ll'}$ or H$_{mm'}$], 1.03[2 H, m (8 lines), H$_{mm'}$ or H$_{ll'}$][b]	151.1 [s, *C*(η^1-C$_9$H$_7$)], 144.5 [s, *C*(η^1-C$_9$H$_7$)], 139.7 [dd, J(Pt–C$_b$) = 41, J(C–H) = 166, C$_b$], 124.6 [d, J(C–H) = 159, C$_e$], 124.1 [dd, J(Pt–C$_c$) = 30, J(C–H) = 165, C$_c$], 123.9 [d, J(C–H) = 158, C$_d$], 122.8 [d, J(C–H) = 157, C$_f$ or C$_g$], 120.9 [d, J(C–H) = 158, C$_f$ or C$_g$], 102.0 [dd, J(Pt–C$_h$) = 81, J(C–H) = 162, C$_{hh'}$ or C$_{ii'}$], 101.75 [dd, J(Pt–C$_{i/h}$) = 85, J(C–H) = 164, C$_{ii'}$ or C$_{hh'}$], 54.0 [dd, J(Pt–C$_a$) = 595, J(C–H) = 145, C$_a$], 31.1 [t, J(C–H) = 131, C$_{j/k}$ or C$_{l/m}$], 27.9 [t, J(C–H) = 131, *C*$_{l/m}$ or C$_{j/k}$][b]
 5b or 5a[d]	7.56 [1 H, m (5 lines), H$_f$], 7.45 [1 H, m (4 lines), H$_d$], 7.23 [1 H, m (5 lines), H$_g$], 7.21 [1 H, m (6 lines), H$_e$], 6.92 [1 H, dd, J(H$_c$–H$_b$) = 6, J(H$_c$–H$_d$) = 2, H$_c$], 6.86 [1 H, dd, J(H$_b$–H$_c$) = 6, J(Pt–H$_b$) = 46, H$_b$], 4.61 [1 H, br, J(Pt–H$_a$) = 164, H$_a$], 3.83 [1 H, br, J(Pt–H$_{h/i}$) = 164, H$_{hh'}$ + H$_{ii'}$], 1.58 (2 H, m br, one of H$_{jj'}$, H$_{kk'}$, or H$_{mm'}$), 1.45 (2 H, m br, one of H$_{jj'}$, H$_{kk'}$, H$_{ll'}$ or H$_{mm'}$), 1.32 [2 H, m br (10 lines), one of H$_{jj'}$, H$_{kk'}$, H$_{ll'}$ or H$_{mm'}$], 1.25 [2 H, m br (7 lines), one of H$_{jj'}$, H$_{kk'}$, H$_{ll'}$, or H$_{mm'}$][b]	151.1 [s, *C*(η^1-C$_9$H$_7$)], 144.3 [s, *C*(η^1-C$_9$H$_7$)], 138.6 [dd, J(Pt–C$_c$) = 43, J(C–H) = 166, C$_c$], 123.2 [dd, J(Pt–C$_b$) = 20, J(C–H) = 165, C$_b$], 124.2 [d, J(C–H) = 158, C$_e$], 124.0 [d, J(C–H) = 158, C$_d$], 123.2 [d, J(C–H) = 159, C$_g$], 120.9 [d, J(C–H) = 160, C$_f$], 102.1 [dd, J(Pt–C$_h$) = 81, J(C–H) = 162, C$_{hh'}$ or H$_{ii'}$], 101.4 [dd, J(Pt–C$_{i/h}$) = 83, J(C–H) = 162, C$_{ii'}$ or C$_{hh'}$], 52.8 [dd, J(Pt–C$_a$) = 608, J(C–H) = 143, C$_a$], 29.4 [t, J(C–H) = 131, C$_{j/k}$], 29.3 [t, J(C–H) = 131, C$_{k/j}$][b]

Table IV (Continued)

compd	NMR data[a] ^{1}H	NMR data[a] ^{13}C
 **6**	7.55 [2 H, m (4 lines), $H_{cc'}$ or $H_{dd'}$], 7.46 [2 H, m (4 lines), $H_{dd'}$ or $H_{cc'}$], 6.69 [3 H, br, J(Pt–H) = 55, H_a + $H_{bb'}$], 5.02 [4 H, br, J(Pt–H) = 82, H_e], 2.35 [4 H, m (9 lines), H_f], 2.07 (4 H, m br, H_g)[c]	101.58 [d, J(C–H) 163, $C_{cc'}$ or $C_{dd'}$], 94.95 [s, $C(\eta^5\text{-}C_5Me_5)$], 92.84 [d, J(C–H) = 169, $C_{dd'}$ or $C_{cc'}$], 73.21 [dd, J(Pt–C) = 65, J(C–H) = 185, C_a], 58.98 [dd, J(Pt–C) = 175, J(C–H) = 162, $CH(\eta\text{-}C_8H_{12})$], 58.8 [dd, J(Pt–C) = 45, J(C–H) = 189, $C_{bb'}$], 32.7 [t, J(C–H) = 131, $CH_2(\eta\text{-}C_8H_{12})$][c]

[a] Data given as chemical shift [intensity, multiplicity, assignment]. Chemical shifts in ppm and coupling constants in Hz. [b] In $[^2H_6]$-benzene at room temperature. [c] In $[^2H_6]$acetone at room temperature. [d] For **5a** and **5b** the resonances assignable to the indenyl ligands cannot be unambiguously determined.

Table V. ^{195}Pt NMR, Mass Spectral, and Analytical Data for Compounds 1–6

compd	^{195}Pt NMR,[a] ppm	mass spectrum, *m/e* (P^+) {^{195}Pt}	analysis. found (calcd) C	analysis. found (calcd) H
1	–5516	573 (P^+)	58.7 (58.6)	7.8 (7.3)
2	–5750		41.7 (41.2)	5.2 (5.2)
3	–4684 (t)[b]		55.8 (56.1)	7.9 (8.5)
4	–3439	453 (P^+), 328 (P^+ – Ind)	45.8 (45.2)	4.2 (4.2); Cl, 7.7 (7.8)
5a,b	–3560, –3562	533 (P^+), 418 (P^+ – Ind)	58.3 (58.3)	4.9 (4.9)
6	–5196		40.0 (40.4)	3.7 (3.7)

[a] Referenced to $H_2[PtCl_6]$ in D_2O (external), Ξ = 21.4971 MHz, spectra measured at room temperature. [b] $\delta(^{31}P)$ –31.2 [J(Pt–P) = 1550 Hz, PMe_3].

house" modifications were made to the radio frequency hardware. For the heteronuclear experiments broad-band ^1H or ^{31}P decoupling was achieved by using WALTZ-16 modulation,[22] in addition a booster amplifier was included to produce short (typically 8 μs; 90°) ^1H pulses via the decoupler on the ^{13}C probe.

The DQPH-COSY experiments described in this paper were acquired by using the time proportional phase increments (TPPI) method of Marion and Wuthrich.[18] Typically 1024 t_1 increments of 1K words were acquired, giving a 4MK word data matrix with equal digital resolution in both f_1 and f_2.

Gaussian multiplication was applied to both dimensions prior to Fourier transformation in both dimensions. The resultant spectra were symmetrized after phase corrections in both dimensions.

Crystal Structure Determination. Crystals of 1 were sealed under nitrogen in Lindemann glass capillaries and were mounted on an Enraf-Nonius CAD4F diffractometer and cell dimensions obtained by least-squares methods from the positions of 25 carefully centered reflections. During data collection three intensity control reflections were measured every hour and four orientation controls checked after every 200 measurements. There was no significant variation in the magnitude of the intensity controls throughout data collection.

Lorentz and polarization corrections were applied together with an empirical absorption correction.[23] Equivalent reflections were merged, and only those for which $I > 3\sigma(I)$ were included in the refinement [where $\sigma(I)$ is the standard deviation based on counting statistics].

The platinum atomic coordinates werre determined by using Patterson methods; subsequent electron density difference syntheses revealed the location of all remaining non-hydrogen atoms. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions (C–H = 0.96 Å) and allowed to ride on their attached carbons.

Corrections for anomalous dispersion and isotropic extinction[24] were made in the final cycles of refinement; a Chebyshev weighting scheme[25] was used with the parameters as in Table I. The final positional parameters are recorded in Table III. All calculations were performed on a VAX 11/750 computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system[26] and plotted by using the CHEMX package.[27] Atomic scattering factors and anomalous dispersion coefficients were taken from ref 28.

Table VI. NMR Coupling Constants for $[Pt(\eta\text{-}C_8H_{12})XY]$ Derivatives

compound	olefinic cyclooctadiene resonances $^2J(^{195}Pt\text{–}H)$	olefinic cyclooctadiene resonances $^1J(^{195}Pt\text{–}C)$	ref
$[Pt(\eta\text{-}C_8H_{12})(Me)Cl]$	35[a] 74		28
$[Pt(\eta\text{-}C_8H_{12})(\eta^1\text{-}Ind)Cl]$	39[b] 80	46[b] 210	this work
$[Pt(\eta\text{-}C_8H_{12})(\eta^1\text{-}Cp)Cl]$	47.5[c] 72		this work
$[Pt(\eta\text{-}C_8H_{12})(\eta^1\text{-}Cp)_2]$	49	110	28
$[Pt(\eta\text{-}C_8H_{12})(\eta^1\text{-}Ind)_2]$	45	164	this work

[a] Trans to Me. [b] Trans to Ind. [c] Trans to Cp.

Experimental Details. Synthesis of $[Pt(\eta\text{-}C_5Me_5)\{\sigma{:}\eta^2\text{-}C_8H_{12}(Cp^*)\}]$ (1). To a suspension of $[Pt(\eta\text{-}C_8H_{12})Cl_2]$ (0.1 g, 0.26 mmol) in THF (50 cm^3) was added NaCp* (0.084 g, 0.52 mmol) in THF (20 cm^3). The mixture was stirred for 12 h during which time the solution turned yellow. The suspension was allowed to settle and the solution filtered. The filtrate was reduced to dryness in vacuo, yielding a yellow oily solid. The oily solid was extracted with pentane (2 × 50 cm^3). The pentane extracts were concentrated under reduced pressure. Cooling to –20 °C and then to –80 °C overnight gave yellow crystals of $[Pt(\eta\text{-}C_5Me_5)\{\sigma{:}\eta^2\text{-}C_8H_{12}(Cp^*)\}]$ (0.1 g, 0.18 mmol, 71%).

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Synthesis of [Pt(η^5-C_5Me_5)(η^4-C_8H_{12})]BF_4 (2). Treatment of **1** (0.1 g, 0.17 mmol) with $HBF_4 \cdot Et_2O$ (2–3 drops) in pentane at −78 °C gives an instantaneous pale yellow precipitate. The suspension was allowed to warm to room temperature, and the solid was collected by filtration. Recrystallization from THF diethyl ether (1:1; 10 cm^3) gave a yellow microcrystalline solid (0.063 g, 0.12 mmol, 70%).

Synthesis of [Pt(PMe_3)$_2${σ^2-C_8H_{12}(Cp*)$_2$}] (3). To a solution of [Pt(η-C_5Me_5){σ:η^2-C_8H_{12}(Cp*)}] (0.05 g, 0.087 mmol) in pentane (30 cm^3) was added trimethylphosphine (1 cm^3) by vacuum transfer. The mixture was allowed to stir at room temperature for 24 h. The solvent and unreacted PMe_3 were removed in vacuo, yielding a colorless oily residue. The residue was extracted with pentane (2 × 20 cm^3), and the solution was filtered and concentrated to ca. 10 cm^3. Cooling initially to −20 °C and then −80 °C gave colorless crystals (0.5 g, 0.068 mmol, 80%).

Synthesis of [Pt(η-C_8H_{12})(η^1-C_9H_7)Cl] (4). To a suspension of [Pt(η-C_8H_{12})Cl_2](0.2 g, 0.53 mmol) in THF (50 cm^3) was added NaInd (0.073 g, 0.53 mmol) in THF (20 cm^3). The mixture was stirred for 12 h during which time the solution turned yellow. The suspension was allowed to settle and the solution filtered. The filtrate was reduced to dryness in vacuo, yielding a yellow solid. The oily solid was extracted with toluene (2 × 50 cm^3). The toluene extracts were concentrated under reduced pressure. Cooling to −20 °C and then to −80 °C overnight gave yellow crystals of [Pt(η-C_8H_{12})(η^1-C_9H_7)Cl] (0.16 g, 0.37 mmol, 70%).

Synthesis of [Pt(η-C_8H_{12})(η^1-C_9H_7)$_2$] (5). To a suspension of [Pt(η-C_8H_{12})Cl_2] (0.1 g, 0.26 mmol) in THF (50 cm^3) was added NaInd (0.096 g, 0.7 mmol) in THF (20 cm^3). The mixture was stirred for 12 h during which time the solution turned yellow in color. The suspension was allowed to settle and the solution filtered. The filtrate was reduced to dryness in vacuo, yielding a waxy red solid. The waxy solid was extracted with toluene (2 × 50 cm^3) giving a dark orange solution. The toluene extracts were concentrated under reduced pressure. Cooling to −20 °C and then to −80 °C overnight gave orange microcrystalline [Pt(η-C_8H_{12})(η^1-C_9H_7)$_2$] (0.097 g, 0.18 mmol, 71%).

Synthesis of [Pt(η^5-C_9H_7)(η^4-C_8H_{12})]BF_4 (6). Method A. Treatment of mixture of **5a** and **5b** (1:1; 0.2 g, 0.53 mmol) with $HBF_4 \cdot Et_2O$ (2–3 drops) in diethyl ether at −78 °C gives an instantaneous pale yellow precipitate. The suspension was allowed to warm to room temperature. The precipitate was collected, washed with diethyl ether (2 × 10 cm^3), and dried in vacuo. Recrystallization from THF/diethyl ether (1:1; 10 cm^3) gave a yellow microcrystalline solid (0.23 g, 0.47 mmol, 90%).

Method B. To a solution of **4** (0.75 g, 0.14 mmol) in CH_2Cl_2 (20 cm^3) was added a solution of $AgBF_4$ (0.027 g, 0.14 mmol) in CH_2Cl_2 at room temperature. The solution was stirred at room temperature for 5–10 min and the solvent removed under reduced pressure to give a yellow waxy solid. Extraction with THF/diethyl ether (1:1; 2 × 10 cm^3) gives an orange solution which on cooling to −20 °C and then −80 °C gives a yellow microcrystalline solid (0.056 g, 0.11 mmol, 80%).

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Registry No. 1, 108818-18-4; 2, 108818-20-8; 3, 108834-57-7; 4, 108818-21-9; 5a, 108818-22-0; 5b, 108942-24-1; 6, 108818-24-2; NaCp*, 40585-51-1; NaInd, 23181-84-2; [Pt(η-C_8H_{12})Cl_2], 12080-32-9.

Supplementary Material Available: Listings of the hydrogen atom positions and anisotropic thermal parameters for all non-hydrogen atoms (2 pages); a listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Reactivity and Mechanism in the Formation of (μ-Hydrocarbyl)diplatinum(IV) Complexes by Oxidative Addition of α,α'-Dibromoxylenes to Dimethylplatinum(II) Complexes

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A study of the formation of binuclear complexes with μ-hydrocarbyl ligands by double oxidative addition of the organic dihalides, α,α'-dibromoxylene (ortho and para isomers), and $I(CH_2)_nI$ to binuclear platinum complexes has been made. In bridged 2,2′-bipyrimidine (bipym) systems it is found that [Me_2Pt(μ-bipym)$PtMe_2$(4-$CH_2C_6H_4CH_2Br$)Br] undergoes rapid intramolecular oxidative addition to give [Me_2BrPt(μ-bipym)(μ-4-$CH_2C_6H_4CH_2$)$PtBrMe_2$] but the analogous complexes [Me_2Pt(μ-bipym)$PtMe_2$(2-$CH_2C_6H_4CH_2Br$)Br] and [Me_2Pt(μ-bipym)$PtMe_2${$(CH_2)_nI$}I] were long-lived and rearranged slowly to tetranuclear complexes. Reasons for these differences are suggested, based on conformational or ring strain effects. Binuclear complexes with μ-hydrocarbyl groups were formed more easily from [Pt_2Me_4(μ-pyen)] (pyen = bis(2-pyridyl)ethylenediimine) as a result of the flexibility of the μ-pyen ligand, but the reagents $I(CH_2)_nI$ failed to give μ-polymethylene derivatives. Kinetic studies of several of these reactions have been carried out, and it is shown that the para isomer of α,α'-$C_6H_4(CH_2Br)_2$ is more reactive than the ortho isomer and that a platinum center can activate a remote C–Br bond by a neighboring group effect. The apparent intermolecular oxidative additions of binuclear complexes to give tetranuclear complexes are shown to follow first-order kinetics and probably involve an intramolecular reaction followed by rapid dimerization. The intramolecular reaction is thought to involve dissociation of platinum(IV) from the diimine ligand.

Introduction

There is considerable interest in μ-hydrocarbyl complexes of transition metals, partly since such compounds can act as models for proposed catalytic intermediates, and this area of chemistry has been reviewed.[1-4] Platinum complexes with $Pt(CH_2)_nPt$ units have been prepared by oxidative addition of $I(CH_2)_nI$ to complexes such as the 2,2′-bipyrimidine derivative [$PtMe_2$(bipym)] (1c).[5,6] The

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