Coordination of Donor-Functionalized Cyclopentadienyl Ligands at Platinum(II) Centers: Syntheses and Molecular Structure of [μ-(1,2-η^2:5,6-η^2-cod){(η^5-$C_5Me_4CH_2CH_2NMe_2$)MePt}$_2$]

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Received February 12, 2001

The syntheses of novel monomeric and dimeric platinum(II) complexes are reported. Modified cyclopentadienyls (Cp^R) such as pentamethylcyclopentadienyl (Cp*) and its functionalized derivatives 1-[2-(dimethylamino)eth-1-yl]-2,3,4,5-tetramethylcyclopentadienyl (Cp^{*N}), 1-(but-3-en-1-yl)-2,3,4,5-tetramethylcyclopentadienyl ($Cp^{*2=}$) and 1-(pent-4-en-1-yl)-2,3,4,5-tetramethylcyclopentadienyl ($Cp^{*3=}$) were reacted with [(η^4-cod)PtMeX] (COD = *cis*,*cis*-1,5-cyclooctadiene, X = halogen) to give the monomeric species [(1,2-η^2:5,6-cod)(η^5-Cp^R)MePt] (Cp^R = Cp* (**1**), Cp^{*N} (**3**), $Cp^{*2=}$ (**5**), $Cp^{*3=}$ (**6**)), wherein the COD ligand is η^2-coordinated to one metal center. Dimerization of **1** or **3** resulted in the COD-bridged species [μ-(1,2-η^2:5,6-η^2-cod){(η^5-Cp^R)MePt}$_2$] (**2**, **4**); the molecular structure of **4** was determined by single-crystal X-ray diffraction. All new compounds were characterized by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopy and by elemental analysis where possible.

Introduction

Platinum(II) and -(IV) complexes containing the cyclopentadienyl (Cp) or the peralkylated pentamethylcyclopentadienyl (Cp*) ligands are well-known in the literature and have still been of increased interest during the past decades. Thereby the Cp ring can either be η^1- or η^5-bound to the metal center.[1−3] For transition metals in general, cyclopentadienyl systems which are functionalized by a side chain containing an additional donor group attract special interest due to structural discussions as well as catalytic applications.[4−9] These modified Cp ligands may either possess two soft donor sites or one hard and one soft donor site at the same time. By choosing appropriate systems and conditions, one can *intra*molecularly stabilize electron-deficient centers in a reversible or an irreversible way so that unusual coordination states and reactions can be observed.[8c] With respect to catalytic processes, donor-functionalized cyclopentadienyls provide the opportunity to temporarily stabilize a reactive metal fragment by an *intra*molecular coordination, to immobilize or to trap the catalytically active complex as well as to vary the solubility.[4c−e,5]

Cyclopentadienyl complexes containing the *intra*-molecularly coordinated side chain are known for group 9 metals[6,7] and even for the group 10 metal nickel,[8b−f]

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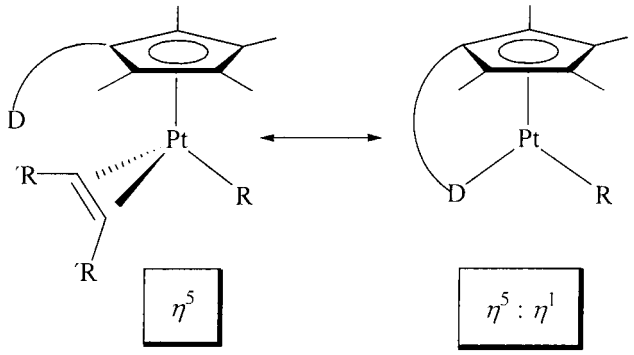
10.1021/om010107a CCC: $20.00
Publication on Web 07/16/2001

Scheme 1



D = two-electron donor

but there is surprisingly no example in the literature of a platinum center and a classical *intra*molecular coordination of a Cp side chain, although synthetic and theoretical investigations on the field of platinum(II)[10] as well as platinum(IV)[11] chemistry with cyclopentadienyl ligands have still continued over the past few years. Most of the complexes have a Cp system without any functionalization; one example was reported with a noncoordinating side chain at a platinum(IV) center[3] and there is one example for an *inter*molecularly coordinated phosphino donor function which is fixed directly at the Cp ring without any spacer group.[2]

In this work, we describe the syntheses of platinum(II) complexes with the Cp* ligand and donor functionalized derivatives, i.e., 1-[2-(dimethylamino)eth-1-yl]-2,3,4,5-tetramethylcyclopentadienyl (Cp^{*N}), 1-(but-3-en-1-yl)-2,3,4,5-tetramethylcyclopentadienyl ($Cp^{*2=}$), and 1-(pent-4-en-1-yl)-2,3,4,5-tetramethylcyclopentadienyl ($Cp^{*3=}$), with special emphasis on the donor properties and the coordination mode of the bidentate ligands. The Cp moiety is always η^5-coordinated to the metal center, but the additional donor competes with the alkene moiety of the COD ligand present in the starting compound for the remaining coordination site (Scheme 1).

To characterize our new species, $^{195}Pt\{^1H\}$ NMR spectroscopy was used in addition to ^1H and ^{13}C NMR techniques, and we will demonstrate the qualitative correlation of the $^{195}Pt\{^1H\}$ NMR shifts with the strength of the resulting platinum(II)−olefin bond, which affects the coordination mode of the bidentate Cp ligands.

Results

Complexes with the Cp* Ligand. Reaction of [(η^4-cod)PtMeI] (COD = *cis,cis*-1,5-cyclooctadiene) with 1 equiv of KCp* in THF leads to a partial displacement of the COD ligand ($\eta^4 \rightarrow \eta^2$) by the η^5-coordinating Cp* and to the formation of the complex [(1,2-η^2:5,6-cod)(η^5-Cp*)MePt] (**1**). Compound **1** is a yellow oil and was characterized by ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR as well as high-resolution mass spectrometry and elemental analysis. When kept in solution, the complex shows partial decomposition after 1 week. However, when the isolated raw product, i.e., the oil, was stored at room temperature under the exclusion of light, a partial dimerization occurred to yield the COD-bridged complex [μ-(1,2-η^2:5,6-η^2-cod){(η^5-Cp*)MePt}$_2$] (**2**) and free COD (Scheme 2). This dimerization is very slow and was therefore not completed after weeks; thus, compound **2** could not be separated from **1**. The workup after weeks was even more difficult because partial decomposition still occurred under these conditions.

In the ^1H and $^{13}C\{^1H\}$ NMR spectra compounds **1** and **2** show similar signals except for the resonances of the diolefin ligand. Dimerization could be concluded from the integration of the ^1H NMR signals and, moreover, the mass spectra, which contained a peak with the mass and isotopic pattern of dimer **2**. The $^{195}Pt\{^1H\}$ NMR spectra are identical; so, obviously, the resulting electronic environments at the platinum centers influenced by either a nonbridged or a bridged COD ligand are very similar and both species have the same ^{195}Pt NMR resonance.

At this point, we were interested to study the effect of a donor-functionalized side chain at the Cp system. In these cases one can either expect the same coordination mode as for the nonfunctionalized Cp* or an *intra*molecular coordination of the donor function and substitution of the olefin ligand which was present in the starting compound. The chelating effect as well as the donor properties of the ligand and the acceptor properties of the metal center have to be taken into account to judge the specific situation in each compound. Therefore, the donor and acceptor properties can be defined by Pearson's concept[12] of hard and soft acids and bases.

Complexes with the Cp^{*N} Ligand. We chose the well-known ligand 1-[2-(dimethylamino)eth-1-yl]-2,3,4,5-tetramethylcyclopentadienyl (Cp^{*N})[13] with an amino group in the side chain representing a hard Lewis base ligand. Our experiments show that reaction between the chloro compound [(η^4-cod)PtMeCl] and the lithium salt $LiCp^{*N}$ as well as reaction between the iodo derivative [(η^4-cod)PtMeI] and the potassium salt KCp^{*N} yield the products **3** and **4**, which are analogous to compounds **1** and **2** (Scheme 2). The dimeric complex [μ-(1,2-η^2:5,6-η^2-cod){(η^5-Cp^{*N})MePt}$_2$] (**4**) could be readily isolated as yellow crystals. However, we found by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and as indicated by elemental analysis that the primary reaction product was the monomer [(1,2-η^2:5,6-cod)(η^5-Cp^{*N})MePt] (**3**), which directly underwent dimerization to give the COD-bridged species and free COD. Now, in the case of the Cp^{*N} ligand

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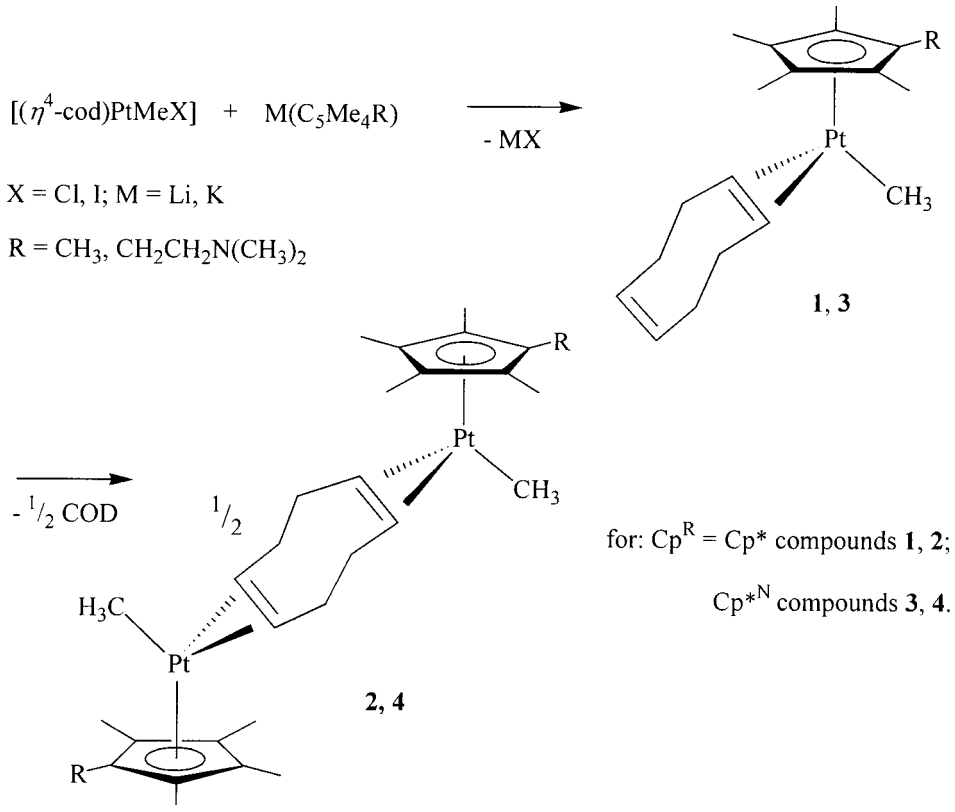
Scheme 2



reaction to product **4** and its simultaneously occurring crystallization took place when compound **3**, a yellow oil, was stored under the exclusion of light at room temperature for 7 days. Completion of the formation of **4** was much faster than that observed for the pentamethylated Cp analogue. Dimerization already started during the preparation of complex **3** so that no suitable elemental analysis could be obtained for the primary reaction product; only elemental analyses for mixtures of **3** and **4** were possible. The dimeric complex **4** is fairly air-stable and was fully characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray structural analysis. Compounds **3** and **4** again show the same ^{195}Pt{^{1}H} NMR signal, and the ^{1}H and ^{13}C{^{1}H} NMR spectra are analogous, as is the case for compounds **1** and **2** (vide supra). Because the spectra contain only one set of signals for the bridging COD ligand, the molecule **2** may exhibit an inversion center.

Molecular Structure of 4. Suitable crystals of **4** were grown from the crude product **3** as described above. The platinum(II) complex crystallizes in the monoclinic space group $P2_1/n$ with no unusual intermolecular contacts (Figure 1, Table 1); selected bond lengths and angles are given in Table 2. The results of the X-ray analysis confirm that the molecule exhibits an inversion center, as proposed on the basis of the ^{1}H and ^{13}C{^{1}H} NMR data. The geometry around the platinum center can be described as a "piano stool" not differing much from the structure of platinum(IV) complexes such as [(η^5-Cp)PtMe$_3$] or derivatives of this complex.[11a,b,14] The structural features in the η^5-coordinated Cp*^{N} are quite

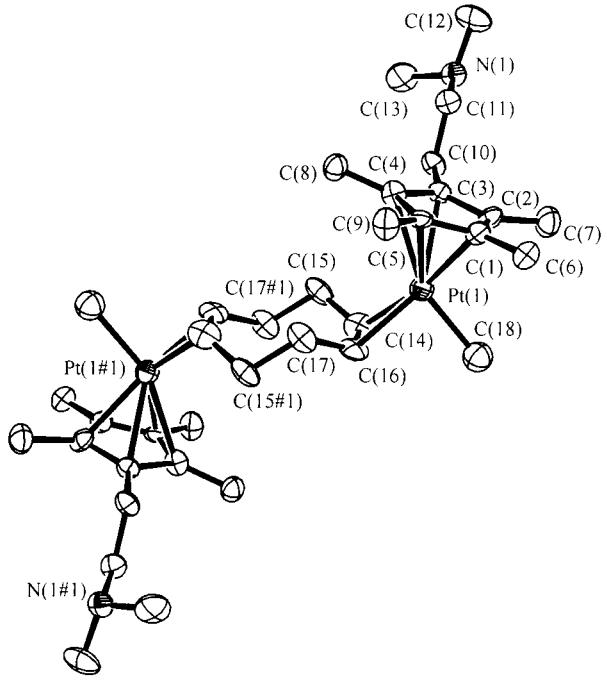


Figure 1. Molecular structure of **4** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

usual: the Pt−(Cp*^{N})$_{centroid}$ distance is 1.98 Å, which is comparable to that in some platinum(IV) complexes,[14] the mean Pt−C$_{Cp}$ distance is 2.245(10)−2.364(10) Å, and the mean C−C−C ring angle is about 108°, which fits well with the internal angles of a regular pentagon. The Pt−C$_{methyl}$ bond length is 2.094(11) Å and is essentially the same as the sum of the appropriate covalent radii

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Table 1. Crystallographic Data for 4

chem formula	$C_{18}H_{31}NPt$
fw	456.53
cryst color, habit	yellow, needle
cryst size, mm^3	$0.05 \times 0.05 \times 0.1$
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	
a, Å	8.4785(17)
b, Å	16.274(3)
c, Å	12.930(3)
β, deg	94.54(3)
V, $Å^3$	1778.4(6)
Z	4
d_{calcd}, Mg/m^3	1.705
μ, mm^{-1}	7.882
no. of params	176
θ range for data collecd, deg	2.02−25.22
no. of rflns collected	9037
no. of indep rflns	3158 (R_{int} = 0.1114)
index ranges	$-10 \le h \le 8$
	$-18 \le k \le 19$
	$-14 \le l \le 15$
transmissn (min/max)	0.504970/1.00000
final R indices ($I > 2\sigma(I)$)	R1 = 0.0472
	wR2 = 0.0909
R_{wF^2} (all data)	R1 = 0.0891
	wR2 = 0.1043
largest diff peak and hole, $e/Å^3$	1.232 and −0.991

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

Pt(1)−C(1)	2.319(10)	C(1)−C(2)	1.441(14)
Pt(1)−C(2)	2.245(10)	C(1)−C(5)	1.364(13)
Pt(1)−C(3)	2.311(9)	C(2)−C(3)	1.418(14)
Pt(1)−C(4)	2.347(10)	C(3)−C(4)	1.435(13)
Pt(1)−C(5)	2.364(10)	C(4)−C(5)	1.457(13)
Pt(1)−C(14)	2.100(11)	C(14)−C(15)	1.474(16)
Pt(1)−C(16)	2.085(10)	C(14)−C(16)	1.395(15)
Pt(1)−C(18)	2.094(11)	C(15)−C(17#1)	1.579(14)
Pt(1)−$Cp^{*N}_{centroid}$	1.98	C(16)−C(17)	1.515(15)
Pt(1)−$(C{=}C)_{centroid}$	1.97		
C(14)−Pt(1)−C(16)	38.9(4)	C(2)−C(3)−C(4)	108.2(8)
C(14)−Pt(1)−C(18)	88.8(5)	C(3)−C(4)−C(5)	106.1(9)
C(16)−Pt(1)−C(18)	88.1(5)	C(14)−C(16)−C(17)	125.0(10)
C(1)−C(2)−C(3)	107.4(8)	C(15)−C(14)−C(16)	125.5(11)
C(1)−C(5)−C(4)	109.1(9)	C(16)−C(17)−C(15#1)	111.9(8)
C(2)−C(1)−C(5)	109.0(9)		

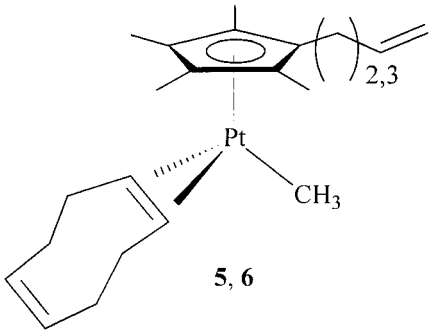
(2.08 Å)[15] within the experimental error. It falls into the range of typical Pt−C_{methyl} distances (2.0−2.2 Å)[16] comparable to the bond length in formally hexacoordinated platinum compounds such as [(η^5-Cp)$PtMe_3$],[14a] [(η^5-MeCp)$PtMe_3$],[14b] and [(η^5-Cp*)$PtMe_2X$][11a,b] as well as various penta- or tetracoordinated complexes [L_3Pt-MeX] and [L_2PtMeX].[16] The Pt−$(C{=}C)_{centroid}$ distance in **4** (1.97 Å) can also be compared with typical platinum−olefin distances (2.00−2.16 Å), although it is little shortened.[17] In the literature there exists only one crystal structure of a closely related compound: [(1-σ:5,6-η^2-C_8H_{12}-2-Cp*)(η^5-Cp*)Pt] (see Chart 1).[18] It is a platinum(II) complex also bearing an η^5-bound Cp ligand, a π-bonded olefin group, and an alkyl group as the σ-ligand. In its molecular structure the Pt−$(C{=}C)_{centroid}$ bond length amounts to 1.96(9) Å as well, and

Scheme 3

$$[(\eta^4\text{-cod})PtMeCl] + LiCp^R \xrightarrow[-LiCl]{}$$

for: $Cp^R = Cp^{*2=}$ compound **5**;

$Cp^{*3=}$ compound **6**.



5, **6**

even the olefin bond with 1.37(2) Å fits well with the data we collected for compound **4** (1.395(15) Å). In platinum(II) complexes in general, when the COD is coordinated in an η^4 fashion as in [(η^4-cod)$PtMe_2$],[19] for example, the olefin bond is about 1.36−1.38 Å and the maximum distance of 1.40 Å is quite rare. However, a comparison with the aforementioned complexes is not really valid, because in compound **4** we have a formally pentacoordinated electron-rich platinum center and an 18-valence-electron complex and not a four-coordinated metal center in a 16-valence-electron complex.

Complexes with the $Cp^{*=}$ Ligands. With both the 1-(but-3-en-1-yl)-2,3,4,5-tetramethylcyclopentadienyl ligand ($Cp^{*2=}$)[8a] and the 1-(pent-4-en-1-yl)-2,3,4,5-tetramethylcyclopentadienyl ligand ($Cp^{*3=}$),[8b] we chose systems that contain the same type of donor−acceptor ligand, i.e., an olefin, that is present in the starting compound. Therefore, we examined whether the chelating effect is strong enough in these compounds to allow a coordination of the side chain and consequently a substitution of COD. The reaction between $LiCp^{*2=}$ and [(η^4-cod)PtMeCl] as well as between $LiCp^{*3=}$ and [(η^4-cod)PtMeCl] proceeds in a similar manner as for the other Cp^R systems, but in contrast with those preceding cases only the monomeric species [(1,2-η^2:5,6-cod)(η^5-$Cp^{*2=}$)MePt] (**5**) and [(1,2-η^2:5,6-cod)(η^5-$Cp^{*3=}$)MePt] (**6**) could be isolated (Scheme 3). Compounds **5** and **6** are likewise yellow oils and were characterized by ^1H, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR. Dimerization as well as the attempted complete displacement of the COD by the olefinic double bond in the $Cp^{*=}$ ligands was not observed independent from the length of the side chain having either a spacer with two carbons or with three carbons.

Displacement of COD by Phosphines. To displace the strongly bound COD from the platinum center, the addition of an even stronger donor such as a phosphine, for example, may be necessary. To test this, compound **3**, [(1,2-η^2:5,6-cod)(η^5-Cp^{*N})MePt], was mixed with approximately 1 equiv of PMe_3 in an NMR tube (solvent

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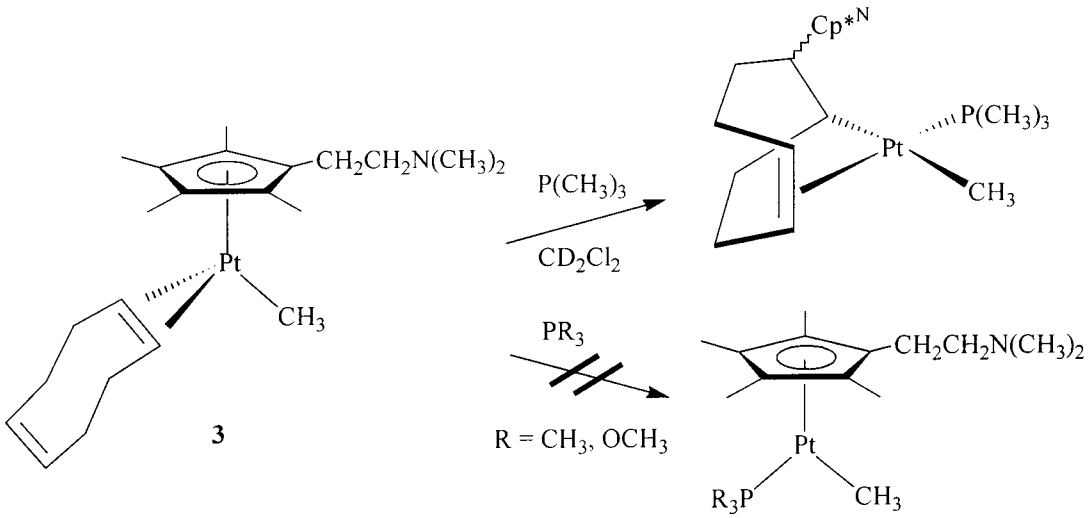
Scheme 4



CD_2Cl_2) and the reaction was observed by $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectroscopy. Within 1 h the signals from the starting compounds decreased and signals for a new compound were detected. The $^{31}P\{^1H\}$ NMR spectrum contains a signal at −18.1 ppm (relative to external 85% H_3PO_4 in D_2O) with ^{195}Pt satellites and a coupling constant of 1256 Hz. The signal in the $^{195}Pt\{^1H\}$ NMR spectrum is at −4023 ppm, and the coupling amounts to 1242 Hz, which is in good agreement with the $^{31}P\{^1H\}$ NMR spectrum. Because the signal appears as a doublet, it belongs to a species where only one phosphino group is bound to a platinum center. These signals and the couplings seem to be similar to those of a complex reported before: the addition of PPh_3 to [(η^4-cod)(η^1-Cp)PhPt] in THF yielded a displacement of the Cp anion followed by an attack of this anion at the coordinated olefin, and the complex [(1-σ:5,6-η^2-C_8H_{12}-2-Cp*)(PPh_3)PhPt] was isolated as the only product.[1d] On changing to the less polar solvent diethyl ether, two products in a 1:1 ratio could be detected. Apart from the reaction product appearing in THF, at this point the COD was completely displaced by the phosphine and [(η^5-Cp)(PPh_3)PhPt] was formed, which is distinguished by a much larger $^{195}Pt-^{31}P$ coupling constant (5680 Hz in comparison with 1318 Hz).[1d] In the NMR experiments with PMe_3 we could not detect any strong coupling of more than 5000 Hz, but the $^{31}P\{^1H\}$ NMR and $^{195}Pt\{^1H\}$ NMR data appeared to be consistent with a species tentatively assigned as "[(1-σ:5,6-η^2-C_8H_{12}-2-Cp*^{N})(PMe_3)MePt]" and not to the COD-free complex [(η^5-Cp*^{N})(PMe_3)MePt], which was the aim of this NMR investigation (Scheme 4).

So as not to end in a complete substitution of the Cp*^{N} ligand as described above, we decided to vary the phosphine, because its electron density was expected to have a decisive influence on the reaction pathway. In comparison with the phosphine PMe_3, the respective phosphinic acid ester $P(OMe)_3$ has a lower electron density at the phosphorus, is a harder electron donor (HSAB), and does not, therefore, stabilize possible cationic transition states as well as PMe_3. In NMR experiments compound **3**, [(1,2-η^2:5,6-cod)bis{(η^5-Cp*^{N})-MePt}], was mixed with approximately 1 equiv of $P(OMe)_3$ (solvent d_8-THF, CD_2Cl_2, or C_6D_6) and the reactions were observed by $^{31}P\{^1H\}$ spectroscopy. After a few hours a new signal in the $^{31}P\{^1H\}$ NMR spectrum appeared at about 134 ppm with ^{195}Pt satellites and a coupling constant of 5400 Hz. The strength of the phosphorus−platinum coupling fits well with a species related to [(η^5-Cp)(PPh_3)PhPt], in accordance with the literature.[1d] In the corresponding $^{195}Pt\{^1H\}$ NMR spectra, besides the resonance belonging to the starting compound **3**, there is a signal at −5793 ppm with a coupling of 5370 Hz, but this signal unfortunately appears as a triplet. Thus, in combining the information on ^{31}P NMR and ^{195}Pt NMR resonances, we have to suggest a structure with two equivalent phosphino moieties at one platinum center, and therefore the species belonging to these signals cannot be the desired product [(η^5-Cp*^{N}){$P(OMe)_3$}MePt] (Scheme 4). In the more polar solvents d_8-THF and CD_2Cl_2 after 1 week the main signal in the $^{31}P\{^1H\}$ NMR spectrum is still the same, but signals with much smaller couplings to the platinum (about 2400 Hz) occur additionally. In the corresponding $^{195}Pt\{^1H\}$ NMR spectra signals with a coupling of approximately 2400 Hz appear as doublets; therefore, the complex with the large $^{195}Pt-^{31}P$ coupling constant is not the only reaction product, but the one which was generated more rapidly and whose formation is clearly favored in nonpolar solvents such as benzene.

Discussion

In platinum(II) complexes with an η^5-coordinated Cp* the η^2-coordinated ancillary olefin COD is surprisingly difficult to displace by *intra*molecular donor functions such as amines or even other olefins linked at the Cp ligand. In fact, this kind of reaction did not take place in our hands. The most important reason for it is probably the strength of the platinum−olefin bond. In the case of the side chain bearing an amino donor this relates to Pearson's concept.[12] With a Cp*−platinum(II) fragment we have a very soft acid, which is in contrast to the amine being a hard base. Additionally there might be a general problem with the size of the particular spacer in a side chain because it can either be too short for an *intra*molecular coordination or too long so that the side chain is too flexible for starting an interaction with the metal center. We can exclude this problem by varying the spacer length from a two-carbon chain to a

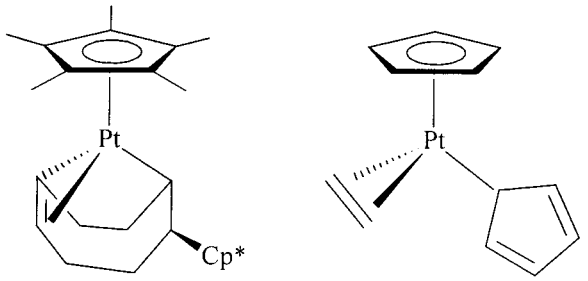
three-carbon chain in the case of the olefinic functionalized side chain at the Cp ligand ($Cp^{*2=}$ and $Cp^{*3=}$). Thus, apparently the chelating effect is not strong enough to cause a displacement of the coordinated olefin by the chosen side-chain donors and additionally the sterically demanding η^2-coordinated COD moiety prevents an attack of the side chain.

Next, we compared the behavior of an olefinic side chain in our Pt case with the reported *intra*molecular coordination of an olefinic side chain to metal centers such as cobalt and nickel.[6a,b,8b] In these latter cases, synthesis started either from the appropriate metal−halogens in the case of nickel or from Cp−cobalt(III) diiodide and Na/Hg so that no other strong donor ligand which was present from the starting compound could compete with the side chain of the Cp system. For the above specified complexes with a coordinated side chain the resonances of the olefin protons and carbons show the same significant upfield shift as we observed for the η^2-coordinated or bridged COD moiety in this work (for details see below), but the effect caused by the complexation of the platinum(II) center is still slightly stronger. This is an indication of the strong bonding between the COD and the Pt(II) center and gives a probable explanation why the COD cannot be displaced even by another olefin function. One may speculate that the use of starting compounds which contain olefins such as ethene or propene instead of COD might effect a better chance to generate the desired *intra*molecularly stabilized Pt(II) species because the olefins are more volatile, less sterically demanding, and therefore easier to displace. Further investigations in this direction have already been started.

When a phosphine is added to a Cp−platinum complex which contains an η^2-coordinated olefin, the phosphine can either displace the olefin or even the Cp moiety. In our system both cases appeared; therefore, the strength of the bond to the olefin seems to be similar to that of the bond to the Cp moiety but a displacement of the Cp ligand is favored in more polar solvents, which was already observed in related cases as reported in the literature.[1d,18] The synthesis of the desired complex, i.e., $[(\eta^5\text{-}Cp^{*N})\{P(OMe)_3\}MePt]$, containing an η^5-coordinated Cp ligand, an alkyl, and the phosphine, could not be carried out in any of our NMR experiment. Varying the electron density at the phosphorus has a clear effect on the reaction, but the COD-free complex with an η^5-coordinated Cp^{*N} ligand could not be detected, and therefore it does not seem to be the favored product.

By discussing the strength of the platinum−olefin bond in compounds **1**−**6**, one can classify this bond by using the Dewar−Chatt−Duncanson model.[20] We first looked at the NMR signals of the olefin protons and carbons and compared them with those of free COD. For the proton resonances of coordinated COD there is a significant upfield shift of about 3 ppm ($^2J_{Pt-H} = 76$ Hz). The same tendency can be found for the carbon signals: the upfield shift here is 78 ppm ($^1J_{Pt-C} = 309-310$ Hz). The $^{195}Pt\{^1H\}$ NMR data offer an additional probe: The signal for each of the new $(\eta^5\text{-Cp})Pt(II)$ species (**1**−**6**) appears between −5467 and −5469 ppm (relative to the external standard H_2PtCl_6 in D_2O).

Chart 1



$[(\eta^5\text{-Cp})(\eta^2\text{-}C_2H_4)(\sigma\text{-Cp})Pt]$

$[(1\text{-}\sigma\text{:}5,6\text{-}\eta^2\text{-}C_8H_{12}\text{-}2\text{-Cp}^*)(\eta^5\text{-Cp}^*)Pt]$

Table 3. $^{195}Pt\{^1H\}$ NMR Data of Complexes 1−6 in Comparison with Related Data[a]

	δ[a]
$[(1,2\text{-}\eta^2\text{:}5,6\text{-cod})(\eta^5\text{-Cp}^*)MePt]$ (**1**)[b]	−5467
$[\mu\text{-}(1,2\text{-}\eta^2\text{:}5,6\text{-}\eta^2\text{-cod})\{(\eta^5\text{-Cp}^*)MePt\}_2]$ (**2**)[b]	−5467
$[(1,2\text{-}\eta^2\text{:}5,6\text{-cod})(\eta^5\text{-Cp}^*N)MePt]$ (**3**)[b]	−5469
$[\mu\text{-}(1,2\text{-}\eta^2\text{:}5,6\text{-}\eta^2\text{-cod})\{(\eta^5\text{-Cp}^*N)MePt\}_2]$ (**4**)[b]	−5469
$[(1,2\text{-}\eta^2\text{:}5,6\text{-cod})(\eta^5\text{-Cp}^{*2=})MePt]$ (**5**)[b]	−5469
$[(1,2\text{-}\eta^2\text{:}5,6-\text{cod})(\eta^5\text{-Cp}^{*3=})MePt]$ (**6**)[b]	−5469
$[(1\text{-}\sigma\text{:}5,6\text{-}\eta^2\text{-}C_8H_{12}\text{-}2\text{-Cp}^*)(\eta^5\text{-Cp}^*)Pt]$[c]	−5516
$[(\eta^5\text{-Cp})(\eta^2\text{-}C_2H_4)(\sigma-\text{Cp})Pt]$[d,e]	−5316
$[(\eta^5\text{-Cp}^*)PtMe_3]$[f]	−5258
$[(\eta^5\text{-Cp}^*N)PtMe_3]$[g]	−5266
$[(\eta^4\text{-cod})PtMeCl]$[h]	−3496
$[(\eta^4\text{-cod})PtMeI]$[h]	−3877

[a] All resonances reported in ppm relative to H_2PtCl_6 in D_2O. [b] Data reported in this paper. [c] Reference 18. [d] Reference 25. [e] Converting of the values (see ref 23c): $\delta(PtCl_6^{2-}) = \delta$(frequency scale) − 4533 ppm. [f] Reference 21. [g] Reference 22. [h] Solvent CD_2Cl_2.

These chemical shifts are quite similar to those of $[(\eta^5\text{-Cp})Pt^{IV}(alkyl)_3]$ complexes,[21] including $[Cp^{*N}PtMe_3]$,[22] and therefore the resonances are all located in a region typical for platinum centers in hexacoordinated CpPt(IV) compounds.[23] To our knowledge only a few platinum(II) complexes are reported which contain a Cp moiety coordinated in an η^5 fashion, an olefin, and an alkyl group,[18,24,25] but two of them were synthesized in a very different way. Chart 1 shows these two examples, which have also been characterized by $^{195}Pt\{^1H\}$ NMR spectroscopy.[18,25]

In Table 3 a survey of ^{195}Pt NMR data is given, also containing the ^{195}Pt NMR signal of the complexes $[(1\text{-}\sigma\text{:}5,6\text{-}\eta^2\text{-}C_8H_{12}\text{-}2\text{-Cp}^*)(\eta^5\text{-Cp}^*)Pt]$ and $[(\eta^5\text{-Cp})(\eta^2\text{-}C_2H_4)(\sigma\text{-Cp})Pt]$ which match our own data and so are in accordance with the way we will describe the platinum−olefin bond.

Summarizing the experimental and analytical data, we have to conclude from the very strong shifts of the olefinic resonances in the NMR spectra as well as

(20) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(21) Boardman, L. D.; Newmark, R. A. *Magn. Reson. Chem.* **1992**, *30*, 481.

(22) Synthesis: see ref 3. The ^{195}Pt NMR resonance we recorded is slightly different from the one reported therein.

(23) (a) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247. (b) Benn, R.; Rufińska, A. *Angew. Chem.* **1986**, *98*, 851; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861. (c) Pregosin, P. S. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 285.

(24) (a) Hill, M. N. S.; Johnson, B. F. G.; Keating, T.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975,** 1197. (b) Clark, H. C.; Shaver, A. *Can. J. Chem.* **1976**, *54*, 2068.

(25) Boag, N. M.; Goodfellow, R. J.; Green, M.; Hessner, B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2585.

from the platinum resonances, which are similar to resonances of typical platinum(IV) centers, that the nature of the platinum−olefin bond has to be described as a metallacyclopropane, and it is thus comparatively stronger.

Dimerization of the monomeric species **1** and **3** to give the COD-bridged structures is clearly driven by entropic effects. This effect was previously proposed for the reaction of a $[(\eta^4\text{-cod})PtR]^+$ fragment with 1 equiv of $Na(S_2CNEt_2)$ to yield COD-bridged species such as $[\mu\text{-}(1,2\text{-}\eta^2\text{:}5,6\text{-}\eta^2\text{-cod})\{(S_2CNEt_2)RPt\}_2]$.[26] Furthermore, there is a nickel complex analogous to compounds **2** and **4**, the $[\mu\text{-}(1,2\text{-}\eta^2\text{:}5,6\text{-}\eta^2\text{-cod})\{(\eta^5\text{-Cp})MeNi\}_2]$, which was synthesized from Cp_2Ni, MeLi, and COD.[9a] Even when 1 equiv of COD was used, only the bridged dimer could be isolated. Unfortunately it was only characterized by ^{13}C NMR, but these data are comparable to the data recorded for the new complexes **2** and **4**. The interesting observation is that the dimerization of **3** to yield **4** occurs faster than the respective formation of **2** from **1**. Therefore, with the Cp* ligand the main reaction product is the monomeric species, but with a small amount of dimer as a side product which may be in equilibrium with the monomer. In comparison with this, the reaction with the Cp^{*N} ligand yielded the dimeric compound as the final reaction product but with the monomer as an intermediate. A probable explanation for this can be a reversible coordination of the side chain, either *intra*molecular or *inter*molecular, so that a 16-electron fragment which would be intermediately formed by decomplexation of the COD can be stabilized before being trapped by another "$Cp^{*N}PtMe(\eta^2\text{-cod})$" moiety. This would also explain why decomposition is a problem for the dimerization of $[(1,2\text{-}\eta^2\text{:}5,6\text{-cod})(\eta^5\text{-Cp*})MePt]$ (**1**). Another possibility is the formation of a 16-electron fragment by a ring slippage of the Cp moiety from η^5 to η^3 and the stabilization of this fragment by a coordination of the side chain followed by a decomplexation of the olefin and ring slippage from η^5 to η^3. The final step would again be the displacement of the amino group by an olefin function of a COD.

Conclusion

It has been demonstrated that platinum(II) complexes containing an η^5-coordinated cyclopentadienyl ligand can be prepared from $[(\eta^4\text{-cod})PtMeX]$ and these reactions result in a new class of complexes where one of the olefinic functions is surprisingly still coordinated to the metal center. It is particularly difficult to displace coordinated COD from Cp^RPt^{II} centers completely so that in investigations of side-chain-functionalized Cp systems neither a pendant amino group nor a pendant olefin will coordinate to the platinum center in addition to the Cp moiety. In general, many different aspects have to be taken into account to predict the coordination mode of bidentate cyclopentadienyl ligands. Probably the most decisive fact here is the type of donor ligand in the starting compound, which has to be replaced, and the strengths of the resulting bond. Sterically less demanding leaving alkenes such as ethene, propene, or even norbornadiene, for example, may be a better choice than COD. Subsequent work will focus on the effect of changing Cp* to Cp as well as evaluating alternative strategies to introduce functionalized Cp groups at Pt(II) centers bearing coordinated ancillary ligands more labile than COD.

Experimental Section

General Comments. All experiments were carried out under a purified argon atmosphere using standard Schlenk techniques. Solvents were dried by using standard procedures, distilled, and stored under argon and molecular sieves (4 Å). The following compounds were synthesized according to the literature: [(cod)PtMeCl],[27] [(cod)PtMeI] (prepared from [(cod)-PtMeCl] using NaI), HCp^{*N},[13] HCp*,[28] $LiCp^{*2=}$,[8a] and $LiCp^{*3=}$.[8b] All other reagents were used as purchased.

NMR spectra were obtained either on a Bruker Advance DRX 400 spectrometer (^1H, 400.13 MHz; ^{13}C, 100.62 MHz) or on a Bruker Advance DPX 250 spectrometer (^{31}P, 101.26 MHz; ^{195}Pt, 53.48 MHz) at ambient temperature. ^1H and ^{13}C chemical shifts are given in ppm, calibrated against residual protons of the deuterated solvents, and referenced to TMS, ^{31}P values are reported relative to the external standard 85% H_3PO_4 in D_2O, and ^{195}Pt values are reported relative to the external standard $[PtCl_6]^{2-}$ in D_2O. The assignments of the ^1H and ^{13}C NMR signals were made with the aid of $^1H/^{13}C$-HMQC experiments. The IR spectra were recorded on a Perkin-Elmer 1720 X-FT spectrometer, and the infrared peaks are given in cm^{-1}. All mass spectra were recorded by the FAB technique with 3-nitrobenzyl alcohol as matrix and performed using a VG Autospec spectrometer. The decomposition point determinations were performed in a glass capillary using a Gallenkamp melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum employing a C-, H-, N-Analysenautomat of the type CHNSO Vario EL.

Preparation of $[(1,2\text{-}\eta^2\text{:}5,6\text{-cod})(\eta^5\text{-Cp*})MePt]$ (1). To a suspension of KCp* (0.18 g, 1.03 mmol) in THF (20 mL) was added 0.44 g (0.99 mmol) of [(cod)PtMeI] in one portion, and the reaction mixture was stirred for 2 days under the exclusion of light at room temperature. Workup was carried out by removing the solvent in vacuo, and the residue was extracted with pentane (3 × 15 mL). All volatile components were removed in vacuo again to yield 0.32 g of **1** (0.71 mmol, 72%) as a yellow oil. Several attempts were made to purify the product, but traces of **2** could not be avoided. Anal. Calcd for $C_{19}H_{30}Pt$ (453.54): C, 50.32; H, 6.67. Found: C, 49.32; H, 6.78. HRMS: *m/z* calcd for $C_{19}H_{30}{}^{195}Pt$, 453.1995; found, 453.1998. MS: *m/z* (relative intensity, %) 453 [M^+ (31)], 438 [M^+ − Me (100)], 345 [M^+ − COD (60)], 330 [M^+ − Me, COD (57)]. ^1H NMR (C_6D_6): δ 0.28 (s, 3 H, $^2J_{Pt-H}$ = 89 Hz, Pt−CH_3), 1.72 (s, 15 H, $^3J_{Pt-H}$ = 11 Hz, Cp CH_3), 1.73−1.85 (m, 2 H, CH_2, cod $H_{4,7}$), 2.03−2.20 (m, 4 H, CH_2, cod $H_{3,4,7,8}$), 2.25−2.40 (m, 2 H, CH_2, cod $H_{3,8}$), 2.69 (br s, 2 H, $^2J_{Pt-H}$ = 76 Hz, CH, cod $H_{1,2}$), 5.67 (br s, 2 H, CH, cod $H_{5,6}$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −14.9 ($^1J_{Pt-C}$ = 886 Hz, Pt−CH_3), 9.1 (Cp CH_3), 30.2 ($^3J_{Pt-C}$ = 40 Hz, CH_2, cod $C_{4,7}$), 31.6 ($^2J_{Pt-C}$ = 68 Hz, CH_2, cod $C_{3,8}$), 51.3 ($^1J_{Pt-C}$ = 309 Hz, CH, cod $C_{1,2}$), 101.4 (C_q, $^1J_{Pt-C}$ = 13 Hz, Cp C_{1-5}), 130.2 (CH, cod $C_{5,6}$). $^{195}Pt\{^1H\}$ NMR (C_6D_6): δ −5467. IR (neat liquid; select.): 3011 (w), 2966 (s), 2924 (s), 2878 (s), 2806 (w), 1645 (w), 1454 (m), 1433 (m), 1379 (m), 1357 (w), 1236 (w), 1214 (w), 1157 (w), 1083 (w), 1025 (w), 940 (w), 796 (w), 718 (m).

Preparation of $[\mu\text{-}(1,2\text{-}\eta^2\text{:}5,6\text{-}\eta^2\text{-cod})bis\{(\eta^5\text{-Cp*})MePt\}]$ (2). By storing reaction product **1** under the exclusion of light and air for about 1 month the formation of **2** took place but it

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(27) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.
(28) Kohl, F. X.; Jutzi, P. *Organomet. Synth.* **1986**, *3*, 489.

could not be separated from **1** completely. MS: *m/z* (relative intensity, %) 798 [M^+ (5)], 768 [M^+ − 2Me (8)], 453 [M^+ − Cp*PtMe (39)], 438 [Cp*Pt(cod) (100)], 345 [Cp*PtMe (75)], 330 [Cp*Pt (63)]. ^{1}H NMR (C_6D_6): δ 0.27 (s, 3 H, $^2J_{Pt-H}$ = 89 Hz, Pt−CH_3), 1.30−1.50 (m, 2 H, CH_2, cod), 1.73 (s, 15 H, $^3J_{Pt-H}$ = 11 Hz, Cp CH_3), 2.30−2.40 (m, 2 H, CH_2, cod), 2.70 (br s, 2 H, $^2J_{Pt-H}$ = 76 Hz, CH, cod). ^{13}C{^{1}H} NMR (C_6D_6): δ −14.7 ($^1J_{Pt-C}$ = 886 Hz, Pt−CH_3), 9.2 (Cp CH_3), 32.1 (CH_2, cod), 51.4 ($^1J_{Pt-C}$ = 309 Hz, CH, cod), 101.5 (C_q, $^1J_{Pt-C}$ = 13 Hz, Cp C_{1-5}). ^{195}Pt{^{1}H} NMR (C_6D_6): δ −5467.

Preparation of [(1,2-η^2:5,6-cod)(η^5-Cp*^{N})MePt] (3). A suspension of 0.20 g (1.00 mmol) of LiCp*^{N} in 15 mL of diethyl ether (freshly prepared by addition of *n*-butyllithium in *n*-hexane (1.6 M; 0.63 mL, 1.01 mmol) to a solution of HCp*^{N} (0.19 g, 1.00 mmol) in diethyl ether) was cooled to −78 °C and an amount of 0.35 g (1.00 mmol) of [(cod)PtMeCl] dissolved in 15 mL of THF was added. While it was stirred overnight, the mixture was warmed to room temperature, resulting in a yellow solution. After all volatile components were removed in vacuo, the residue was extracted three times with 20 mL of pentane. The combined extracts were again evaporated in vacuo, leaving 0.47 g (0.92 mmol, 92%) of **3** as a yellow oil. MS: *m/z* (relative intensity, %) 510 [M^+ (7)], 495 [M^+ − Me (86)], 402 [M^+ − COD (75)], 385 (100). ^{1}H NMR (C_6D_6): δ 0.32 (s, 3 H, $^2J_{Pt-H}$ = 89 Hz, Pt−CH_3), 1.72 (s, 6 H, $^3J_{Pt-H}$ = 12 Hz, Cp CH_3), 1.81 (s, 6 H, $^3J_{Pt-H}$ = 11 Hz, Cp CH_3), 1.75−1.85 (m, 2 H, CH_2, cod $H_{4,7}$), 2.13 (s, 6 H, CH_3, NMe_2), 2.05−2.20 (m, 4 H, CH_2, cod $H_{3,4,7,8}$), 2.25−2.40 (m, 4 H, CH_2, $H_{2'}$ and cod $H_{3,8}$), 2.45−2.55 (m, 2 H, CH_2, $H_{1'}$), 2.72 (br s, 2 H, $^2J_{Pt-H}$ = 76 Hz, CH, cod $H_{1,2}$), 5.67 (br s, 2 H, CH, cod $H_{5,6}$). ^{13}C{^{1}H} NMR (C_6D_6): δ −15.4 ($^1J_{Pt-C}$ = 884 Hz, Pt−CH_3), 9.1 and 9.2 (Cp CH_3), 23.6 (CH_2, $C_{1'}$), 30.3 ($^3J_{Pt-C}$ = 40 Hz, CH_2, cod $C_{4,7}$), 31.6 ($^2J_{Pt-C}$ = 68 Hz, CH_2, cod $C_{3,8}$), 45.6 ($N(CH_3)_2$), 51.7 ($^1J_{Pt-C}$ = 309 Hz, CH, cod $C_{1,2}$), 60.5 (CH_2, $C_{2'}$), 101.4 (C_q, $^1J_{Pt-C}$ = 20 Hz, Cp $C_{3,4}$), 102.1 (C_q, $^1J_{Pt-C}$ = 19 Hz, Cp $C_{2,5}$), 103.9 (C_q, Cp C_1), 130.1 (CH, cod $C_{5,6}$). ^{195}Pt{^{1}H} NMR (C_6D_6): δ −5469.

The result of a typical elemental analysis was as follows. Anal. Calcd for a mixture (1:1) of **3** and **4**: $C_{22}H_{37}NPt/0.5\ C_{36}H_{62}N_2Pt_2$ (510.64/456.54): C, 49.56; H, 7.07; N, 2.91. Found: C, 49.46; H, 6.95; N, 2.93.

The preparation of compound **3** starting from [(cod)PtMeI] could be carried out analogously to the preparation of compound **1**.

Preparation of [μ-(1,2-η^2:5,6-η^2-cod)bis{(η^5-Cp*^{N})MePt}] (4). When reaction product **3** was stored with the exclusion of light and air for about 1 week, the formation and crystallization of **4** occurred. Compound **4** was collected as yellow crystals in almost quantitative yield. Washing the crystalline product with a small amount of cold methanol (0 °C) and toluene led to 0.40 g (0.88 mmol, 96%; mp 148 °C dec) of **4**. These crystals were suitable for X-ray diffraction analysis. Anal. Calcd for $C_{36}H_{62}N_2Pt_2$ (913.09): C, 47.36; H, 6.84; N, 3.07. Found: C, 47.84; H, 6.84; N, 2.86. MS: *m/z* (relative intensity, %) 913 [M^+ + H (3)], 510 [M^+ − Cp*^{N}PtMe (7)], 495 [Cp*^{N}Pt(cod) (87)], 402 [Cp*^{N}PtMe (75)], 385 (100). ^{1}H NMR (C_6D_6): δ 0.35 (s, 3 H, $^2J_{Pt-H}$ = 89 Hz, Pt−CH_3), 1.45−1.60 (m, 2 H, CH_2, cod), 1.75 (s, 6 H, $^3J_{Pt-H}$ = 11 Hz, CH_3, Cp CH_3), 1.83 (s, 6 H, $^3J_{Pt-H}$ = 10 Hz, Cp CH_3), 2.15 (s, 6 H, CH_3, NMe_2), 2.25−2.35 (m, 2 H, CH_2, CH_2NMe_2), 2.40−2.50 (m, 2 H, CH_2, cod), 2.50−2.60 (m, 2 H, Cp CH_2), 2.78 (br s, 2 H, $^2J_{Pt-H}$ = 75 Hz, CH, cod). ^{13}C{^{1}H} NMR (C_6D_6): δ −15.5 ($^1J_{Pt-C}$ = 882 Hz, Pt−CH_3), 9.2 and 9.3 (Cp CH_3), 23.6 (CH_2, Cp CH_2), 33.3 (CH_2, cod), 45.6 ($N(CH_3)_2$), 52.3 ($^1J_{Pt-C}$ = 310 Hz, CH, cod), 60.7 (CH_2, CH_2-NMe_2), 101.2 (C_q, Cp $C_{3,4}$), 102.4 (C_q, Cp $C_{2,5}$), 104.1 (C_q, Cp C_1). ^{195}Pt{^{1}H} NMR (C_6D_6): δ −5469. IR (KBr; select.): 2919 (s), 2873 (s), 2812 (s), 2776 (s), 1464 (s), 1427 (m), 1379 (w), 1262 (w), 1237 (m), 1211 (w), 1181 (m), 1052 (m), 1039 (m), 1010 (w), 955 (m), 865 (w), 592 (w), 550 (w).

Preparation of [(1,2-η^2:5,6-cod)(η^5-Cp*$^{2=}$)MePt] (5). To 0.14 g (0.76 mmol) of LiCp*$^{2=}$, suspended in 10 mL of diethyl ether, was added 0.24 g (0.68 mmol) of [(cod)PtMeCl]. The mixture was cooled to −78 °C, and after the addition of 8 mL of THF the resulting solution was stirred overnight and warmed to room temperature. Removing the solvents in vacuo followed by extraction of the yellow residue with 3 × 15 mL of pentane and evaporation of the combined pentane extracts led to 0.20 g (0.42 mmol, 64%) of **5** as a yellow oil. Anal. Calcd for $C_{22}H_{34}Pt$ (493.60): C, 53.53; H, 6.94. Found: C, 53.89; H, 6.81. MS: *m/z* (relative intensity, %) 493 [M^+ (5)], 478 [M^+ − Me (48)], 385 [M^+ − COD (34)], 369 [M^+ − COD, CH_4 (100)]. ^{1}H NMR (C_6D_6): δ 0.29 (s, 3 H, $^2J_{Pt-H}$ = 89 Hz, Pt−CH_3), 1.71 (s, 6 H, $^3J_{Pt-H}$ = 11 Hz, Cp CH_3), 1.76 (s, 6 H, $^3J_{Pt-H}$ = 10 Hz, Cp CH_3), 1.70−1.85 (m, 2 H, CH_2, cod $H_{4,7}$), 2.00−2.20 (m, 6 H, CH_2, $H_{2'}$ and cod $H_{3,4,7,8}$), 2.25−2.40 (m, 4 H, CH_2, $H_{1'}$ and cod $H_{3,8}$), 2.70 (br s, 2 H, $^2J_{Pt-H}$ = 75 Hz, CH, cod $H_{1,2}$), 4.95−5.05 (m, 2 H, CH_2, $H_{4'}$), 5.67 (br s, 2 H, CH, cod $H_{5,6}$), 5.75−5.85 (m, 1 H, CH, $H_{3'}$). ^{13}C{^{1}H} NMR (C_6D_6): δ −15.3 ($^1J_{Pt-C}$ = 885 Hz, Pt−CH_3), 9.1 and 9.2 (2 s, Cp CH_3), 24.6 (CH_2, $C_{1'}$), 30.2 ($^3J_{Pt-C}$ = 38 Hz, CH_2, cod $C_{4,7}$), 31.6 ($^2J_{Pt-C}$ = 68 Hz, CH_2, cod $C_{3,8}$), 35.1 (CH_2, $C_{2'}$), 51.6 ($^1J_{Pt-C}$ = 309 Hz, CH, cod $C_{1,2}$), 101.1 (C_q, $^1J_{Pt-C}$ = 13 Hz, Cp $C_{3,4}$), 102.0 (C_q, $^1J_{Pt-C}$ = 11 Hz, Cp $C_{2,5}$), 105.0 (C_q, $^1J_{Pt-C}$ = 17 Hz, Cp C_1), 114.9 (CH_2, $C_{4'}$), 130.1 (CH, cod $C_{5,6}$), 138.6 (CH, $C_{3'}$). ^{195}Pt{^{1}H} NMR (C_6D_6): δ −5469. IR (neat liquid; select.): 3076 (w), 2956 (s), 2926 (s), 2878 (s), 2859 (m), 1713 (w), 1683 (w), 1640 (m), 1455 (m), 1378 (m), 1238 (w), 1214 (w), 1159 (w), 1085 (w), 1019 (w), 993 (m), 910 (m), 719 (w).

Preparation of [(1,2-η^2:5,6-cod)(η^5-Cp*$^{3=}$)MePt] (6). To 0.25 g (1.27 mmol) of LiCp*$^{3=}$ suspended in 10 mL of diethyl ether, 0.45 g (1.27 mmol) of [(cod)PtMeCl] was added, and the mixture was cooled to −78 °C. The addition of 5 mL of THF yielded a clear, yellow solution after 1 h, which was stirred overnight while being warmed to room temperature. Removing the solvents in vacuo followed by extracting the yellow residue with 3 × 15 mL of pentane and evaporating the combined pentane extracts led to 0.47 g (0.93 mmol, 73%) of **6** as a yellow oil. Anal. Calcd for $C_{23}H_{36}Pt$ (507.63): C, 54.42; H, 7.15. Found: C, 54.79; H, 6.98. MS: *m/z* (relative intensity, %) 507 [M^+ (5)], 492 [M^+ − Me (35)], 399 [M^+ − COD (42)], 383 [M^+ − COD,CH_4 (100)]. ^{1}H NMR (C_6D_6): δ 0.31 (s, 3 H, $^2J_{Pt-H}$ = 89 Hz, Pt−CH_3), 1.40−1.55 (m, 2 H, $H_{2'}$), 1.72 (s, 6 H, $^3J_{Pt-H}$ = 12 Hz, Cp CH_3), 1.77 (s, 6 H, $^3J_{Pt-H}$ = 11 Hz, Cp CH_3), 1.80−1.90 (m, 2 H, CH_2, cod $H_{4,7}$), 1.95−2.05 (m, 2 H, $H_{3'}$), 2.05−2.20 (m, 4H, CH_2, cod $H_{3,4,7,8}$), 2.20−2.30 (m, 2 H, $H_{1'}$), 2.30−2.40 (m, 2 H, CH_2, cod $H_{3,8}$), 2.72 (br s, 2 H, $^2J_{Pt-H}$ = 75 Hz, CH, cod $H_{1,2}$), 4.95−5.05 (m, 2 H, $H_{5'}$), 5.68 (br s, 2 H, CH, cod $H_{5,6}$), 5.70−5.85 (m, 1 H, $H_{4'}$). ^{13}C{^{1}H} NMR (C_6D_6): δ −15.3 ($^1J_{Pt-C}$ = 884 Hz, Pt−CH_3), 9.1 and 9.2 (Cp CH_3), 24.4 (CH_2, $C_{1'}$), 30.0 (CH_2, $C_{2'}$), 30.3 ($^3J_{Pt-C}$ = 40 Hz, CH_2, cod $C_{4,7}$), 31.6 ($^2J_{Pt-C}$ = 66 Hz, CH_2, cod $C_{3,8}$), 34.0 (CH_2, $C_{3'}$), 51.6 ($^1J_{Pt-C}$ = 309 Hz, CH, cod $C_{1,2}$), 101.0 (C_q, Cp $C_{3,4}$), 102.0 (C_q, Cp $C_{2,5}$), 105.6 (C_q, Cp C_1), 114.8 (CH_2, $C_{5'}$), 130.1 (CH, cod $C_{5,6}$), 138.7 (CH, $C_{4'}$). ^{195}Pt{^{1}H} NMR (C_6D_6): δ −5469. IR (neat liquid; select.): 3076 (w), 3010 (w), 2956 (s), 2929 (s), 2878 (s), 2860 (m), 2809 (w), 1641 (w), 1583 (w), 1457 (m), 1439 (m), 1378 (m), 1239 (w), 1213 (w), 1084 (w), 991 (w), 910 (m), 804 (w), 719 (w).

X-ray Structure Determination. Geometry and intensity data were collected with Mo Kα radiation at 203(2) K on a Bruker-axs-SMART diffractometer equipped with a graphite monochromator (λ = 0.71073 Å). A summary of crystal data, data collection parameters, and convergence results is compiled in Table 1. A semiempirical absorption correction was applied. The structure was solved by direct methods (SHELXS 86). Refinements were carried out with the SHELXL-97 package. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions and refined isotropically in riding mode. All refinements were made by full-matrix least squares on F^2. Crystallographic data (excluding structure factors) for the structure of **4** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication

no. CCDC 156541. Copies of the data can be obtained free of charge by application to the CCDC, 12 Union Road, Cambridge CB2, 1EZ, U.K. (fax, int. code +44-1223/336-001; e-mail, deposit@ccdc.cam.ac.uk).

Acknowledgment. The support of this work by Degussa-Hüls AG and W. C. Heraeus GmbH is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010107A