Consecutive Cyclometalation by Platinum(II)

Milko E. van der Boom,[†] Shyh-Yeon Liou,[†] Linda J. W. Shimon,[‡] Yehoshoa Ben-David, † and David Milstein *,†

Departments of Organic Chemistry and Chemical Services, The Weizmann Institute of Science, 76100 Rehovot, Israel

Received January 23, 1996[®]

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 sp³ C-H activation of the ligand DIPPIDH (α^2 -(diisopropylphosphino)isodurene; 1) and (1,5cyclooctadiene)dimethylplatinum(II) ((COD)PtMe₂) at room temperature by ${}^{31}P{}^{1}H{}$ 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 CH₄. 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*- $(DIPPID)_{2}Pt$ (**3b**) with liberation of CH₄ in parallel pathways. Continuous heating results in the quantitative formation of the thermally stable **3b**. Mechanistically, the second C-Hactivation 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 sp²-sp³ 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 sp³ 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)

$$\mathbf{R} - \mathbf{CH}_{3} + \mathbf{ML}_{n} \xrightarrow{-\mathbf{H} - \mathbf{L}} \mathbf{R} - \mathbf{CH}_{2} - \mathbf{ML}_{n-1} \xrightarrow{+\mathbf{A} - \mathbf{B}} \mathbf{R} - \mathbf{ML}_{n-1} + \mathbf{A} - \mathbf{CH}_{2} - \mathbf{B}$$
(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 -(diisopropylphosphino)isodurene; 1) and (1,5-cyclooctadiene)dimethylplatinum(II) ((COD)PtMe2).

The chelating diene in (COD)PtMe₂ can be displaced by phosphine ligands.^{3,4} Reaction with **1** followed by cyclometalation of a benzylic C-H bond by the electronrich metal center is expected to result in the formation of a six-membered ring and CH₄, rendering the overall process irreversible. Our system allows a second mol-



ecule of 1 to coordinate to the metal, resulting in the formation of a second six-membered chelating ring with liberation of CH₄. Previous studies on cyclometalation provided much information on intra- and intermolecular C–H activation.⁵ It is known that σ -bonded Pt–CH₃^{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 sixmembered 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.

Experimental Section

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

^{*} To whom correspondence should be addressed.

[†] Department of Organic Chemistry.

[‡] Department of Chemical Services.

 [®] Abstract published in Advance ACS Abstracts, April 15, 1996.
 (1) (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. Nature
 1993, 364, 699. (b) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. Nature 1994, 370, 42

⁽²⁾ Van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D. To be submitted for publication.

⁽³⁾ Clark, H. C.; Manzer, L. E. J. Organomet. Chem. 1973, 59, 411. (4) Fallis, S.; Anderson, G. K.; Rath, N. P. Organometallics 1991, 10. 3180.

^{(5) (}a) Crabtree, R. H. Angew. Chem., Int. Ed. Engl. **1993**, *32*, 789. (b) Chipperfield, J. R. In Chemistry of the Platinum Group Metals, Hartley, F. R., Ed.; Elsevier: Amsterdam, The Netherlands, 1991; Chapter 7. (c) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, Chapter 39, pp 592–606. (d) Ryabov, A. D. Chem. Rev. **1990**, *90*, 403. (e) Evans, D. W.; Baker, G. R.; Newkome, G. R. Coord. Chem. Rev. **1989**, *93*, 155. (f) Dehand, J.; Pfeffer, M. Coord. Chem. Rev. **1976**, *18*, 344. (g) Omae, I. Coord. Chem. Rev. 1988, 83, 137. (h) Shaw, B. L. J. Organomet. Chem. 1980, 200,

⁽a) Cheney, A. J.; Shaw, B. L. J. Chem. Soc., Dalton Trans. 1972, 754.
(b) Cheney, A. J.; Shaw, B. L. J. Chem. Soc., Dalton Trans. 1972, 754.
(b) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. J. Chem. Soc., Chem. Commun. **1970**, 1176. (c) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. J. Chem. Soc. A **1971**, 3833.

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)PtMe2 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, ³¹P, and ¹³C 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 ¹³C 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. ³¹P{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 ¹³C $\{^{1}H\}$ NMR were made using ¹H{³¹P}, ¹H-¹H COSY, and ¹³C-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)-PtMe₂ (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 CH₄. FDMS analysis showed m/z 709 (calcd M⁺⁺ 709. Anal. Calcd for C₃₃H₅₆P₂Pt: C, 55.84; H, 7.95. Found: C, 56.20; H, 8.25. ¹H NMR (C₆D₆): δ 6.7 (m, 4H, Ar*H*), 3.26 (d, 2H, ²*J*_{PH} = 9.0 Hz, ${}^{3}J_{\text{PtH}} = 19.0$ Hz, ArCH₂P), 2.84 (vt, 2H, ${}^{3}J_{\text{PH}} = 10.4$ Hz, ${}^{2}J_{\text{PtH}}$ = 89.0 Hz, ArC H_2 Pt), 2.82 (d, 2H, $^2J_{PH}$ = 9.2 Hz, $^3J_{PPt}$ = 29.2 Hz, ArCH2P), 2.4-2.2 (m, 15H, ArCH3), 2.0 (m, 4H, PCH(CH3)2), 1.2–0.9 (m, 24 H, PCH(CH₃)₂), 0.90 (vt, 3H, ${}^{3}J_{PH} = 6.4$ Hz, $^{2}J_{\text{PtH}} = 66.9 \text{ Hz}, \text{PtC}H_{3}$). $^{31}\text{P}\{^{1}\text{H}\} \text{ NMR} (C_{6}D_{6})$: $\delta 65.97 \text{ (s, 1P, 1P)}$ ${}^{1}J_{\text{PtP}} = 2270.6 \text{ Hz}$, 31.21 (s, 1P, ${}^{1}J_{\text{PtP}} = 1889.9 \text{ Hz}$). ${}^{13}C{}^{1}H{}$ -NMR (C₆D₆): δ 150.2 (vt, ${}^{3}J_{PC} = 7.1$ Hz, ${}^{2}J_{PtC} \approx 56$ Hz, C_{ipso} -CH₂Pt), 138–124 (m, not resolved, C_{Ar}), 30–16 (m, not resolved totally, Ar CH₃ and P CH(CH₃)₂), 30.63 (dd, ${}^{3}J_{PC} = 7.6$ Hz, ${}^{1}J_{PC}$ = 248.9 Hz, ${}^{2}J_{PtC}$ = 497.8 Hz, Ar*C*H₂PPt), 10.89 (vt, ${}^{2}J_{PC,cis}$ = 6.5 Hz, Ar*C*H₂Pt), 5.02 (dd, ${}^{2}J_{PC,cis} = 10.4$ Hz, ${}^{2}J_{PC,trans} = 90.3$ Hz, ${}^{1}J_{PtC} = 621.9$ Hz, Pt*C*H₃).

Synthesis of *trans*-(DIPPID)₂Pt (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)PtMe₂ (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 ³¹P{¹H} NMR of the mother liquid showed only complex **3b**. Quantitative analysis of the gas phase by GC showed formation of 2 equiv of CH₄. 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 CH₄. 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, Ar*H*), 6.40 (s, 2H. Ar*H*), 2.91 (br s, 4H, ArC*H*₂P), 2.54 (br s, 4H, PC*H*(CH₃)₂), 2.25 (s, 6H, ArC*H*₃), 2.18 (br s, 4H, ArC*H*₂Pt), 2.05 (s, 6H, ArC*H*₃), 1.21 (dd, 12H, ³*J*_{HH} = 6.9 Hz, ³*J*_{PH} = 6.8 Hz), 0.91 (br m, 12H, PCH(C*H*₃)₂). ³¹P{¹H} NMR (C_6D_6): δ 73.26 (s, 2P, ¹*J*_{PtP} = 3270.2 Hz).

Follow-up of the Formation of cis-(DIPPIDH)(DIP-PID)PtMe (2a). A solution of DIPPIDH (1; 45 mg, 0.180 mmol) in 0.6 mL of C₆D₆ was added to (COD)PtMe₂ (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 ³¹P{¹H} NMR, showing the presence of free ligand 1 and intermediate A, δ 26.64 (s, ${}^{1}J_{PtP} = 1765.1$ 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 CH4, which was also observed by ${}^{\hat{1}}H$ and ${}^{13}C\{{}^{1}H\}$ NMR. This experiment was repeated under the same conditions at 58 °C and monitored by ³¹P{¹H} NMR measurements at room temperature. The results are presented in Figure 4.

Follow-up of the Formation of trans-(DIPPIDH)(DIP-PID)PtMe (2b) and trans-(DIPPID)2Pt (3b). A solution of DIPPIDH (1; 32 mg, 0.128 mmol) in 0.6 mL of C₆D₆ was added to (COD)PtMe₂ (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 ³¹P{¹H} NMR at room temperature. ³¹P{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 C₆D₆ at 109 °C and monitored by ${}^{31}P{}^{1}H$ 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 \times 0.5 mm) was mounted on a glass fiber and flash-frozen under a cold nitrogen stream (at 110 K) on a Rigaku AFC5R fourcircle diffractometer mounted on a rotating anode with Mo K α 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 $2.1^{\circ} \leq \theta \leq 27.5^{\circ}$. The SHELXS-92⁸ and SHELXL-93⁹ 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 F² (SHELXL-93). The final cycle of the leastsquares 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)PtMe₂

⁽⁸⁾ Sheldrick, G. M. SHELXS-92 Program for Crystal Structure Determination. University of Göttingen, Göttingen, Germany, 1992.
(9) Sheldrick, G. M. SHELXL-93 Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.

TADIE I. CIVSIAI DALA IUI <i>LI ALIS</i> -(DIFFID)9FL (J	Table 1	. Crystal	Data for	trans-	DIPPID) ₂ Pt ((3b)
--	---------	-----------	----------	--------	--------	---------------------	---------------

formula	$C_{32}H_{52}P_2Pt$
fw	693.77
space group	<i>P</i> 1
cryst system	triclinic
a, Å	8.238(2)
<i>b</i> , Å	9.677(2)
<i>c</i> , 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)
$D_{\rm calcd}$, g cm ⁻³	1.503
Ζ	1
μ (Mo K α), cm ⁻¹	47.0
crystal size, mm ³	0.9 imes 0.5 imes 0.5
-	

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

compd	P : δ, ppm (¹ <i>J</i> _{PPt} , Hz)	$\begin{array}{l} \mathbf{P}_{\mathrm{ring}}: \ \delta, \ \mathbf{ppm} \\ (^{1}J_{\mathrm{PPt}}, \ \mathbf{Hz}) \end{array}$	Δ (complex-ligand 1), ppm
1 A 2a 2b ^a 3b	4.60 26.64 (1765.1) 31.21(1889.9) 22.92 (2876.9)	65.97 (2270.6) 71.85 (3319.5) 73 26 (3270 2)	22.40 (P) 26.61 (P), 61.37 (P _{ring}) 18.32 (P), 67.25 (P _{ring}) 68 66 (P)

 $^{a 2}J_{\rm PP} = 419.1$ Hz.

in benzene at room temperature by the aromatic phosphine 1 results in quantitative formation of the sp³ C-H activated *cis* product **2a** (Figure 1) and 1 equiv of CH₄. 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. CH₄ was unambiguously detected by ¹H and ${}^{13}C{}^{1}H$ NMR and quantified by GC. In the ${}^{31}P{}^{1}H$ 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 ¹⁹⁵Pt 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 ³¹P-³¹P coupling is observed, indicating that both phosphorus atoms are coordinated mutually cis, which is in agreement with the observed platinum-phosphorus coupling constants (${}^{1}J_{PtP} = 2270.6$ 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 ¹³C{¹H} NMR. For instance, the Pt-CH₃ group appears in the ${}^{13}C{}^{1}H{}$ NMR spectrum as a double doublet at 5.02 ppm, flanked by ¹⁹⁵Pt satellites $(^{1}J_{\text{PtC}} = 621.9 \text{ Hz})$ with trans $^{2}J_{\text{PC}} = 90.3 \text{ Hz}$ and cis ${}^{2}J_{PC} = 10.4$ Hz. In ¹H NMR this alkyl group appears



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

as a virtual triplet at δ 0.90 with ${}^{2}J_{PtH} = 66.9$ Hz and ${}^{3}J_{PH} = 6.4$ Hz, which collapses into a singlet upon ${}^{31}P$ decoupling.

Reacting (COD)PtMe₂ with the ligand **1** in benzene at higher temperatures (100–130 °C) in a pressure flask results in quantitative formation of the double-C-Hactivated complex 3b and 2 equiv of CH₄. 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**. ${}^{31}P{}^{1}H{}$ NMR exhibits one sharp singlet at δ 73.26 for both ³¹P nuclei, flanked by ¹⁹⁵Pt satellites, indicating that both phosphorus atoms are magnetically equivalent. The observed ${}^{1}J_{PPt} =$ 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 ${\bf 3b}$ from ${\bf 1}$ and (COD)PtMe₂ by ${}^{31}P{}^{1}H$ 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 ³¹P{¹H} NMR and are accompanied by satellites due to coupling with ¹⁹⁵Pt. The large phosphorus–phosphorus coupling (²J_{PP} = 419.1 Hz) indicates that both nuclei are mutually *trans*, which is in agreement with the observed ¹⁹⁵Pt–³¹P coupling

^{(10) (}a) Pregosin, P. S. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987. (b) Pregosin, P. S.; Kunz, R. W. ³¹P and ¹³C NMR of Transition Metal Complexes, Springer-Verlag: Berlin, 1979.

⁽¹¹⁾ Allen, F. H.; Pidcock, A. J. Chem. Soc. A 1968, 2700.

^{(12) (}a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Linder, E.; Fawzi, R.; Hermann, A. M.; Eichele, K.; Hiller, W. Organometallics **1992**, *11*, 1033.

^{(13) (}a) Perera, S. D.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1993**, 3653. (b) Hii, K. K.; Perera, S. D.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1994**, 103.

⁽¹⁴⁾ Perera, S. D.; Shaw, B. L. J. Chem. Soc., Dalton Trans. 1995, 641 and references therein.



Figure 2. ${}^{31}P{}^{1}H$ NMR Follow-up of the reaction of **1** (2.1 equiv) with (COD)PtMe₂ (1 equiv) in C₆D₆ 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 (${}^{1}J_{PtP} = 3319.5$ and 2876.9 Hz). 10,11 The lowfield 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-CH₃ group appears in 1 H NMR as a virtual triplet at δ 0.24 (${}^{3}J_{PH} = 5.3$ Hz) with platinum satellites (${}^{2}J_{PtH} = 53.2$ Hz), which collapsed into a singlet upon 31 P decoupling. 13

b. X-ray Crystal Structure of (DIPPID)₂Pt (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 squareplanar 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

		- I					
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)				
	Rond	Angles					
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(2)	6) 119.1(10)	C(312) - C(37) - C(36)	116.5(11)				

interesting to note that the sp²-sp³ 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(36)-P(3)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 leastsquares 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.** ${}^{31}P{}^{1}H{}$ NMR follow-up of the reaction of (COD)PtMe₂ 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 ³¹P{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 platinum¹⁰ and is similar to the ones assigned to the η^1 -bound phosphines in complexes **2a**,**b**. In addition the platinum-phosphorus coupling $(^{1}J_{PtP} =$ 1765.1 Hz) is characteristic of phosphines trans to a strong σ donor such as a CH₃ 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)-PtMe₂. 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

⁽¹⁵⁾ International Tables for Crystallography, Wilson, Ed.; A. T. C., Kluwer Academic: Dordrecht, The Netherlands, **1992**; Vol. C, Mathematical, Physical and Chemical Tables.

⁽¹⁶⁾ Chaloner, P. A.; Broadwood-Strong, G. T. L. J. Organomet. Chem. 1989, 362, C21.





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 CH₄. 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 ${}^{31}P{}^{1}H{}$ 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 $(1 \rightarrow 2a)$ was also monitored by ¹H NMR at room temperature, no evidence was obtained for the presence of so-called "agostic" interactions. A plausible oxidativeaddition-reductive-elimination pathway is presented in Scheme 1. Cope and Siekmann¹⁸ 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 d⁸ L₄ species generally requires an unsaturated, three-coordinated, 14-electron complex (d⁸ L₃), as exemplified in many stoichiometric reactions¹⁹ and supported by theoretical studies,²⁰ although direct C-H activations by square-planar 16electron complexes (which are likely to have a relative large kinetic barrier) have also been reported.²¹ For

(17) Crabtree, R. H. Chem. Rev. $1985,\ 85,\ 245$ and references therein.

(20) Saillard, J.-Y.; Hoffmann, R. J. Am. Chem. Soc. 1984, 106, 2006.



Figure 4. ${}^{31}P{}^{1}H{}$ NMR follow-up of a reaction of **1** (3 equiv) with (COD)PtMe₂ (1 equiv) at 58 °C in C₆D₆.

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 14electron 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 CH₄, 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 Bercaw²⁵ 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 ArCH₂Pt^{IV}, which is formed upon C-H activation, labilizes the Pt-CH₃ bond trans to it. Formation of CH₄ by C-H reductive elimination involving this alkyl group is therefore preferred over the CH₃ group trans to P. Since CH₄ 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, com*pound is obtained.* Since intermediate **A** is observed prior to the C-H activation step, the rate-determining

⁽¹⁸⁾ Cope, A. C.; Siekmann, R. W. J. Am. Chem. Soc. 1965, 87, 3272.
(19) (a) Jones, W. D.; Kosar, W. P. J. Am. Chem. Soc. 1986, 108, 5640. (b) Neve, F.; Ghedini, M.; Tiripicchio, A.; Ugozzoli, F. Inorg. Chem. 1989, 28, 3084. (c) Farnetti, E.; Nardin, G.; Graziani, M. J. Chem Soc., Chem. Commun. 1989, 1264. (d) Jones, W. D.; Feher, F. J. Acc. Chem. Res. 1989, 22, 91 and references therein. (e) Ghosh, C. K.; Hogano, J. K.; Krentz, K.; Graham, W. A. G. J. Am. Chem. Soc. 1989, 111, 5480. (f) Price, R. T.; Andersen, R. A.; Muetterties, E. L. J. Organomet. Chem. 1989, 376, 407. (g) Hoffmann, P.; Heiss, H.; Neiteler, P.; Muller, G.; Lachmann, J. Angew. Chem., Int. Ed. Engl. 1990, 29, 880. (h) Maguire, J. A.; Boese, W. T.; Goldman, M. E.; Goldman, A. S. Coord. Chem. Rev. 1990, 97, 179. (i) McCamley, A.; Perutz, R.; Stahl, S.; Werner, H. Angew. Chem., Int. Ed. Engl. 1989, 28, 1690. (j) Freedman, D. A.; Mann, K. R. Inorg. Chem. 1991, 30, 836. (k) Cavell, K. J.; Jin, H. J. Chem. Soc., Dalton Trans. 1995, 4081.

⁽²¹⁾ Gregory, T.; Harper, P.; Desrosiers, P. J.; Flood, T. C. Organometallics **1990**, *9*, 2523 and references therein.

^{(22) (}a) Foley, P.; Whitesides, G. M. J. Am. Chem. Soc. **1979**, 101, 2732. (b) Foley, P.; Whitesides, G. M. J. Am. Chem. Soc. **1980**, 102, 6713.

⁽²³⁾ Canty, A. J.; van Koten, G. Acc. Chem. Res. 1995, 28, 406 and references therein.

⁽²⁴⁾ De Felice, V.; De Renzi, A.; Panunzi, A.; Tesauro, D. J. Organomet. Chem. **1995**, 488, C13.

⁽²⁵⁾ Stahl, S.; Labinger, J. A.; Bercaw, J. E. J. Am. Chem. Soc. 1995, 117, 9371.

⁽²⁶⁾ Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. Organometallics 1995, 14, 4966.



Figure 5. ${}^{31}P\{{}^{1}H\}$ NMR follow-up of thermolysis of 2a at 109 ${}^{\circ}C$ 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 $(\mathbf{A} \rightarrow \mathbf{B})$ by dissociation of the olefin or the C–H cleavage itself $(\mathbf{B} \rightarrow \mathbf{C})$.

d. Mechanism of the Formation of Complex 2b. ³¹P{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-CH₃ 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 ³¹P{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 CH₄ 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 ${}^{31}P{}^{1}H{}$ 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

³¹P{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 sixmembered chelate, although the latter is expected to open readily in order to reduce the steric hindrance. Our observations show that the isomerization process **2a** \rightarrow **2b** is faster than the irreversible cyclometalation reaction **2a** \rightarrow **3b**, which suggests that formation of an unsaturated 14-electron Pt(II) complex (**D** or **F**) by disassociation of the bulky ligand **1** (**2a** \rightarrow **2b**) or opening of the chelate (**2a** \rightarrow **3b**) is rate determining. This process is first order in **2a** with $k_{obs} = 2.3 \times 10^{-3} \text{ s}^{-1}$ at 109 °C (Figure 6).

It is tempting to assume that this isomerization process is reversible ($2a \leftrightarrow 2b$) and that 2a is the only precursor of **3b**. Chatt and Wilkins²⁸ showed that the cis isomers of (R_3P)₂PtCl₂ complexes are in equilibrium with their trans isomers. However, we cannot exclude the possibility that **3b** is formed by two parallel pathways ($3b \leftarrow 2a \leftrightarrow 2b \rightarrow 3b$). 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

⁽²⁷⁾ Cheney, A. J.; Shaw, B. L. J. Chem. Soc., Dalton Trans. 1972, 754.
(28) Chatt, J.; Wilkins, R. G. J. Chem. Soc. 1952, 273, 4300.



Figure 6. ${}^{31}P{}^{1}H$ NMR follow-up of thermolysis of **2a** at 109 °C in C₆D₆.

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 sp³ C–H activation using (phosphino)arenes such as DIPPIDH (**1**) and (COD)-PtMe₂. Activation of two benzylic C–H bonds with formation of two new M–C(sp³) σ -bonds results in selective loss of 2 equiv of methane, with retention of the metal oxidation state (eq 2).

$$2R-CH_3 + M^{II}(CH_3)_2 \rightarrow (R-CH_2)_2M^{II} + 2CH_4$$
 (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 CH₄. 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** \rightarrow **2b** is kinetically preferable over the second cyclometalation **2a** \rightarrow **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** \rightarrow **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 (ArCH₂Pt) has a major electronic effect on the course of the reaction but at the end steric demands prevail over the electronic ones.

Acknowledgment. We thank Roel H. Fokkens (University of Amsterdam) for performing the FDMS experiments. This work was supported by the U.S.-Israel Binational Science Foundation, Jerusalem, Israel. D.M. is the holder of the Israel Matz professorial chair of organic chemistry.

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.

OM9600452