Consecutive Cyclometalation by Platinum(II)

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The mechanism of the selective formation of the new benzylic mono- and bicyclometalated platinum(II) complexes **2a**,**b** and **3b** has been studied. Monitoring the initial sp^3 C−H activation of the ligand DIPPIDH (α^2-(**di**i**so**propyl**p**hosphino)**iso****d**urene; **1**) and (1,5-cyclooctadiene)dimethylplatinum(II) ((COD)$PtMe_2$) at room temperature by $^{31}P\{^1H\}$ NMR reveals that, after displacement of 1,5-cyclooctadiene, the complex *cis*-(DIPPIDH)(DIPPID)-PtMe (**2a**) is formed selectively by oxidative addition of a benzylic C−H bond and subsequent reductive elimination of CH_4. This reaction is controlled by electronic factors. Heating of **2a** results in isomerization to the thermodynamically more stable isomer *trans*-(DIPPIDH)-(DIPPID)PtMe (**2b**) as well as the formation of the double-C−H activated complex *trans*-$(DIPPID)_2Pt$ (**3b**) with liberation of CH_4 in parallel pathways. Continuous heating results in the quantitative formation of the thermally stable **3b**. Mechanistically, the second C−H activation proceeds analogously to the first one. The molecular structure of **3b**, possessing two six-membered metallacycles, two methylene bridges, and two phosphines in mutually *trans* positions, was determined by complete single-crystal diffraction studies.

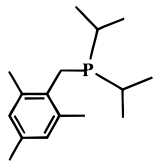
Introduction

Recently we demonstrated the selective activation and functionalization of unstrained sp^2-sp^3 C−C bonds by rhodium(I)[1] and platinum(II),[2] using bis(phosphino)-xylene substrates under mild homogeneous conditions. It was shown that the competing, kinetically favorable benzylic C−H activation can be reversed or suppressed by utilizing nonpolar or polar substrates. The sp^3 C−H activation precedes an interesting overall process, which includes (i) the selective demethylation of an aromatic system and (ii) transferring of the methylene group to another substrate (eq 1)

$$R-CH_3 + ML_n \xrightarrow{-H-L} R-CH_2-ML_{n-1} \xrightarrow{+A-B} R-ML_{n-1} + A-CH_2-B \quad (1)$$

To extend our findings and to obtain insight into the nature of the bond activation processes involved, we studied the formation of new methylene-bridged metal complexes using the phosphine ligand DIPPIDH (α^2-(**di**i**so**propyl**p**hosphino)**iso****d**urene; **1**) and (1,5-cyclo-octadiene)dimethylplatinum(II) ((COD)$PtMe_2$).

The chelating diene in (COD)$PtMe_2$ can be displaced by phosphine ligands.[3,4] Reaction with **1** followed by cyclometalation of a benzylic C−H bond by the electron-rich metal center is expected to result in the formation of a six-membered ring and CH_4, rendering the overall process irreversible. Our system allows a second molecule of **1** to coordinate to the metal, resulting in the formation of a second six-membered chelating ring with liberation of CH_4. Previous studies on cyclometalation provided much information on intra- and intermolecular C−H activation.[5] It is known that σ-bonded Pt−CH_3[6a] groups and bulky substituents promote C−H activation.[6b,c] In this paper we report on the mechanism of two consecutive C−H activation processes involving Pt(II), displaying interesting steric and electronic effects. The synthesis and the crystal structure of the double-cyclometalated complex **3b,** possessing two six-membered chelates, two methylene bridges, and two phosphines in mutually *trans* positions, are described. Furthermore, the isolation (**2a**) and formation (**2a**,**b**) of two monocyclometalated products are discussed.



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Experimental Section

General Procedures. All reactions were carried out under nitrogen in a Vacuum Atmospheres glovebox (DC-882) equipped

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with a recirculation (MO-40) "Dri-Train" or under argon using standard Schlenk techniques. Solvents were reagent grade or better. Benzene was dried (Frutarom, Na/benzophenone), distilled, and degassed before introduction into the glovebox, where it was stored over activated 4 Å molecular sieves. Deuterated solvents were purchased from Aldrich and were degassed and stored over 4 Å activated molecular sieves in the glovebox. (COD)$PtMe_2$ and DIPPIDH (**1**) were prepared by published procedures.[3,7] Reaction flasks were washed with water and acetone and oven-dried prior to use. GC analyses were performed on a Varian 3300 gas chromatograph equipped with a molecular sieve column. Field desorption (FD) mass spectra were measured on a Varian MAT 711 double-focused mass spectrometer at The Institute of Mass Spectrometry, University of Amsterdam, Amsterdam, The Netherlands. Elemental analyses were carried out at the Hebrew University, Jerusalem, Israel.

Spectroscopic Analysis. The ^1H, ^{31}P, and ^{13}C NMR spectra were recorded at 400.19, 161.9, and 100.6 MHz, respectively, on a Bruker AMX 400 NMR spectrometer. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. The ^1H and ^{13}C NMR chemical shifts are relative to tetramethylsilane; the resonance of the residual protons of the solvent was used as an internal standard h_1 (7.15 ppm benzene) and all-d solvent peaks (128.00 ppm benzene), respectively. $^{31}P\{^1H\}$ NMR chemical shifts are relative to 85% H_3PO_4 in D_2O at δ 0.0 (external reference), with shifts downfield of the reference considered positive. Screw-cap 5 mm NMR tubes were used in NMR follow-up experiments. Assignments in the ^1H and $^{13}C\{^1H\}$ NMR were made using $^1H\{^{31}P\}$, $^1H-^1H$ COSY, and ^{13}C-DEPT-135 NMR (distortionless enhancement by polarization transfer). All measurements were carried out at 298 K unless otherwise specified.

Synthesis of *cis*-(DIPPIDH)(DIPPID)PtMe (2a). A solution of DIPPIDH (**1**; 60 mg, 0.240 mmol) in 10 mL of benzene was added dropwise to a stirred solution of (COD)-$PtMe_2$ (40 mg, 0.120 mmol) in 10 mL of benzene. After 3 days of stirring at room temperature, the colorless solution was submitted to high vacuum, yielding a colorless oil (80 mg, 94%). Prolonged stirring for another 2 days did not result in the formation of other products. Quantitative analysis of the gas phase by GC showed formation of 1 equiv of CH_4. FDMS analysis showed m/z 709 (calcd $M^{\bullet+}$ 709. Anal. Calcd for $C_{33}H_{56}P_2Pt$: C, 55.84; H, 7.95. Found: C, 56.20; H, 8.25. ^1H NMR (C_6D_6): δ 6.7 (m, 4H, ArH), 3.26 (d, 2H, $^2J_{PH}$ = 9.0 Hz, $^3J_{PtH}$ = 19.0 Hz, ArCH_2P), 2.84 (vt, 2H, $^3J_{PH}$ = 10.4 Hz, $^2J_{PtH}$ = 89.0 Hz, ArCH_2Pt), 2.82 (d, 2H, $^2J_{PH}$ = 9.2 Hz, $^3J_{PPt}$ = 29.2 Hz, ArCH_2P), 2.4−2.2 (m, 15H, ArCH_3), 2.0 (m, 4H, PCH(CH_3)$_2$), 1.2−0.9 (m, 24 H, PCH(CH_3)$_2$), 0.90 (vt, 3H, $^3J_{PH}$ = 6.4 Hz, $^2J_{PtH}$ = 66.9 Hz, PtCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 65.97 (s, 1P, $^1J_{PtP}$ = 2270.6 Hz), 31.21 (s, 1P, $^1J_{PtP}$ = 1889.9 Hz). $^{13}C\{^1H\}$-NMR (C_6D_6): δ 150.2 (vt, $^3J_{PC}$ = 7.1 Hz, $^2J_{PtC} \approx$ 56 Hz, C_{ipso}-CH_2Pt), 138−124 (m, not resolved, C_{Ar}), 30−16 (m, not resolved totally, ArCH$_3$ and PCH(CH_3)$_2$), 30.63 (dd, $^3J_{PC}$ = 7.6 Hz, $^1J_{PC}$ = 248.9 Hz, $^2J_{PtC}$ = 497.8 Hz, ArCH$_2$PPt), 10.89 (vt, $^2J_{PC,cis}$ = 6.5 Hz, ArCH$_2$Pt), 5.02 (dd, $^2J_{PC,cis}$ = 10.4 Hz, $^2J_{PC,trans}$ = 90.3 Hz, $^1J_{PtC}$ = 621.9 Hz, PtCH$_3$).

Synthesis of *trans*-(DIPPID)$_2$Pt (3b). A solution of DIPPIDH (**1**; 30 mg, 0.120 mmol) in 10 mL of benzene was added dropwise to a stirred solution of (COD)$PtMe_2$ (20 mg, 0.060 mmol) in 10 mL of benzene. The solution was heated to 110−120 °C using a pressure flask. After 3 days the colorless solution was cooled to room temperature and was concentrated in vacuo to approximately 1 mL, resulting in the formation of colorless crystals of pure **3b**, which were isolated by filtration (25 mg, yield 59%). The $^{31}P\{^1H\}$ NMR of the mother liquid showed only complex **3b**. Quantitative analysis of the gas phase by GC showed formation of 2 equiv of CH_4. Complex **3b** is also formed by heating a benzene solution of complex **2a** to 130 °C for 2 days. Quantitative analysis of the gas phase of the latter reaction by GC showed formation of 1 equiv of CH_4. Anal. Calcd for $C_{32}H_{52}P_2Pt$: C, 55.40; H, 7.55. Found: C, 55.70; H, 7.80. ^1H NMR (C_6D_6): δ 6.55 (s, 2H, ArH), 6.40 (s, 2H. ArH), 2.91 (br s, 4H, ArCH_2P), 2.54 (br s, 4H, PCH(CH_3)$_2$), 2.25 (s, 6H, ArCH_3), 2.18 (br s, 4H, ArCH_2Pt), 2.05 (s, 6H, ArCH_3), 1.21 (dd, 12H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 6.8 Hz), 0.91 (br m, 12H, PCH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 73.26 (s, 2P, $^1J_{PtP}$ = 3270.2 Hz).

Follow-up of the Formation of *cis*-(DIPPIDH)(DIPPID)PtMe (2a). A solution of DIPPIDH (**1**; 45 mg, 0.180 mmol) in 0.6 mL of C_6D_6 was added to (COD)$PtMe_2$ (20 mg, 0.060 mmol) and loaded in a 5 mm screw-cap NMR tube, which was equipped with a septum and tightly closed using Teflon tape and Parafilm. After approximately 1 h at room temperature the reaction mixture was monitored by $^{31}P\{^1H\}$ NMR, showing the presence of free ligand **1** and intermediate **A**, δ 26.64 (s, $^1J_{PtP}$ = 1765.1 Hz). The reaction mixture was heated for 10 min at 80 °C, resulting in the formation of complex **2a**. Analysis of the gas phase by GC and comparison with an authentic sample showed the formation of CH_4, which was also observed by ^1H and $^{13}C\{^1H\}$ NMR. This experiment was repeated under the same conditions at 58 °C and monitored by $^{31}P\{^1H\}$ NMR measurements at room temperature. The results are presented in Figure 4.

Follow-up of the Formation of *trans*-(DIPPIDH)(DIPPID)PtMe (2b) and *trans*-(DIPPID)$_2$Pt (3b). A solution of DIPPIDH (**1**; 32 mg, 0.128 mmol) in 0.6 mL of C_6D_6 was added to (COD)$PtMe_2$ (20 mg, 0.060 mmol) and loaded in a 5 mm screw-cap NMR tube which was firmly sealed using Teflon tape and Parafilm. The NMR tube was placed in an oil bath at 100 °C and monitored by $^{31}P\{^1H\}$ NMR at room temperature. $^{31}P\{^1H\}$ NMR first showed formation of complex **2a** and intermediate **A**; the latter was only observed during the start of the reaction. After prolonged heating, formation of complexes **3b** and **2b** became visible, while complexes **2a** and **A** disappeared. The results are presented in Figure 2. Raising the temperature to 130 °C resulted in disappearance of complex **2b** and an increase in the amount of **3b**. This process was completed within 2 h. This experiment was repeated by starting with **2a** (42 mg, 0.060 mmol) in 0.6 mL of C_6D_6 at 109 °C and monitored by $^{31}P\{^1H\}$ NMR at room temperature. The results are presented in Figures 5 and 6.

X-ray Crystal Structure Determination of *trans*-(DIPPID)$_2$Pt (3b). A colorless transparent crystal (0.9 × 0.5 × 0.5 mm) was mounted on a glass fiber and flash-frozen under a cold nitrogen stream (at 110 K) on a Rigaku AFC5R four-circle diffractometer mounted on a rotating anode with Mo Kα radiation and a graphite monochromator. Accurate unit-cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections in the range $2.1° \leq \theta \leq 27.5°$. The SHELXS-92[8] and SHELXL-93[9] program packages installed on a Silicon Graphics workstation were used for structure solution and refinement. Structure **3b** was solved using direct methods (SHELXS-92) and refined by full-matrix least-squares techniques based on F^2 (SHELXL-93). The final cycle of the least-squares refinement gave an agreement factor R of 0.0294 (based on F^2) for all data. Hydrogens were calculated from difference Fourier maps and refined in a riding mode with individual temperature factors. An ORTEP view of the molecular structure and the adopted numbering scheme is shown in Figure 3. Table 1 gives details of the crystal structure determination. Selected bond angles and distances are listed in Table 3.

Results and Discussion

a. Formation and Identification of Complexes 2a,b and 3b. Displacement of COD from (COD)$PtMe_2$

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Table 1. Crystal Data for *trans*-(DIPPID)$_2$Pt (3b)

formula	$C_{32}H_{52}P_2Pt$
fw	693.77
space group	*P*1
cryst system	triclinic
a, Å	8.238(2)
b, Å	9.677(2)
c, Å	10.806(2)
α, deg	66.07(3)
β, deg	77.70(3)
γ, deg	89.39(3)
V, Å^3	766.5 (3)
D_{calcd}, g cm^{-3}	1.503
Z	1
μ(Mo Kα), cm^{-1}	47.0
crystal size, mm^3	0.9 × 0.5 × 0.5

Table 2. $^{31}P\{^1H\}$ NMR Data

compd	P: δ, ppm ($^1J_{PPt}$, Hz)	P_{ring}: δ, ppm ($^1J_{PPt}$, Hz)	Δ(complex−ligand **1**), ppm
1	4.60		
A	26.64 (1765.1)		22.40 (P)
2a	31.21(1889.9)	65.97 (2270.6)	26.61 (P), 61.37 (P_{ring})
2b[a]	22.92 (2876.9)	71.85 (3319.5)	18.32 (P), 67.25 (P_{ring})
3b		73.26 (3270.2)	68.66 (P_{ring})

[a] $^2J_{PP}$ = 419.1 Hz.

in benzene at room temperature by the aromatic phosphine **1** results in quantitative formation of the sp^3 C−H activated *cis* product **2a** (Figure 1) and 1 equiv of CH_4. Prolonged stirring, as well as changes in the metal/ligand ratio, did not result in the formation of other products. Compound **2a** has been fully characterized by various NMR techniques, FDMS, and elemental analysis. CH_4 was unambiguously detected by ^1H and $^{13}C\{^1H\}$ NMR and quantified by GC. In the $^{31}P\{^1H\}$ NMR (Table 2) two slightly broadened resonances of equal intensity appear at δ 65.97 and 31.21 ($w_{1/2}$ = 10 and 40 Hz, respectively), flanked by ^{195}Pt satellites. These signals sharpen upon heating to 333 K. The broadening is assumed to be a result of restricted bond rotation caused by steric hindrance of the bulky phosphine ligands in *cis* positions and due to fluxionality of the ring. The low-field chemical shift of δ 65.97 reflects a deshielding effect of this phosphorus atom due to the formation of the six-membered chelated ring.[10,11,14] No $^{31}P-^{31}P$ coupling is observed, indicating that both phosphorus atoms are coordinated mutually *cis*, which is in agreement with the observed platinum−phosphorus coupling constants ($^1J_{PtP}$ = 2270.6 and 1889.9 Hz). In addition, these coupling constants are characteristic of phosphines *trans* to a strong σ donor such as an alkyl.[10−13] The structure of complex **2a** is fully supported by ^1H and $^{13}C\{^1H\}$ NMR. For instance, the Pt−CH_3 group appears in the $^{13}C\{^1H\}$ NMR spectrum as a double doublet at 5.02 ppm, flanked by ^{195}Pt satellites ($^1J_{PtC}$ = 621.9 Hz) with *trans* $^2J_{PC}$ = 90.3 Hz and *cis* $^2J_{PC}$ = 10.4 Hz. In ^1H NMR this alkyl group appears as a virtual triplet at δ 0.90 with $^2J_{PtH}$ = 66.9 Hz and $^3J_{PH}$ = 6.4 Hz, which collapses into a singlet upon ^{31}P decoupling.

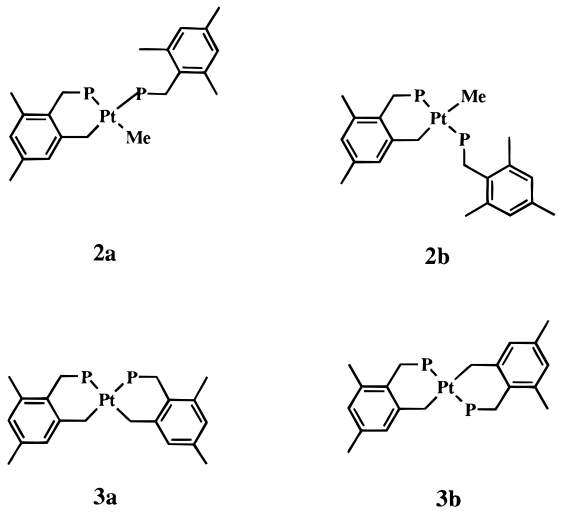

Figure 1. Complexes **2a**,**b** and **3a**,**b** (**3a** is not observed; the isopropyl substituents on P are omitted for clarity).

Reacting (COD)PtMe$_2$ with the ligand **1** in benzene at higher temperatures (100−130 °C) in a pressure flask results in quantitative formation of the double-C−H-activated complex **3b** and 2 equiv of CH_4. Colorless prismatic crystals are readily formed upon slow concentration of the reaction mixture. Complex **3b** was fully characterized by NMR, X-ray (*vide infra*), and elemental analysis. Changing the metal/ligand ratio does not influence the product formation, as observed also in the formation of **2a**. $^{31}P\{^1H\}$ NMR exhibits one sharp singlet at δ 73.26 for both ^{31}P nuclei, flanked by ^{195}Pt satellites, indicating that both phosphorus atoms are magnetically equivalent. The observed $^1J_{PPt}$ = 3270.2 Hz is typical of two mutually *trans* phosphorus atoms.[10] The low-field chemical shift of δ 73.26 reflects a deshielding effect of both phosphorus atoms due to the formation of two six-membered rings.[10,11,14] The ^1H NMR shows slightly broadened resonances, which are probably caused by fluxional behavior of these two rings. The thermal stability of the double-cyclometalated complex **3b** is likely to be due to the presence of the chelating rings, but it may be also kinetically inert due to steric factors. The sterically hindered, but electronically favorable, *cis* isomer **3a** was never observed. However, monitoring the formation of **3b** from **1** and (COD)PtMe$_2$ by $^{31}P\{^1H\}$ NMR at 100 °C (Figure 2) shows the formation and disappearance of two species: (i) the short-lived intermediate **A**, which is probably a result of partial or full displacement of the diene by the ligand(s) (Scheme 1), and (ii) the complex **2a**. Meanwhile, complexes **2b** and **3b** are formed in parallel pathways (*vide infra*). Raising the temperature to 130 °C at the end of the experiment for approximately 2 h results in the disappearance of **2b**.

Although complex **2b** was not isolated, the structure of **2b** is unambiguous. Two different phosphorus signals of equal intensity appear as sharp doublets at δ 71.85 and 22.92 in the $^{31}P\{^1H\}$ NMR and are accompanied by satellites due to coupling with ^{195}Pt. The large phosphorus−phosphorus coupling ($^2J_{PP}$ = 419.1 Hz) indicates that both nuclei are mutually *trans*, which is in agreement with the observed $^{195}Pt-^{31}P$ coupling

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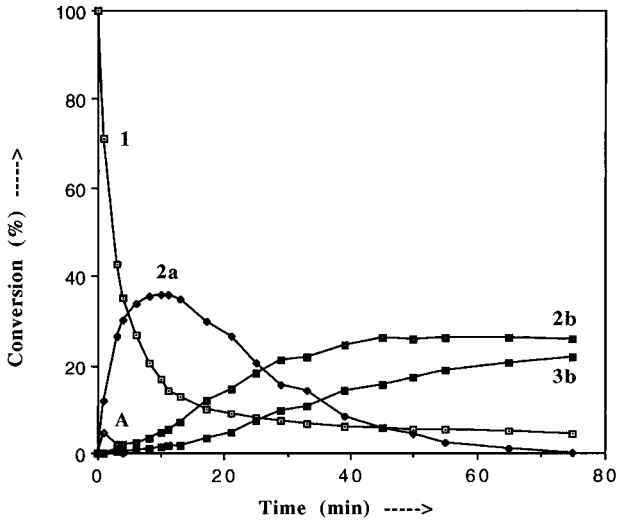

Figure 2. $^{31}P\{^1H\}$ NMR Follow-up of the reaction of **1** (2.1 equiv) with (COD)$PtMe_2$ (1 equiv) in C_6D_6 at 100 °C.

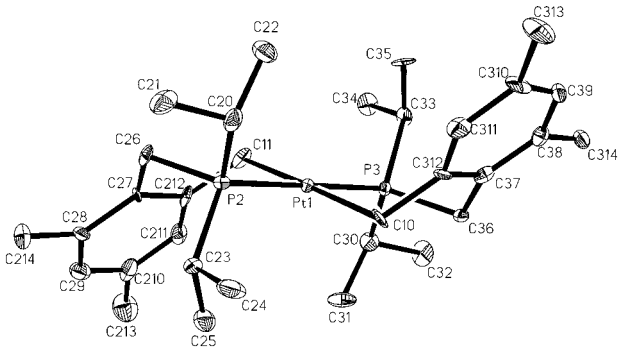

Figure 3. ORTEP view of complex **3b**, showing that the platinum atom has inserted into two C−H bonds, with retention of the metal oxidation state.

constants ($^1J_{PtP}$ = 3319.5 and 2876.9 Hz).[10,11] The low-field chemical shift of δ 71.85 reflects the deshielding effect of this phosphorus atom due to the six-membered chelated ring,[10,11,14] as also observed with **2a** and **3b**. The chemical shift of δ 22.92 is similar to the one assigned to the η^1-bound phosphine **1** in **2a** and **A** (Table 2). The σ-bonded Pt−CH_3 group appears in ^1H NMR as a virtual triplet at δ 0.24 ($^3J_{PH}$ = 5.3 Hz) with platinum satellites ($^2J_{PtH}$ = 53.2 Hz), which collapsed into a singlet upon ^{31}P decoupling.[13]

b. X-ray Crystal Structure of (DIPPID)$_2$Pt (3b). Single-crystal X-ray diffraction of complex **3b** unambiguously confirms its structure and also indirectly supports the structure of precursors **2a**,**b**. An ORTEP view of the molecular structure and the adopted numbering scheme is shown in Figure 3. Table 1 gives details of the crystal structure determination. Selected bond angles and distances are listed in Table 3. The structure of **3b** shows a monomeric neutral complex in which the Pt(II) center has an almost perfect square-planar coordination geometry. The phosphines as well as the methylene groups are in a *trans* arrangement with almost perfect linear angles of P(3)−Pt(1)−P(2) (179.9°) and C(11)−Pt(1)−C(10) (178.4°). The Pt(1)−P(2) (2.273 Å), Pt(1)−P(3) (2.262 Å), Pt(1)−C(10) (2.149 Å), and Pt(1)−C(11) (2.146 Å) distances are in the range normally found for such bonds.[15] The ligand arrangement is the one expected on steric grounds; however, the strongest *trans* directors, the methylene groups, are situated *trans*, which is unfavored electronically. It is

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 3b

Bond Lengths			
Pt(1)−C(11)	2.146(11)	P(3)−C(36)	1.838(12)
Pt(1)−C(10)	2.149(12)	P(3)−C(33)	1.853(12)
Pt(1)−P(3)	2.262(3)	P(3)−C(30)	1.86(2)
Pt(1)−P(2)	2.273(3)	C(10)−C(312)	1.52(2)
P(2)−C(20)	1.82(2)	C(11)−C(212)	1.47(2)
P(2)−C(26)	1.843(12)	C(36)−C(37)	1.54(2)
P(2)−C(23)	1.866(12)	C(26)−C(27)	1.47(2)

Bond Angles			
C(11)−Pt(1)−C(10)	178.4(6)	P(3)−Pt(1)−P(2)	179.9(2)
C(11)−Pt(1)−P(3)	91.8(3)	C(10)−Pt(1)−P(2)	92.5(3)
C(11)−Pt(1)−P(2)	88.3(3)	C(10)−Pt(1)−P(3)	87.4(3)
C(26)−P(2)−Pt(1)	110.9(4)	C(36)−P(3)−Pt(1)	112.2(4)
C(212)−C(11)−Pt(1)	113.7(7)	C(312)−C(10)−Pt(1)	112.4(8)
C(212)−C(27)−C(26)	119.1(10)	C(312)−C(37)−C(36)	116.5(11)

interesting to note that the sp^2−sp^3 carbon−carbon bond lengths between C(10)−C(312) and C(11)−C(212) (1.52 and 1.47 Å, respectively) are significantly different. The Pt(1)···C(312) and the Pt(1)···C(212) distances are relatively short (3.066 and 3.047 Å, respectively), although there is no additional spectroscopic evidence for any metal−carbon interaction and the aromaticity is not distorted in this complex. The C(312)−C(10)−Pt(1) and C(212)−C(11)−Pt(1) angles (112.4 and 113.7°, respectively) are indicative of an approximate tetrahedral geometry around C(10) and C(11). The X-ray crystal structure shows that both of the six-membered rings Pt(1)−C(10)−C(312)−C(37)−C(36)−P(3) and Pt(1)−C(11)−C(212)−C(27)−C(26)−P(2) have a distorted-boat configuration. The planarity of the coordination geometry around platinum has been determined by least-squares plane analysis through the atoms Pt(1), P(2), P(3), C(10), C(11), C(26), and C(36), which showed deviations from the plane of 0.011, 0.010, 0.032, −0.004, −0.030, 0.016, and −0.017 Å, respectively (mean deviation from plane 0.0171 Å). The aromatic backbones of both cyclometalated ligands are mutually trans.

c. Mechanism of the Formation of Complexes 2a,b and 3b. $^{31}P\{^1H\}$ NMR follow-up of the reaction of (COD)$PtMe_2$ with **1** in benzene at room temperature shows the formation of intermediate **A** by coordination of the ligand **1** to the metal center (Scheme 1). The postulated structure of **A** is analogous to those of previously reported platinum−olefin complexes.[16] $^{31}P\{^1H\}$ NMR shows the presence of free **1** and **2a** and a broad singlet at δ 26.64 ppm ($w_{1/2}$ = 37 Hz), flanked with its platinum satellites. This chemical shift is in the normal range found for similar phosphine ligands coordinated to platinum[10] and is similar to the ones assigned to the η^1-bound phosphines in complexes **2a**,**b**. In addition the platinum-phosphorus coupling ($^1J_{PtP}$ = 1765.1 Hz) is characteristic of phosphines trans to a strong σ donor such as a CH_3 group (as in complex **2a**).[10−13] The ^1H NMR is not conclusive but shows the presence of a new signal at 4.79 ppm which is partially overlapped with a signal of the starting material (COD)-$PtMe_2$. However, the structure of the postulated **A** might also consist of two ligands **1** coordinated mutually *cis* to the metal center, although this is not expected to be favorable for steric reasons. Raising the temperature

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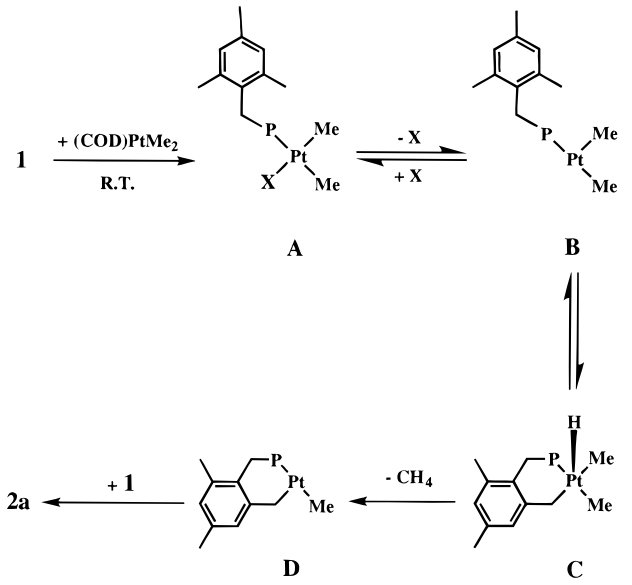
Scheme 1. Proposed Mechanism for the Selective Formation of 2a (X = COD, DIPPIDH (1))



to 80 °C for 10 min results in the disappearance of **A**, the quantitative formation of complex **2a**, and the production of 1 equiv of CH_4. Thus, association of **1** and opening of the chelated olefinic ring occurs before the rate-determining step. Monitoring the disappearance of **1** at 58 °C by $^{31}P\{^1H\}$ NMR shows formation of **2a** as the only product (Figure 4).

Bulky phosphines promote C−H activation by stabilizing a conformation in which the C−H bond is in proximity or in direct contact with the metal.[6b,c] In many reported cases the C−H bond approaches the metal at a short M···H distance, which may be viewed as a bent three-center−two-electron (3c−2e) bond including C, H, and the metal.[17] Although this process (**1** → **2a**) was also monitored by ^1H NMR at room temperature, no evidence was obtained for the presence of so-called "agostic" interactions. A plausible oxidative-addition−reductive-elimination pathway is presented in Scheme 1. Cope and Siekmann[18] reported for the first time cyclometalation involving aryl C−H bond activation by platinum(II). Oxidative addition and reductive elimination of C−H bonds by d^8 L_4 species generally requires an unsaturated, three-coordinated, 14-electron complex (d^8 L_3), as exemplified in many stoichiometric reactions[19] and supported by theoretical studies,[20] although direct C−H activations by square-planar 16-electron complexes (which are likely to have a relative large kinetic barrier) have also been reported.[21] For

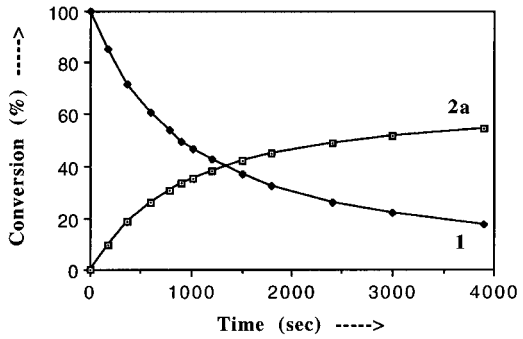


Figure 4. $^{31}P\{^1H\}$ NMR follow-up of a reaction of **1** (3 equiv) with $(COD)PtMe_2$ (1 equiv) at 58 °C in C_6D_6.

example, Whitesides and co-workers reported that bis(neopentyl)platinum(II) complexes undergo facile cyclometalation.[22] The reaction proceeds by initial dissociation of a phosphine ligand to generate a 14-electron intermediate, followed by oxidative addition of a C−H bond and finally by reductive elimination of neopentane. Dissociation of the monocoordinated COD or ligand **1** from **A** results in the formation of the unsaturated 14-electron complex **B**, which undergoes oxidative addition of the C−H bond to give the five-coordinated alkyl hydride **C**. Rapid C−H reductive elimination gives 1 equiv of CH_4, rendering the overall process irreversible. Complexes such as **C** are proposed as intermediates in the protonolysis of platinum(II)−carbon σ-bonds, which is a subject of current interest.[23−26] A six-coordinated alkyl(hydrido)platinum(IV) complex was isolated recently by Tesauro.[24] However, five-coordinate alkyl(hydrido)platinum(IV) species such as **C** are expected to be very unstable toward C−H reductive elimination, as reported very recently by Bercaw[25] and Puddephatt.[26] The resulting 14-electron complex **D** forms the more stable 16-electron complex **2a** by coordination of the additional ligand **1**. We believe that the selective formation of the sterically hindered *cis* isomer **2a** is due to strong electronic effects in the proposed Pt(IV) intermediate **C**. The σ-bonded benzyl ligand $ArCH_2Pt^{IV}$, which is formed upon C−H activation, labilizes the Pt−CH_3 bond trans to it. Formation of CH_4 by C−H reductive elimination involving this alkyl group is therefore preferred over the CH_3 group trans to P. Since CH_4 formation is irreversible, only intermediate **D** is likely to be formed, which is captured by **1** to form complex **2a** at a rate higher than its isomerization. An alkyl(hydrido)platinum(IV) intermediate having one methyl in the apical position will lead to the formation of compound **2b**. *This selective transformation represents an unusual case of an organometallic reaction which is entirely driven by electronic factors. Only the sterically hindered, but electronically preferred, compound is obtained.* Since intermediate **A** is observed prior to the C−H activation step, the rate-determining

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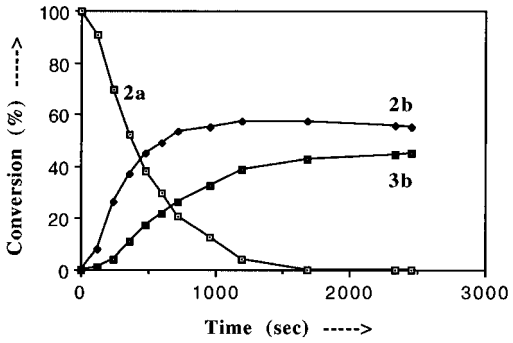
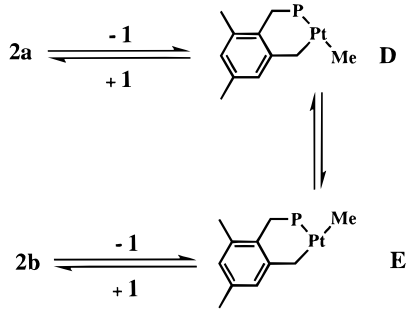


Figure 5. $^{31}P\{^1H\}$ NMR follow-up of thermolysis of **2a** at 109 °C in C_6D_6.

Scheme 2. Proposed Mechanism for the Isomerization of Complexes 2a ↔ 2b.



step probably involves a later step such as the formation of a 14-electron complex (**A** → **B**) by dissociation of the olefin or the C−H cleavage itself (**B** → **C**).

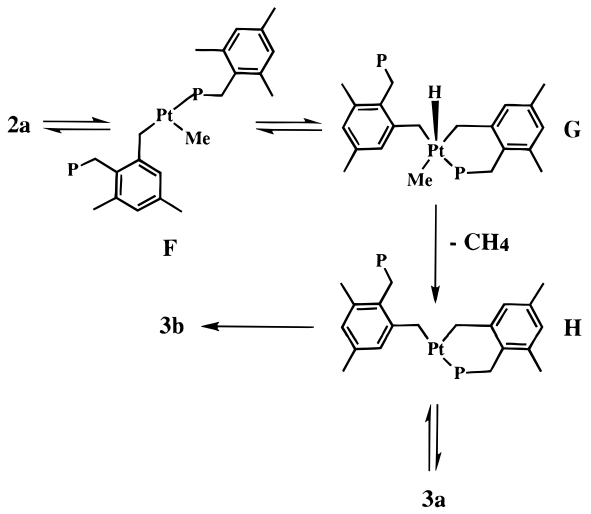
d. Mechanism of the Formation of Complex 2b. $^{31}P\{^1H\}$ NMR follow-up of the second C−H activation process shows that the *cis* complex **2a**, which is formed selectively at room temperature, undergoes two parallel reactions upon heating: isomerization to the *trans* complex **2b** and C−H activation to form the double-cyclometalated *trans* **3b** (Figures 1, 2 and 5). Thus, complex **2b** is thermodynamically more stable than its *cis* isomer **2a**.

A plausible mechanism of this isomerization process is presented in Scheme 2. Upon mild heating of the kinetic isomer **2a**, the η^1-coordinated ligand **1** is likely to dissociate due to (i) the strong *trans* influence of the σ-bonded Pt−CH_3 group and (ii) the steric hindrance of the mutually *cis* phosphine ligands. We propose that the trigonal species **D** is formed again and isomerizes to **E**. Coordination of DIPPIDH (**1**) gives the observed *trans* square-planar complex **2b**.

The driving force of this isomerization process is undoubtedly the decrease of steric hindrance between the mutually *cis* phosphines in **2a**. Complex **2a**, having two high *trans*-effect alkyls mutually *cis*, is favored electronically. Compatible with the reduced steric hindrance in complex **2b**, the $^{31}P\{^1H\}$ NMR spectrum of **2b** exhibits sharp resonances, as compared with the broad ones observed with complex **2a**, indicating no restriction of bond rotation. Thus, in this isomerization process steric factors prevail over electronic ones in controlling the relative stability of the products.

e. Mechanism of the Formation of Complex 3b. Complex **3b** can be formed from **2a** (Scheme 3) by following almost the same argumentation as in the formation of complexes **2a**,**b** (Schemes 1 and 2). Upon moderate heating, the six-membered ring opens up,

Scheme 3. Proposed Mechanism for the Selective Formation Of Complex 3b



forming the 14-electron complex **F**, which readily undergoes C−H oxidative addition of the second η^1-coordinated ligand **1** to form the Pt(IV) species **G**. Reductive elimination of CH_4 gives **H**, which is followed by association of the phosphine to give the thermally stable complex **3b.** It is likely that, in analogy with the formation of **2b** from **2a**, first the *cis* isomer **3a** is formed, which isomerizes to the thermally stable *trans* **3b**. However, **3a** was not detected upon monitoring of the second cyclometalation by $^{31}P\{^1H\}$ NMR. *Only the electronically unfavorable, but sterically preferred, compound is obtained.* Shaw and co-workers reported the synthesis of two analogous *cis* and *trans* Pt(II) complexes bearing two chelating five-membered rings.[27]

$^{31}P\{^1H\}$ NMR follow-up of this process shows that the isomerization process forming **2b** is kinetically preferable over formation of the double-cyclometalated **3b** (Figures 2 and 5). Dissociation of the η^1-coordinated phosphine from **2a** is preferable over opening of the six-membered chelate, although the latter is expected to open readily in order to reduce the steric hindrance. Our observations show that the isomerization process **2a** → **2b** is faster than the irreversible cyclometalation reaction **2a** → **3b**, which suggests that formation of an unsaturated 14-electron Pt(II) complex (**D** or **F**) by disassociation of the bulky ligand **1** (**2a** → **2b**) or opening of the chelate (**2a** → **3b**) is rate determining. This process is first order in **2a** with $k_{obs} = 2.3 \times 10^{-3}$ s^{-1} at 109 °C (Figure 6).

It is tempting to assume that this isomerization process is reversible (**2a** ↔ **2b**) and that **2a** is the only precursor of **3b**. Chatt and Wilkins[28] showed that the cis isomers of $(R_3P)_2PtCl_2$ complexes are in equilibrium with their trans isomers. However, we cannot exclude the possibility that **3b** is formed by two parallel pathways (**3b** ← **2a** ↔ **2b** → **3b**). The direct formation of **3b** from **2a** and not from **2b** is preferable if we consider the loss of rotational entropy of the phosphine ligand **1**, which occurs on cyclometalation. In **2a** rotation is restricted due to steric interaction, whereas in **2b** it is not. Thus, metalation of **2a** will cause a relatively small loss of rotational entropy compared to cyclometalation

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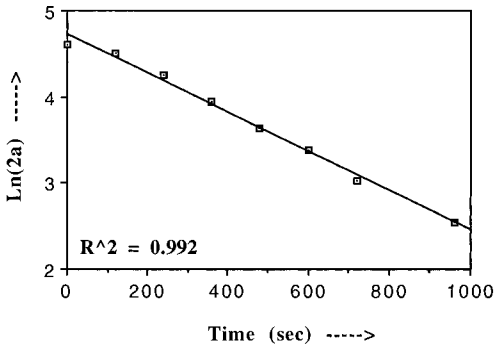

Figure 6. $^{31}P\{^1H\}$ NMR follow-up of thermolysis of **2a** at 109 °C in C_6D_6.

of **2b**. The chelated ring of **2a** is also expected to open more readily, reducing the larger steric hindrance. Therefore, the barrier to form **3b** directly from **2b** is higher, if it occurs at all, which agrees with our observations.

Conclusions

Six-membered chelated benzylic platinum(II) complexes are easily accessible by sp^3 C−H activation using (phosphino)arenes such as DIPPIDH (**1**) and (COD)-$PtMe_2$. Activation of two benzylic C−H bonds with formation of two new M−C(sp^3) σ-bonds results in selective loss of 2 equiv of methane, with retention of the metal oxidation state (eq 2).

$$2R{-}CH_3 + M^{II}(CH_3)_2 \rightarrow (R{-}CH_2)_2M^{II} + 2CH_4 \quad (2)$$

Our results indicate that the stepwise metal insertion into both C−H bonds proceeds by a similar mechanism. We believe that in both cases a coordinatively unsaturated 14-electron complex is involved, possessing three relatively strong σ-donors (two alkyl groups and one phosphine ligand), which undergoes oxidative addition to form alkylhydridoplatinum(IV) intermediates. This process is followed by C−H reductive elimination to give the ring-closed platinum(II) products and CH_4. The initial C−H activation takes places at room temperature due to the relatively easy dissociation of the coordinated olefin; the second C−H activation follows first-order kinetics and requires more vigorous conditions, since opening up of the six-membered platinacycle is involved. The second cyclometalation is expected to be more favorable for entropic reasons, although the first cyclometalation reaction involves formation of two relatively strong phosphorus−platinum(II) bonds. Both C−H activation processes proceed in a regioselective manner; whereas the first process is directed by electronic factors

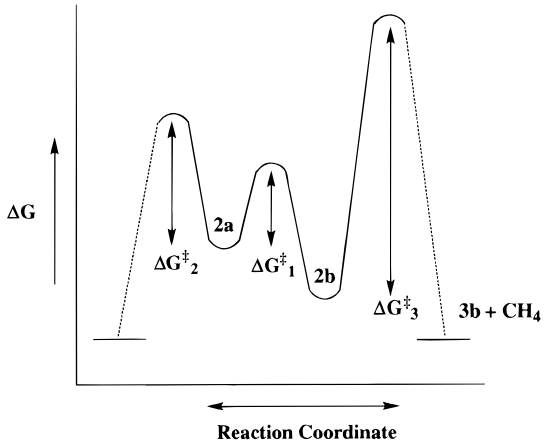

Figure 7. Relative free energy barriers for the formation of complexes **2a**,**b** and **3b**.

at the transition state, the second C−H activation is directed by steric factors. The monometalated *cis* complex **2a** reacts in two competing pathways to give the *trans* complex **2b** and the double-cyclometalated *trans* complex **3b**. The cis-trans isomerization of the monometalated complexes **2a** → **2b** is kinetically preferable over the second cyclometalation **2a** → **3b**. Eventually the *trans* complex **2b** is also selectively converted to **3b**. Complex **3b** is directly generated from **2a** and might be directly generated form **2b**, although the isomerization process (**2a** → **2b**) is likely to be reversible. Our observations lead to the following estimations for the relative free energy barriers for the formation of **2a,b** and **3b**: $\Delta G^{\ddagger}_1 < \Delta G^{\ddagger}_2 << \Delta G^{\ddagger}_3$ (Figure 7).

At relatively low temperatures, the distribution of the products is governed by their relative rates of formation (the order of rates of formation being **2a** > **2b** > **3b**), because under these conditions the rates of the reverse reactions are negligible. The overall process shows that the σ-bonded methylene group ($ArCH_2Pt$) has a major electronic effect on the course of the reaction but at the end steric demands prevail over the electronic ones.

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Supporting Information Available: X-ray structure analysis of **3b**, including tables of crystal data and structure refinement of **3b**, atomic coordinates, bond lengths and bond angles, and anisotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

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