Mechanisms of Thermolytic Rearrangement of Dineophylplatinum(II) Complexes via Intramolecular C–H Activation

David C. Griffiths and G. Brent Young*

Inorganic Chemistry Laboratories, Imperial College of Science, Technology and Medicine, London, SW7 2AY, U.K.

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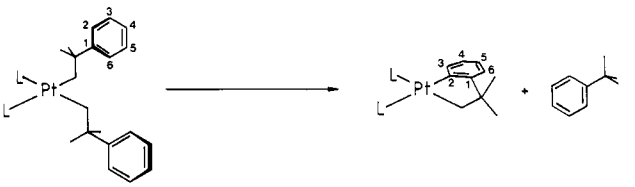
Dineophylplatinum(II) complexes $Pt(CH_2CMe_2Ph)_2L_2$ with bidentate, N-donor ligands (L_2 = 2,2′-bipyridyl, 2,2′-bipyrimidyl, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline) and with P-donor ligands (L = PEt_3, PPh_3) undergo quantitative thermolytic metallacyclization via aromatic δ-hydrogen transfer, generating *tert*-butylbenzene and 3,3-dimethylplatinaindan, $Pt(2\text{-}C_6H_4CMe_2CH_2)L_2$. The facility of reaction is dependent on L (or L_2). Among N-donors, bipyridyl and bipyrimidyl confer identical lability, and neophyl deuteration generates only a small kinetic isotope effect (k^H/k^D = 1.26). The more inert phenanthroline derivatives display stronger isotopic inhibition (k^H/k^D = 3.4). A mechanism is indicated in which prior Pt–N scission is rate-controlling for the flexible bipyridyl and bipyrimidyl ligands but not for the rigid phenanthrolines. Complexes with monodentate phosphine ligands are most labile; when L = Ph_3P, the dialkyl complex cannot be isolated. Detailed studies of *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$ reveal that cyclometalation rate shows a strong inverse dependence on phosphine concentration and a substantial deuterium isotope effect ($k^H/k^D \simeq 3.4$). A mechanism is proposed in which preliminary phosphine dissociation is a prerequisite, but not the rate-limiting, process.

Introduction

Reactions involving the cleavage and formation of C–H bonds at transition-metal centers are currently of great interest because of their relevance to metal-mediated organic synthesis. Recently, several organometallic systems have emerged that will attack aromatic and/or aliphatic C–H bonds of otherwise inert hydrocarbons.[1] The factors controlling the nature and selectivity of these intermolecular reactions are still poorly understood but may be increased by systematic study of related intramolecular cyclometalation reactions.[2]

Here, we describe mechanistic studies on a series of dineophylplatinum(II) complexes $Pt(CH_2CMe_2Ph)_2L_2$ [L_2 = 2,2′-bipyridyl (bpy); 2,2′-bipyrimidyl (bipym); 1,10-phenanthroline (phen); 4,7-diphenyl-1,10-phenanthroline (Ph_2phen); 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen)]. These derivatives, in toluene solutions, undergo a thermolytic metallacyclization (Scheme I) involving aromatic δ-C–H activation, yielding the corresponding platinaindans $Pt(2\text{-}C_6R_4CMe_2CH_2)_2L_2$ (R = H, D).

Scheme I



Previous mechanistic studies on organotransition metals, particularly those involving H-migrations, have focused mainly on complexes with ancillary phosphine ligands.[2] The role of the bidentate N-donor ligands, bpy, bipym, and phen, in such systems has received scant attention.[3] Some evidence has been presented for radical intermediates during reactions of $PtMe_2L_2$ (L_2 = bpy, phen),[4] while complete dissociation of bpy is thought to occur during thermolysis of $Pt(CH_2CH_2CH_2)Cl_2(bpy)$.[5] Bipyridyl itself may act as a source of transferrable hydrogen via rollover 3-metalation.[6]

In parallel, the corresponding reaction of dineophyl compounds with phosphine ligands has also been investigated, particularly *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$. As well as correlations with the N-donor complexes, we compare the results closely with those of related intramolecular aliphatic C–H activations;[2a] metal discrimination between aromatic and aliphatic sites for C–H activation[7] is an im-

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portant aspect of this type of reactivity. A preliminary account of this work has appeared,[8] and a brief independent report of related observations has also been published.[2g]

Experimental Section

General and Instrumental Data. Elemental analyses were by Imperial College Microanalytical Laboratories. NMR spectra were recorded on Brüker WM250 (^{1}H, 250.13 MHz; ^{13}C, 62.9 MHz; ^{31}P, 101.27 MHz), JEOL FX90Q (^{1}H, 89.55 MHz; ^{13}C, 22.13 MHz; ^{31}P) and Perkin-Elmer R-32 (^{1}H, 90 MHz) spectrometers. IR data were collected on a Perkin-Elmer 683 instrument using 4% KBr dispersions of complexes.

All reactions were carried out under nitrogen or argon unless otherwise noted, using standard anerobic techniques.[9] Solvents were distilled under nitrogen prior to use: diethyl ether and tetrahydrofuran (THF) from sodium/benzophenone; toluene and toluene-d_8 from sodium.

Neophyl chloride (1-chloro-2-methyl-2-phenylpropane) and 2,2′-bipyrimidyl were used as supplied by Lancaster Synthesis. 4,7-Diphenyl- and 3,4,7,8-tetramethyl-1,10-phenanthrolines as well as 2,2′-bipyridyl and 1,5-cyclooctadiene (cod) were supplied by Aldrich Chemical Co. and were used without further purification.

Triethylphosphine was obtained from Strem Chemicals and was distilled prior to use. Triphenylphosphine and 1,2-bis(diphenylphosphino)ethane were supplied by Aldrich Chemical Co. and were recrystallized from 2-propanol. The precursor $PtCl_2$(cod) was prepared by using a published method,[10] and 1-chloro-2-methyl-2-phenylpropane-d_5 was prepared from benzene-d_6 and methylallyl chloride by an established procedure.[11]

Preparation of (2-Methyl-2-phenylpropyl)magnesium Chloride. A solution of 1-chloro-2-methyl-2-phenylpropane (3.37 g, 20 mmol) in THF (15 mL) containing a small amount of 1,2-dibromoethane (0.3 mL) as initiator was added dropwise to a stirred suspension of magnesium turnings (0.55 g, 22.6 mg-atom) in THF (15 mL). The mixture was refluxed for 30 h by which time most of the magnesium had dissolved and the solution was grayish yellow. Titration of the supernatant solution (after aqueous quenching) showed a concentration of 0.35 mol L (ca. 85%). After filtration, the solution was stored under argon at −20 °C.

(Cycloocta-1,5-diene)dineophylplatinum(II). To a stirred suspension of $PtCl_2$(cod) (0.93 g, 2.5 mmol) in THF (15 mL) at −20 °C was added dropwise a solution of $Mg(CH_2CMe_2Ph)Cl$ (7.5 mmol) in THF (35 mL). The mixture was allowed to reach room temperature and stirred for a further 6 h. The solvent was removed from the clear dark yellow solution in vacuo and diethyl ether (40 mL) added. The resulting stirred suspension was cooled to −15 °C and hydrolyzed by dropwise addition of degassed saturated ammonium chloride solution (ca. 10 mL). The dark colored ethereal layer was separated, dried over magnesium sulfate, and decolorized with activated charcoal to give a pale yellow solution. Concentration to ca. 10 mL and addition of methanol (ca. 2 mL) afforded large colorless prisms of the product (yield 0.9 g, 63%). (IR: 3099 w, 3084 w, 3084 w, 2958 m, 2950 m, 2810 m, 1600 m, 1495 s, 1375 m, 1280 m, 1070 m, 1030 m, 977 m, 788 m, 764 vs, 700 vs, 565 m cm^{-1}.)

(Cycloocta-1,5-diene)di(neophyl-d_5)platinum(II). This analogue was prepared exactly as above using $Mg(CH_2CMe_2C_6D_5)Cl$ and $PtCl_2$(cod). (IR: 3095 w, 3060 w, 3005 vw, 2955–2850 m, 2810 w, 2151 w, 1566 w, 1484 mw, 1375 mw, 1368 mw, 1355 m, 1312 w, 980 mw, 865 m, 829 mw, 763 m, 570 s, 525 m, 500 ms, 450 w cm^{-1}.)

(Cycloocta-1,5-diene)-3,3-dimethyl-1-platinaindan. A solution of $Pt(CH_2CMe_2Ph)_2$(cod) in toluene was heated to 60 °C for 48 h. Removal of the solvent in vacuo gave a yellowish semisolid. This was crystallized from a 1:1 diethyl ether/hexane mixture as large colorless prisms. (IR: 3055 mw, 3000 mw, 2950 m, 2875 m, 1530 w, 1450 m, 1371 m, 1350 m, 1341 m, 1135 m, 1042 m, 968 m, 860 m, 818 m, 763 s, 746 s, 735 vs, 563 m, 450 w cm^{-1}.)

(2,2′-Bipyridyl)dineophylplatinum(II). 2,2′-Bipyridyl (5.46 g, 35 mmol) and $Pt(CH_2CMe_2Ph)_2$(cod) (0.4 g, 0.7 mmol) were dissolved in the minimum amount of toluene (ca. 30 mL). The solution was stirred at ambient temperature for 4 days. The bright red solution was transferred via steel tubing into a stirred solution of $FeSO_4$ (8.5 g, ca. 56 mmol) in distilled water (50 mL). The aqueous phase immediately became dark red due to formation of $Fe(bpy)_3^{2+}$. The mixture was cooled to −78 °C and the toluene layer filtered off from the frozen aqueous layer. The latter, upon thawing, was washed with toluene (2 × 30 mL), and the organic extracts were combined. Removal of the toluene in vacuo gave analytically pure bright red crystalline product (yield 0.36 g, 83%). (IR: 3100 w, 3080 w, 3046 w, 2950 m, 2855 m, 2790 m, 1598 s, 1492 m, 1465 m, 1440 s, 1355 m, 750 vs, 746 m, 728 s, 695 vs, 563 m cm^{-1}.)

(2,2′-Bipyridyl)di(neophyl-d_5)platinum(II). The deuterated derivative was synthesized by the procedure above, using $Pt(CH_2CMe_2C_6D_5)_2$(cod). (IR: 3105 vw, 3055 vw, 2950–2840 mw, 2268 mw, 2100 w, 1600 ms, 1492 w, 1468 s, 1442 vs, 1353 mw, 1310 w, 1260 mw, 1156 m, 1045 mw, 750 vw, 740 ms, 730 w, 650 w, 566 vs, 500 ms, 480 m, 427 mw cm^{-1}.)

(2,2′-Bipyridyl)-3,3-dimethyl-1-platinaindan. $Pt(CH_2CMe_2Ph)_2$(bpy) was heated for 18 h at 80 °C in toluene solution. Filtration, concentration of the solution, and cooling at −25 °C yielded the product, containing toluene of crystallization, as red prisms (yield 80%, after purification). (IR: 3035 w, 2940 mw, 2845 w, 1600 m, 1468 m, 1442 s, 1425 m, 1384 mw, 1157 mw, 1028 mw, 748 s, 726 m, 698 mw, 556 m cm^{-1}.)

(2,2′-Bipyrimidyl)dineophylplatinum(II). 2,2′-Bipyrimidyl (0.14 g, 0.886 mmol) was dissolved in the minimum amount of toluene (ca. 35 mL), and $Pt(CH_2CMe_2Ph)_2$(cod) (0.50 g, 0.878 mmol) was added to the stirred solution under air. The solution immediately became red, and after 10 days at room temperature, concentration of the solution yielded fine wine-red needles (yield 0.32 g, 59%). (IR: 3083 w, 3058 w, 3040 w, 2970 mw, 2920 w, 2890 m, 2788 ms, 1598 w, 1574 s, 1550 s, 1495 s, 1417 s, 1403 vs, 807 ms, 758 ms, 729 m, 692 vs, 682 m, 562 s cm^{-1}.)

(2,2-Bipyrimidyl)-3,3-dimethyl-1-platinaindan. $Pt(CH_2CMe_2Ph)_2$(bipym) was heated at 80 °C in toluene for 18 h. Removal of the solvent in vacuo and extraction of the residue into diethyl ether gave a dark red solution from which the product was isolated as a red, microcrystalline solid by concentration and cooling at −25 °C. (IR: 3053 w, 2953 mw, 2852 mw, 1573 s, 1550 ms, 1448 m, 1402 vs, 1024 w, 752 s, 736 m, 659 mw, 562 w cm^{-1}.)

(1,10-Phenanthroline)dineophylplatinum(II). A suspension of 1,10-phenanthroline monohydrate (0.8 g, 4 mmol) in diethyl ether (50 mL) was added to $Pt(CH_2CMe_2Ph)_2$(cod) (0.25 g, 0.44 mmol). The mixture was stirred vigorously for 20 h. The microcrystalline orange product was filtered, washed twice with aqueous $FeSO_4$, distilled water, and finally diethyl ether (yield 0.25 g, 89%). (IR: 3080 mw, 3054 w, 3013 w, 2970 m, 2885 ms, 2790 ms, 1626 vw, 1600 w, 1495 ms, 1475 m, 1425 ms, 1395 ms, 1395 m, 1035 m, 843 vs, 760 ms, 724 s, 699 vs, 572 m cm^{-1}.)

(1,10-Phenanthroline)-3,3-dimethyl-1-platinaindan. A suspension of $Pt(CH_2CMe_2Ph)_2$(phen) (0.1 g) in toluene (65 mL) was heated at 95 °C for 48 h. During this time the orange microcrystalline solid dissolved to give a deep red solution. The hot solution was filtered, concentrated to ca. 40 mL, and cooled at −25 °C. This caused the product to separate as bright red crystals in almost quantitative yield (98%). (IR: 3050 w, 3028 w, 2950 mw, 2845 m, 2780 w, 2775 w, 1624 w, 1573 mw, 1494 w, 1445 mw, 1424 s, 1405 ms, 1339 mw, 1143 mw, 1025 m, 835 vs, 753 s, 740 s, 717 vs, 478 w, 453 w cm^{-1}.)

(3,4,7,8-Tetramethyl-1,10-phenanthroline)dineophylplatinum(II). $Pt(CH_2CMe_2Ph)_2$(cod) (0.42 g, 0.74 mmol) and Me_4phen (0.21 g, 0.89 mmol) were dissolved in the minimum amount of toluene (ca. 100 mL). After 5 days of stirring at ambient temperature a yellow powder had formed. The orange supernatant was filtered off, washed with aqueous ferrous sulfate solution, and concentrated to yield more of the orange-yellow solid (overall yield 0.4 g, 57%). (IR: 3065 w, 3040 w, 3000 w, 2950 m, 2875 m, 2776

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m, 1627 w, 1612 w, 1592 w, 1490 ms, 1420 m, 1382 m, 1353 m, 1055 m, 920 m, 822 ms, 764 ms, 730 s, 700 vs, 560 mw cm^{-1}.)

(3,4,7,8-Tetramethyl-1,10-phenanthroline)-3,3-dimethyl-1-platinaindan. $Pt(CH_2CMe_2Ph)_2(Me_4phen)$ (ca. 0.05 g) was dissolved in toluene (50 mL) and heated at 95 °C for 48 h. On cooling the product separated as a yellow-orange microcrystalline solid in almost quantitative yield. (IR: 3043 mw, 2945 m, 2844 m, 2780 w, 1620 w, 1575 mw, 1425 s, 1384 s, 1345 w, 1026 mw, 912 w, 811 ms, 754 ms, 736 vs, 716 s, 693 w, 585 vw, 475 w cm^{-1}.)

(4,7-Diphenyl-1,10-phenanthroline)dineophylplatinum(II). $Pt(CH_2CMe_2Ph)_2(cod)$ (0.02 g, 0.35 mmol) and Ph_2phen (0.16 g, 0.25 mmol) were allowed to react in toluene (20 mL) for 13 days at ambient temperature. The toluene was removed in vacuo and the red residue extracted into diethyl ether (10 mL). Slight concentration of the solution and cooling to −25 °C caused formation of bright orange/red needles of the product (0.2 g, 71%). (IR: 3080 mw, 3054 w, 3013 w, 2970 m, 2885 ms, 2790 ms, 1626 vw, 1600 w, 1495 ms, 1475 m, 1425 ms, 1395 m, 1035 m, 843 vs, 760 ms, 724 s, 699 vs, 572 m cm^{-1}.)

(4,7-Diphenyl-1,10-phenanthroline)di(neophyl-d_5)platinum(II). Using the above procedure, the deuterated analogue was accessible from $Pt(CH_2CMe_2C_6D_5)_2(cod)$. (IR: 3063 vw, 2962 m, 2920 m, 2870 m, 2785 mw, 2270 w, 1625 w, 1598 w, 1564 mw, 1450 mw, 1426 m, 850 vs, 836 ms, 770 vs, 740 s, 710 vs, 637 m, 566 m, 500 m cm^{-1}.)

(4,7-Diphenyl-1,10-phenanthroline)-3,3-dimethyl-1-platinaindan. $Pt(CH_2CMe_2Ph)_2(Ph_2phen)$ (0.15 g, 0.19 mmol) was heated at 90 °C for 2 days in toluene (50 mL). The bright red solution was filtered while still hot. The product crystallized as a bright orange solid on cooling (yield 0.1 g, 55%). (IR: 3035 w, 2932 w, 2837 mw, 1620 mw, 1589 mw, 1570 mw, 1552 mw, 1489 mw, 1440 m, 847 s, 832 ms, 765 s, 730 s, 703 vs, 560 mw, 550 w, 500 mw cm^{-1}.)

***cis*-Dineophylbis(triethylphosphine)platinum(II).** To a suspension of $Pt(CH_2CMe_2Ph)_2(cod)$ (0.43 g, 0.76 mmol) in hexane (10 mL) at room temperature was added by syringe Et_3P (0.4 mL, 2.7 mmol). The $Pt(CH_2CMe_2Ph)_2(cod)$ dissolved and the solution was allowed to stand overnight at ambient temperature. Removal of the hexane in vacuo gave a colorless oil. The oil was cooled at −25 °C for 48 h by which time it afforded a crystalline mass. The colorless solid was extracted into the minimum amount of hexane (ca. 5 mL). Concentration of this solution to ca. 3 mL and cooling at −25 °C caused the product to form as large colorless prisms (yield 0.44 g 83%).

***cis*-Di(neophyl-d_5)bis(triethylphosphine)platinum(II).** This analogue was prepared exactly as above by using $Pt(CH_2CMe_2C_6D_5)_2(cod)$. (IR: 2965 s, 2930 s, 2904 s, 2269 m, 2160 w, 1563 m, 1449 s, 1430 ms, 1400 s, 1374 s, 1253 m, 1031 vs, 1023 s, 754 vs, 710 vs, 618 m, 552 ms, 519 m, 466 m, 405 mw cm^{-1}.)

***cis*-Bis(triethylphosphine)-3,3-dimethyl-1-platinaindan.** *cis*-$Pt(CH_2CMe_2Ph)_2(Et_3P)_2$ was heated in toluene at 50 °C and the solvent removed in vacuo to leave a colorless oil or semisolid. Extraction into the minimum amount of hexane, concentration, and cooling (−25 °C) yielded the product almost quantitatively as large colorless prisms. (IR: 3060 w, 3030 w, 2960–2870 s, 1572 w, 1405 s, 1415 s, 1373 s, 1362 m, 1340 m, 1144 w, 1089 w, 1030 vs, 1018 vs, 760 vs, 745 s, 739 vs, 712 vs, 625 ms, 563 w, 465 w, 413 mw cm^{-1}.)

***cis*-Bis(triphenylphosphine)-3,3-dimethyl-1-platinaindan.** $Pt(CH_2CMe_2Ph)_2(cod)$ and 2 equivs of Ph_3P were reacted in chloroform or benzene for 2 days. Removal of the solvent in vacuo, extraction into the minimum amount of diethyl ether, concentration, and cooling to −25 °C gave the product as a white crystalline solid. (IR: 3075 w, 3050 w, 2948 m, 2920 w, 2790 w, 1480 s, 1433 vs, 1400 s, 1393 s, 1349 m, 1310 m, 1260 ms, 1200 s, 1180 s, 1150 ms, 1118 vs, 1089 vs, 1025 m, 996 m, 800 mw, 750 ms, 740 s, 720 vs, 693 vs, 520 vs, 450 w cm^{-1}.)

[1,2-Bis(diphenylphosphino)ethane]dineophylplatinum(II). Both $Pt(CH_2CMe_2Ph)_2(cod)$ (0.22 g, 0.39 mmol) and dppe (0.16 g, 0.4 mmol) were dissolved in the minimum amount of toluene (30 mL) and allowed to stand at ambient temperature for 3 days.

Concentration of the solution and cooling to −25 °C gave the product as a white powder (0.24 g, 72%). This may be recrystallized as large colorless prisms by redissolving in warm toluene, adding hexane, and cooling. (IR: 3058 mw, 2957 m, 2860 m, 2810 mw, 1598 mw, 1490 m, 1436 s, 1386 m, 1375 m, 1207 mw, 1190 m, 1100 s, 1030 m, 1000 m, 820 ms, 742 s, 693 vs, 679 s, 560 mw, 538 vs, 490 ms, 424 mw cm^{-1}.)

[1,2-Bis(diphenylphosphino)ethane]-3,3-dimethyl-1-platinaindan. $Pt(CH_2CMe_2Ph)_2(dppe)$ (0.06 g, 0.07 mmol) was refluxed in toluene (50 mL) for 24 h. Removal of the solvent gave a white crystalline solid (0.05 g, 95%). (IR 3060 w, 3043 w, 2940 mw, 2912 mw, 2850 w, 2790, 1484 ms, 1432 vs, 1400 vs, 1100 vs, 1024 m, 995 m, 870 m, 813 s, 745 s, 730 s, 695 vs, 646 mw, 530 vs, 500 s, 485 s cm^{-1}.)

Kinetic Studies. (a) N-Donor Complexes. All complexes were recrystallized before use. $Pt(CH_2CMe_2Ph)_2(Ph_2phen)$ was isolated as a diethyl ether solvate, and so pure samples were dissolved in toluene and flash-evaporated in vacuo prior to kinetic determinations.

All experiments were carried out by using a JEOL FX90Q NMR spectrometer fitted with a precision thermoregulated probe. A solution of $Pt(CH_2CMe_2Ph)_2L_2$ (ca. 0.02 mol dm^{-3}) in degassed toluene-d_8 (ca. 0.5 mL) was prepared and cannulated into a 5-mm NMR tube fitted with a rubber septum. Kinetics were determined by equilibrating the probe at the required temperature and recording the ^1H spectrum at regular intervals (±1 s). Calibration[11] showed the accuracy of temperature control to be ±1 °C, with the precision being ±0.1 °C. Data accumulation times of ca. 5 min. and pulse delays of 2 s were employed. Relative concentrations were measured by integration of the resonances due to the α-methylene protons in $Pt(CH_2CMe_2Ph)_2L_2$ and $Pt(2\text{-}C_6H_4CMe_2CMe_2CH_2)L_2$; values of k_{obsd} were obtained from standard first-order plots. Two or more measurements were performed at each temperature to ensure reproducibility. The presence of even low concentrations of dioxygen profoundly affects the rate and the course of thermolytic decay. Metallacycle is not formed, but otherwise the products have not been investigated fully.

(b) *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$. Using the same instrument, kinetics were determined by recording the $^{31}P\{^1H\}$ NMR spectrum of the sample at regular intervals during the experiment (±1 s). Concentrations of the solution were tailored to give short accumulation times relative to this time interval (typically 5 min in 30 min). A pulse delay of 2 s was again employed; variation between 1 and 9 s produced no change in the relative integrals due to *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$ and *cis*-$Pt(2\text{-}C_6H_4CMe_2CH_2)(PEt_3)_2$ indicating that the phosphorus nuclei in both compounds have similar relaxation times and experience similar NOE from ^1H decoupling. ^{31}P in free Et_3P, however, experiences less than half the enhancement of the coordinated ligand,[12] and so $^{31}P\{^1H\}$ NMR cannot be used to determine the concentration of the free phosphine; this was achieved volumetrically.

Results and Discussion

General Information. Diene displacement from $Pt(CH_2CMe_2Ph)_2(cod)$ is slower for N-donors than for P-donors. For N-donors, a large ligand excess (10–50-fold) accelerates reaction. The residual free ligand is readily separable from organometallic product by extraction into aqueous $FeSO_4$ as $Fe(L_2)_3^{2+}$ except for Ph_2phen due to low solubility of the ligand and its iron complex in the aqueous phase.

Reaction of $Pt(CH_2CMe_2Ph)_2(cod)$ with Ph_3P in toluene, even at 0 °C, leads only to isolation of $Pt(2\text{-}C_6H_4CMe_2CH_2)(PPh_3)_2$. The dineophyl complex cannot be detected by ^1H NMR during the reaction but has been observed as a transient intermediate in the ^{31}P-NMR spectrum of freshly mixed solutions of a large excess (ca. 20-fold) of Ph_3P and $Pt(CH_2CMe_2Ph)_2(cod)$.

All these new dialkylplatinum and platinaindan compounds have been characterized by elemental analysis

(12) See, e.g.: Pregosin, P. F.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*: Springer-Verlag Berlin, 1979.

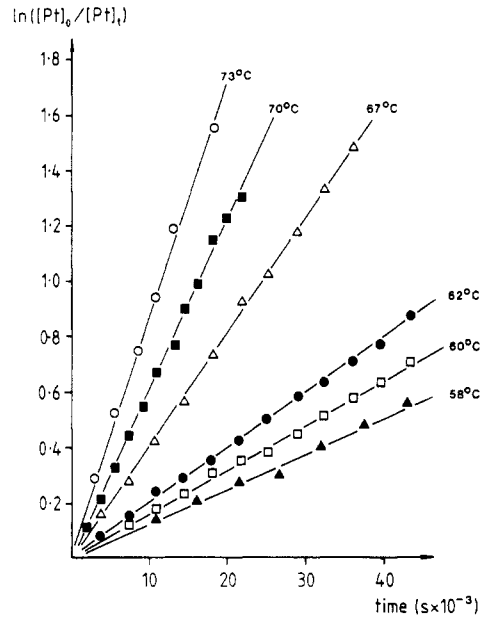


Figure 1. Effect of temperature on cyclization of Pt-$(CH_2CMe_2Ph)_2$(bpy).

(Table I) by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (^1H, Table II; ^{13}C, Table III). Phosphine complexes were also analyzed by $^{31}P\{^1H\}$ NMR (Table IV) and salient features in the electronic spectra of N-donor complexes are presented (Table V).

IUPAC conventions are adopted for numbering of heteroaromatic N-donor ligands. A different convention has been adopted as more convenient for the numbering of the aromatic rings in neophylplatinum(II) and platinaindan compounds. Here the alkyl-substituted aromatic carbon is designated as C_1. In platinaindans, C_2 is Pt-bound (see Scheme I).

Metallacyclization Reactions. In toluene solution under an inert atmosphere (Ar or N_2), all the dineophylplatinum(II) species, including $Pt(CH_2CMe_2Ph)_2$(cod), undergo clean thermolytic rearrangement exclusively to the platinaindan $Pt(2\text{-}C_6H_4CMe_2CH_2)L_2$, with elimination of 1 equiv of *tert*-butylbenzene (Scheme I). Various alternative pathways can be excluded on the basis of this simple product distribution. In particular, products derived from the benzyldimethylcarbinyl radical—the ready rearrangement product of the neophyl radical[13]—were absent. There was no incidence of 2,5-dimethyl-2,5-diphenylhexane (bineophyl). Primary Pt–C homolysis is not, therefore, a significant mechanistic contributor to the product distribution. Neither isomeric (2-*tert*-butylphenyl)platinum complexes[7] nor their products were detected. There was no metalation at an aliphatic γ-C site. The only reaction is a quantitative metal-induced transfer of hydrogen from an aromatic δ-C–H site to a metal-bound aliphatic carbon. This is confirmed by examination of selectively deuterated analogues $Pt(CH_2CMe_2C_6D_5)_2L_2$, from which the only organic product is $C_6D_5CMe_2CH_2D$. Hydrogen transfer by ligand metalation, possible for bpy[6] and PEt_3, also can be ruled out.

N-Donors: $Pt(CH_2CMe_2C_6H_5)_2L_2$ (L_2 = bpy, bipym, Ph_2phen, Me_4phen). (i) Thermolytic Kinetics. Metallacyclizations of all four compounds conformed to first-order rate laws for at least 3 half-lives; representative first-order decay of $Pt(CH_2CMe_2C_6H_5)_2$(bpy) at various temperatures is depicted in Figure 1.

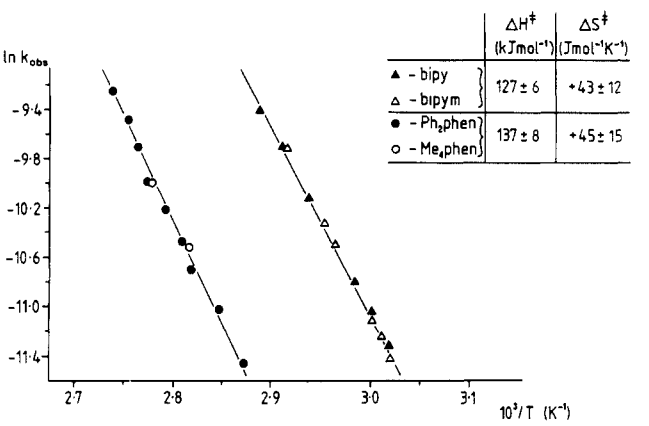


Figure 2. Arrhenius plots and activation parameters for cyclizations of $Pt(CH_2CMe_2Ph)_2L_2$.

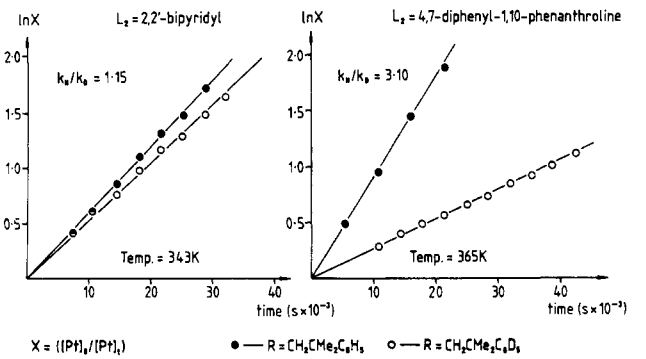


Figure 3. Deuterium isotope effect on cyclizations of Pt-$(CH_2CMe_2Ph)_2L_2$.

The nature of L_2 profoundly affects the rate of rearrangement, with bipyridyl and bipyrimidyl conferring greater lability. We examined the effects on the rates of (a) temperature, (b) deuteration at the H-transfer site, and (c) the presence of coordinating agents.

(a) The variations of k with temperature (Table VI) show linear Arrhenius correlations from which activation parameters ΔH^* and ΔS^* may be calculated (Figure 2).[14] The rearrangements of the bpy and bipym complexes are governed by activation parameters which are indistinguishable within experimental uncertainty. The greater lability of these two systems arises, superficially, from a lower ΔH^* (127 kJ mol^{-1}); ΔS^* for the phenanthroline derivatives is comparably favorable (ca. +44 J mol^{-1} K^{-1}).

(b) Deuterium-labeling provides further evidence that these differing activation characteristics reflect mechanistic variations. Metallacyclization of $Pt(CH_2CMe_2C_6D_5)_2$(bpy) reveals only a small, temperature-independent kinetic isotope effect: $k^H/k^D = 1.26 \pm 0.10$ (Figure 4). Corresponding reaction of $Pt(CH_2CMe_2C_6D_5)_2(Ph_2phen)$, however, exhibits a substantial effect: mean $k^H/k^D = 3.30 \pm 0.20$.

(13) See, for example: Whitesides, G. M.; Panek, E. J.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 232.

(14) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, Wiley: London, 1961; Chapter 5; Alder, R. W.; Baker, R. W.; Brown, J. M. *Mechanism in Organic Chemistry*; Wiley-Interscience: London, 1970; Chapter 1.

Table I. Analytical Data for Dineophylplatinum and Platinaindan Complexes

complex	color	Anal. found (calcd) C	H	N
$Pt(CH_2CMe_2Ph)_2(cod)$	colorless	58.80 (59.01)	6.70 (6.68)	
$Pt(CH_2CMe_2Ph)_2(bpy)$	red	58.36 (58.33)	5.47 (5.54)	4.47 (4.61)
$Pt(CH_2CMe_2Ph)_2(bipym)$	maroon	54.01 (54.27)	5.09 (5.17)	8.91 (9.05)
$Pt(CH_2CMe_2Ph)_2(phen)$	red	59.24 (59.89)	5.28 (5.34)	4.36 (4.37)
$Pt(CH_2CMe_2Ph)_2(Me_4phen)$	orange	61.88 (61.96)	5.91 (6.07)	4.10 (4.01)
$Pt(CH_2CMe_2Ph)_2(Ph_2phen)$	red	66.42 (66.57)	5.17 (5.33)	3.89 (3.58)
$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$	colorless	55.17 (55.08)	8.18 (8.09)	
$Pt(CH_2CMe_2Ph)_2(dppe)$	colorless	63.55 (64.25)	5.76 (5.86)	
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(cod)$	colorless	49.10 (49.60)	5.51 (5.52)	
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(bpy)^4/_7$toluene	red	53.93 (53.77)	4.58 (4.62)	5.21 (5.23)
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(bipym)$	maroon	44.17 (44.53)	3.88 (3.77)	11.37 (11.54)
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(phen)$	red	52.70 (52.07)	3.99 (3.97)	5.37 (5.52)
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(Me_4phen)$	orange	54.93 (55.41)	4.94 (5.01)	4.93 (4.97)
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(Ph_2phen)$	red	61.38 (61.90)	4.25 (4.28)	4.04 (4.25)
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(PEt_3)_2$	colorless	47.06 (46.88)	7.57 (7.51)	
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(PPh_3)_2$	colorless	64.51 (64.86)	5.24 (4.97)	
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(dppe)$	colorless	59.33 (59.58)	5.00 (5.00)	

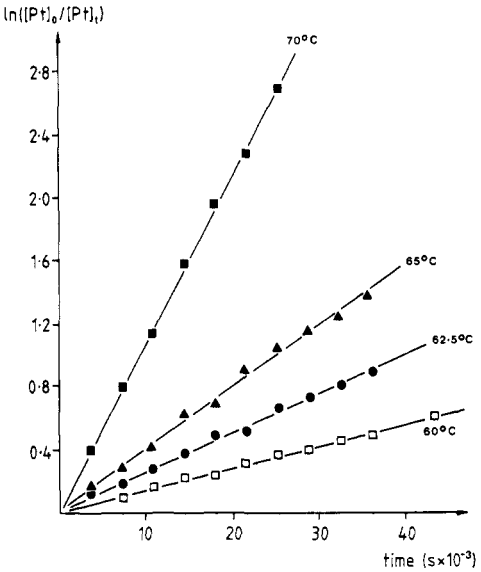
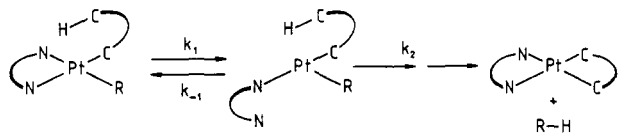


Figure 4. Effect of temperature on metallacyclization rate for *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)_2$ with 0.037 M PEt_3 present.

(c) Thermally or photochemically induced dissociation of ancillary ligands prior to hydrogen transfer (or indeed other reactions of organotransition metals) is often a prerequisite, notably in d^8 metal complexes. It is best documented for monodentate phosphine complexes,[2a-c,15] but complete dissociation of bipyridyl has been proposed to occur in thermolytic rearrangement of $\overline{Pt[(CH_2)_2CH_2]}Cl_2(bpy)$, via mainly reductive C–C elimination.[5] Ligand loss has often been regarded simply as creation of necessary coordination vacancies, but it (or ligand addition[16]) might also serve to impose, on the frontier orbitals, crucially destabilizing ligand-field effects which facilitate the transformation.[17] We examined the effects of several potential ligands on metallacyclization rates.

Scheme II



Cyclization of $Pt(CH_2CMe_2Ph)_2(bpy)$ in the presence of bpy (0.06 M) at 65 °C exhibits a rate ($k = 2.6 \times 10^{-5}$ s^{-1}) virtually identical with that in the absence of free ligand ($k = 3.1 \times 10^{-5}$ s^{-1}, from Figure 4). Similarly, reaction of $Pt(CH_2CMe_2Ph)_2(Ph_2phen)$ at 92 °C (ca. 0.04 M) is unaffected by the presence ($k = 2.74 \times 10^{-5}$ s^{-1}) or absence ($k = 2.53 \times 10^{-5}$ s^{-1}) of added ligand (0.04 M). Complete dissociation of the neutral ligands is clearly not a prerequisite for these rearrangements.

Addition of pyridine to solutions of $Pt(aryl)_2(bpy)$ altered the thermolytic product distribution and intercepted coordinatively unsaturated intermediates.[6] Cyclization of $Pt(CH_2CMe_2Ph)_2(Ph_2phen)$ (0.01 M) at 90 °C with pyridine (ca. 0.04 M) present shows only minor rate sensitivity ($k = 9.02 \times 10^{-5}$ s^{-1}, cf. 7.57×10^{-5} s^{-1} in the absence of pyridine), and metallacycle and *tert*-butylbenzene are the only products detected.

(ii) Mechanistics. The preceding results suggest that the bipyridyl and bipyrimidyl compounds cyclize via a pathway energetically different from that followed by phenanthroline complexes. The large kinetic isotope effect displayed by the latter (3.30) compared with the relatively small effect on the bipyridyl system (1.26) is the most unequivocal evidence that the controls differ for the two. A similarly large value (3.0) was observed for cyclization of *cis*-$Pt(CH_2CMe_3)_2(PEt_3)_2$,[2a] proposedly reflecting a rate-limiting C–H elimination. The comparatively minor effect on metallacyclization rate of $Pt(CH_2CMe_2Ph)_2(bpy)$, conversely, would suggest substantial rate control by a process which does not feature hydrogen (or deuterium)

(15) See, for example: (a) Grubbs, R. H.; Miyashita, A.; Lui, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418. (b) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (c) Moravskiy, A.; Stille, J. K. *Ibid.* **1981**, *103*, 4182. (d) Ozawa, K.; Ito, T.; Nakamura, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (e) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258. (f) DiCosimo, R.; Whitesides, G. M. *Ibid.* **1982**, *104*, 3601. (g) McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *Ibid.* **1981**, *103*, 3396. (h) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982**, *1*, 1528. (i) Komiya, S.; Albright, R.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255; see also ref 25.

(16) (a) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 892. (b) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181.

(17) Cf. Tatsumi, K.; Hoffman, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857 and ref 21k.

Table II. ^{1}H NMR Characteristics of Dineophylplatinum and Platinaindan Complexes

complex	$\delta(^1H)$, ppm, for Ligands (J_{Pt-H})			^{1}H, ppm, for neutral donor ligands (J_{Pt-H}) [assignmt]
	CH_2	CH_3	aromatic	
$Pt(CH_2CMe_2Ph)_2(cod)$	2.23 (88)	1.53 (8)	7.45 dd (J_{H2-H3} = 8) [H2], 7.17–6.92 m [H3, H4]	3.87 (38) [CH], 1.46 t (18) [CH_2]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(cod)$	2.29 (89)	1.44	7.26–7.00 m	5.08 (38), 4.64 (42) [CH], 1.82 [CH_2]
$Pt(CH_2CMe_2Ph)_2(bpy)$	2.78 (86)	1.78	7.68 dd (J_{H2-H3} = 7) [H2], 7.04–6.64 [H3, H4]	8.48 dd (21) (J_{H6-H5} = 6) [H6], 6.28 dd [H5], obscured [H3, H4]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(bpy)$	2.91 (96)	1.81	7.31–6.84 m	9.22 dd (17) ($J_{H6'-H5'}$ = 6, $J_{H6'-H4'}$ = 2) [H6'], 8.73 dd (24) (J_{H6-H5} = 6, J_{H6-H4} = 2) [H6], 7.70 dd ($J_{H3'-H4'} = J_{H3-H4}$ = 6] [H3', H3], 6.35 dd [H5], 6.40 dd [H5]
$Pt(CH_2CMe_2Ph)_2(bipym)$	2.74 (87)	1.78	7.68 dd (J_{H2-H3} = 8) [H2], 6.78–6.60 m [H3, H4]	8.16 m [H4, H6], 5.93 dd ($J_{H4-H5} = J_{H5-H6}$ = 6) [H5]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(bipym)$	2.87 (97)	1.76	7.25–6.98 m	9.16 dd (~15) ($J_{H6'-H5'}$ = 6, $J_{H6'-H4'}$ = 2) [H6'], 8.62 dd (21) (J_{H6-H5} = 6, J_{H6-H4} = 2) [H6], 8.20–8.15 m [H4, H4'], 6.09 dd ($J_{H5'-H4'} = J_{H5'-H6'}$ = 6) [H5'], 6.03 dd ($J_{H5-H4} = J_{H5-H6}$ = 6) [H5]
$Pt(CH_2CMe_2Ph)_2(phen)^c$	2.52 (87)	1.52	7.62 dd (J_{H2-H3} = 8) [H2], 7.07–6.88 m [H3, H4]	9.11 dd (20) ($J_{H9(2)-H7(4)}$ = 15, $J_{H9(2)-H8(3)}$ = 5) [H2, H9], 8.52 dd ($J_{H8(4)-H7(3)}$ = 8, $J_{H9(2)-H7(4)}$ = 1.5) [H4, H7], 7.88 s [H5, H6], 7.6 [H3, H8]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(phen)^d$	2.88 (95)	1.48	7.21–7.03 m	9.91 dd (16) (J_{H2-H3} = 5, J_{H2-H4} = 1.5) [H2], 9.56 dd (24) (J_{H9-H8} = 5, J_{H9-H7} = 1.5) [H9], 8.63 dd (J_{H4-H3} = 4) [H4], 8.54 dd (J_{H7-H8} = 4) [H7], 7.93 s [H5, H6], 8.00–7.75 m [H3, H8]
$Pt(CH_2CMe_2Ph)_2(Ph_2phen)$	3.08 (88)	1.96	7.89 dd (J_{H2-H3} = 6) [H2], 7.33–6.70 m [H3, H4]	8.93 dd (20) ($J_{H2(9)-H4(8)}$ = 5) [H2, H9], 7.54 s [H5, H6], obscured [H3, H8], 7.14 [C_6H_5]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(Ph_2phen)^d$	2.95 (94)	1.55, 1.52	7.20–7.09 m	9.08 dd (16) (J_{H2-H4} = 5) [H2], 8.89 dd (24) (J_{H9-H8} = 5) [H9], 8.00 s [H5, H6], 7.87 d (J_{H3-H2} = 6) [H3], 7.77 d (J_{H8-H9} = 6) [H8], 7.59 [C_6H_5]
$Pt(CH_2CMe_2Ph)_2(Me_4phen)$	2.87 (88)	1.85	7.89 dd (J_{H2-H3} = 8) [H2], 7.04–6.81 m [H3, H4]	8.50 (20) [H2, H9], 7.37 s [H5, H6], 1.75, 1.81 [CH_3]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(Me_4phen)^d$	2.77 (95)	1.49	7.24–6.99 m	9.59 (16) [H2], 9.20 (23) [H9], 8.05 s [H5, H6], 2.64 [CH_3]
cis-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2^e$	2.26 (64)	1.73	7.65 dd (J_{H2-H3} = 7) [H2], 7.38–7.15 m	1.65–1.15 m [CH_2], 0.78–0.61 [CH_3]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(PEt_3)_2^e$	2.18 (56) ($^3J_{P-H}$ = 6)	1.78	7.82 td (53) ($^1J_{H-H}$ = 7, $^2J_{H-H}$ = 1.5) [H6], 7.34–7.03 m	1.64 quintet [P^1–CH_2], 1.50 quintet [P^2–CH_2], 0.92–0.78 app sextet [CH_3]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(PEt_3)_2$	2.03 (56) ($^3J_{P-H}$ = 6)	1.62	7.65 td (53) ($^1J_{H-H}$ = 7, $^2J_{H-H}$ = 1.5) [H6], 7.23–6.94 m	1.56 quintet [P^1–CH_2], 1.50 quintet [P^2–CH_2], 0.88–0.73 app sextet [CH_3]
cis-$Pt(CH_2CMe_2Ph)_2(PPh_3)_2$			*f*	
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(PPh_3)_2$	2.37 (62)	1.71	*g*	7.48 m, 6.73 m [C_6H_5]
$Pt(CH_2CMe_2Ph)_2(dppe)$	2.37 (76)	1.21	*g*	7.35–7.24 m 6.07–6.88 m [C_6H_5], 1.86 t ($^2J_{P-H}$ = 7) [CH_2]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(dppe)$	2.64 (64) ($^3J_{P-H}$ = 6)	1.60	*g*	7.72–7.22 m, 7.00–6.90 [C_6H_5], 1.94 m [CH_2]
$Pt(CH_2CMe_2Ph)_2(dppm)$	2.51 (75)	1.38	*g*	7.39–7.29 m, 7.04–6.82 m [C_6H_5], 3.81 t ($^2J_{P-H}$ = 9) [CH_2]

[a] Recorded in toluene-d_8, unless otherwise noted. [b] Coupling constants J in Hz, where observed. [c] Recorded in dichloromethane-d_2. [d] Recorded in chloroform-d. [e] Recorded in benzene-d_6. [f] Too labile for observation, see text and Table IV. [g] Obscured, by phosphine aromatic resonances.

transfer. This might plausibly be dissociation of *one* of the Pt–N bonds.

Scheme II represents a simple view of such a path in which preliminary, reversible Pt–N cleavage precedes collapse of a tricoordinate intermediate via H transfer. Assuming a steady-state concentration of tricoordinate intermediate, then a first-order rate law is predicted where $k_{obsd} = k_1k_2/(k_2 + k_{-1})$. The isotope effect on k_{obsd} has the form

$$\frac{k^H_{obsd}}{k^D_{obsd}} = \frac{k^H_1k^H_2(k^D_2 + k^D_{-1})}{k^D_1k^D_2(k^H_2 + k^H_{-1})}$$

The isotope effect on any k is independent of the size of $\Delta G^\ddagger$ associated with that step.[18] Further, in the present case, since a Pt–N vibration is the relaxation mode for the transition state, the isotope effects on k_1 and k_{-1} are expected to be small (secondary) or zero ($k^H_1/k^D_1 = k^H_{-1}/k^D_{-1} = 1$). The observed isotope effect can on this basis be simplified to

$$\frac{k^H_{obsd}}{k^D_{obsd}} = \frac{k^H_2}{k^D_2}\left(\frac{1 - k^D_2/k^D_{-1}}{1 + k^H_2/k^H_{-1}}\right)$$

(18) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1979; Chapter 2.2.

Table III. ^{13}C NMR Characteristics of Dineophylplatinum(II) and 1-Platinaindan Complexes

complex	$\delta(^{13}C)$, ppm, for hydrocarbyl ligands (J_{Pt-C}) [assignmt]				$\delta(^{13}C)$, ppm, for ancillary ligands (J_{Pt-C}) [assignmt]
	Pt–CH_2	Pt–CH_2C	Pt–CH_2CCH_3	aromatic	
$Pt(CH_2CMe_2Ph)_2(cod)$	38.9 (897)	42.6	34.0 (60)	133.7 (30.8) [C1], 127.4, 125.9 [C2, C3], 124.5 [C4]	99.9 (43) [CH], 29.3 [CH_2]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(cod)$[b]	50.2 (775)	49.8 (43)	35.0 (44)	168.8 [C1], 156.9 [C2], 134.0 (30), 126.2, 123.8 (54)	99.6 (62), 96.9 (47) [CH], 30.2, 29.2 [CH_2]
$Pt(CH_2CMe_2Ph)_2(bpy)$	24.0 (931)	42.9	32.8 (55)	158.0 [C1], 126.9, 126.7 [C2, C3], 124.1 [C4]	156.0 [C2], 147.9 (30) [C6], 135.2 [C4], 125.9 (20) [C3], 121.6 (10) [C5]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(bpy)$	32.1	47.6	34.0 (52)	*c*, 134.1, 123.9, 123.2, 121.8	150.1 [C6], 149.4 [C6′], 136.6 [C4, C4′], 126.6 [C3], 126.4 [C3′], 122.4 [C5, C5′]
$Pt(CH_2CMe_2Ph)_2(bipym)$	24.4 (958)	42.9 (21)	32.7 (63)	154.3 (24) [C1], 127.1, 126.9 [C2, C3], 124.4 [C4]	155.0 [C4], 162.0 [C2], 153.6 (26) [C6], 122.8 [C5]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(bipym)$	31.7 (833)	47.6 (41)	33.9 (52)	168.9 [C1], 142.8 [C2], 133.7 (34), 124.1 (66), 123.8 (66), 122.2	158.0 [C2, C2′], 156.9 [C4, C4′], 155.9 (26) [C6], 155.4 (32) [C6′], 121.5 [C5, C5′]
$Pt(CH_2CMe_2Ph)_2(phen)$				*d*	
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(phen)$	31.6 (828)	47.9 (42)	34.2 (53)	169.3 [C1], 143.9 [C2], 134.2 (37), 123.9 (66), 123.2, 122.1 (70)	149.9 (32), 149.2 (37) [C2, C9], 148.3, 148.0 [C11, C12], 135.9, 135.7 [C4, C7], 130.5 [C13, C14], 127.2, 127.0 [C5, C6], 125.5, 125.4 [C3, C8]
$Pt(CH_2CMe_2Ph)_2(Me_4phen)$	23.5	42.9	32.9 (58)	155.0 [C1, 126.8 [C2, C3], 123.7 [C4]	148.9 [C2, C9], 141.0 [C4, C7], 134.6 [C3, C8], 122.4 [C5, C6], 18.0, 14.9 [CH_3]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(Me_4phen)$	31.5	47.8	34.2 (52)	169.4 [C1], *c*, 133.4, 123.8, 123.0, 121.9	150.8, 150.0 [C2, C9], 142.6 [C4, C7] 134.0 [C3, C8], 122.8 [C5, C6], 17.7, 15.0 [CH_3]
$Pt(CH_2CMe_2Ph)_2(Ph_2phen)$	24.1 (938)	431 (19)	33.0 (55)	134.3 (31) [C1], 126.9 [C2, C3], 124.5 [C4]	155.0 (34) [C11, C12], 147.3 (25) [C2, C9], 137.4 [C4, C7] 128.1 (8) [C13, C14], 125.4 (16) [C3, C8], 126.9 [C5, C6], 148.0 [C1′], 129.1 [C2′], 129.0 [C3′], 124.1 [C4′]
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(Ph_2phen)$	32.0	47.9 (42)	34.3 (53)	169.4 [C1], 144.5 [C2], 134.3 (36), 123.9 (66), 123.2, 122.1 (66)	149.3, 148.7 (27) [C2, C9], 148.9, 148.8 [C11, C12] 136.9, [C4, C7], 128.8 [C13, C14], 125.9, 125.7 [C5, C6], 125.2, 125.0 [C3, C8],[e] 129.3, 129.0 [C_6H_5]
cis-$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(PEt_3)_2$	48.3 (600) ($^2J_{P_c-C}$ = 87, $^2J_{P_c-C}$ = 7)	50.0 (13) ($^2J_{P_t-C}$ = 7, $^2J_{P_c-C}$ = 6)	35.1 (46) ($^2J_{P_t-C}$ = 6)	121.8 (55) (J_{P-C} = 3) [C4 or C6], 122.7 [C5], 123.6 (59) (J_{P-C} = 8) [C4 or C6], 137.1 (48) (J_{P-C} = 5, J_{P-C} = 5) [C3], 163.0 (906) (J_{P-C} = 110, J_{P-C} = 8) [C2], 167.0 (73) (J_{P-C} = 5) [C1]	17.1 (17) (J_{P-C} = 26) [P_a–CH_2], 18.3 (17) (J_{P-C} = 23) [P_b–CH_2)], 8.6 (10) (J_{PC} = 12) [P–CH_2–CH_3]
$Pt(CH_2CMe_2Ph)_2(dppe)$	30.7 (17) ($^2J_{P_t-C}$ = 100, $^2J_{P_c-C}$ = 7)	43.5	33.7 (42)	156.9 (42) [C1], 126.4 [C2, C3], 124.4 [C4]	26.4 [P–CH_2], 134.6 (24) [C2], 130.1 [C4], *f*
$\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}(dppe)$	45.8 (ca. 600) (J_{P_t-C} = 87, J_{P_c-C} = 7)	50.5 ($^2J_{P_t-C}$ = 7, $^2J_{P_c-C}$ = 4)	35.5 (41) ($^2J_{P_t-C}$ = 5)	*f*, 141.1 (52) [C3], 169.8 [C1]	*f*

[a] Recorded in chloroform-*d*, unless otherwise noted, coupling constants *J* in Hz where observed. [b] Recorded in toluene-d_8, one aromatic resonance is solvent-obscured. [c] C_1 and/or C_2 in metallacycle unresolved due to poor solubility. [d] Insufficiently soluble. [e] Quaternary C of phenyl obscured by C_2, C_9, C_{11}, and C_{12} of phenanthroline. [f] Assignments uncertain.

Table IV. ^{31}P NMR Characteristics of Dineophylplatinum(II) and 1-Platinaindan Complexes with Tertiary Phosphine Ligands[a,b]

complex	δ(P)	^1J(Pt–P), Hz	^2J(P–P), Hz
cis-Pt(CH_2CMe_2Ph)$_2$(PEt_3)$_2$	0.7	1678	
cis-Pt(2-$C_6H_4CMe_2CH_2$)-(PEt_3)$_2$	13.3, 10.6	1833, 1857	13
cis-Pt(CH_2CMe_2Ph)$_2$(PPh_3)$_2$	27.2	1668	
cis-Pt(2-$C_6H_4CMe_2CH_2$)-(PPh_3)$_2$	35.0, 34.7	1949, 1813	9
Pt(CH_2CMe_2Ph)$_2$(dppe)	39.3	1584	
Pt(2-$C_6H_4CMe_2CH_2$)(dppe)	50.1, 49.5	1753, 1882	8
Pt(CH_2CMe_2Ph)$_2$(dppm)	−37.8	1263	
Pt(CH_2CMe_2Ph)$_2$(dmpe)	22.7	1634	

[a] Recorded in toluene-d_8 with broad-band ^1H decoupling. [b] Coupling constants J in Hz.

Table V. Lowest Energy MLCT Transition of PtRR′L$_2$[a]

	λ_{max}, nm	
L_2	R = R′ = CH_2CMe_2Ph	RR′ = 2-$C_6H_4CMe_2CH_2$
bpy	477	467
bipym	502	492
phen	482	463
Me_4phen	454	434
Ph_2phen	487	472

[a] Recorded from freshly prepared dichloromethane solutions.

Table VI. First-Order Metallacyclization Rates of Pt(CH_2CMe_2Ph)$_2$L$_2$

L_2	temp, °C	$10^5 k_{obsd}$, s^{-1}
bpy	73.0	8.22
	70.0	6.02
	67.0	4.07
	62.0	2.03
	60.0	1.62
	58.0	1.26
bipym	70.0	6.07
	65.0	3.25
	60.0	1.53
	59.1	1.32
	58.0	1.10
Ph_2phen	92.0	9.09
	90.0	7.57
	88.5	6.04
	87.0	4.52
Ph_2phen	85.0	3.64
	82.9	2.82
	82.0	2.23
	78.0	1.64
	75.0	1.06
Me_4phen	87.0	4.48
	82.0	2.81

There are two limiting extremes. (1) When $k_{-1} \gg k_2$, then $k^H_{obsd}/k^D_{obsd} = k^H_2/k^D_2$. Even with preliminary Pt–N dislocation, a full isotope effect is expected. (2) If $k_{-1} \ll k_2$, it now follows that $k^H_{obsd}/k^D_{obsd} = k^H_1/k^D_1 = 1$; i.e., a zero isotope effect emerges. Between (1) and (2) the observed isotope effect will vary in the range $k^H_2/k^D_2 \geq k^H_{obsd}/k^D_{obsd} \geq 1$, depending on the ratio k_2/k_{-1}.

Rearrangement of the phenanthroline complex, with its significant isotope effect, clearly resembles (1) more closely. The most energetic transition state involves hydrogen transfer. For the bipyridyl system, although there is a detectable isotope effect, the energetics are more akin to those in (2).

In the (rather unlikely) event that $k^H_2 = k^H_{-1}$ (and $k^H_2 = k^D_{-1}$), the rate ratio becomes

$$\frac{k^H_{obsd}}{k^D_{obsd}} = \frac{k^H_2}{k^D_2}\left\{\frac{1 + k^D_2/k^D_{-1}}{2}\right\} = \tfrac{1}{2}[(k^H_2/k^D_2) + 1]$$

Assuming $k^H_2/k^D_2 = 3.0$ as a reasonable *lower* limit, based on these and related observations, the corresponding lower limit for primary isotope effect k^H_{obsd}/k^D_{obsd} is 2.0. This hypothetical case represents the condition at which H migration ceases to be "rate limiting" in the sense that its transition state is no longer the most energetic along the reaction coordinate (*all* of k_1, k_{-1}, and k_2 will influence the rate, of course). Extending the same assumption ($k^H_2/k^D_2 = 3.0$) to the *observed* isotope effect of 1.26 affords a *lower* limit, $k^H_2/k^H_{-1} = 6.7$ (whence $k_{obsd} = 0.87k_1$), a relatively close approach to (1), where Pt–N scission *is* truly rate-limiting.

Conformational flexibility is the most obvious explanation for the mechanistic differences. Bipyridyl (and bipyrimidyl) has the capacity to rotate not only out of the coordination plane (about a Pt–N bond) but also to rotate the dissociating ring out of coplanarity with its coordinated neighbor (about the C_2–C'_2 bond), allowing the free nitrogen a more extended lifetime beyond recoordination range (Scheme III). Hence k_{-1} is less significant and the tricoordinate intermediate successively adds oxidatively into the C_2–H bond of the phenyl ring and reductively eliminates *tert*-butylbenzene via relatively less energetic summits. The molecular freedom so gained during the η^2–η^1 transformation of bipyridyl is consistent with the positive activation entropy ($\Delta S^\ddagger = +43 \pm 10$ J mol^{-1} K^{-1}) deriving from k_{obsd} (whose activation parameters should reflect mainly k_1). A similar value ($\Delta S^\ddagger = +34 \pm 13$ J mol^{-1} K^{-1}) is observed for the thermolytic rearrangement of Pt(4-$C_6H_4Bu^t$)$_2$(bpy) via rollover C-3-metalation. This clearly does require preliminary Pt–N dissociation.[6] The indistinguishable activation parameters for Pt(CH_2CMe_2Ph)$_2$(bipym) suggest the same mechanistic controls on its rearrangement.

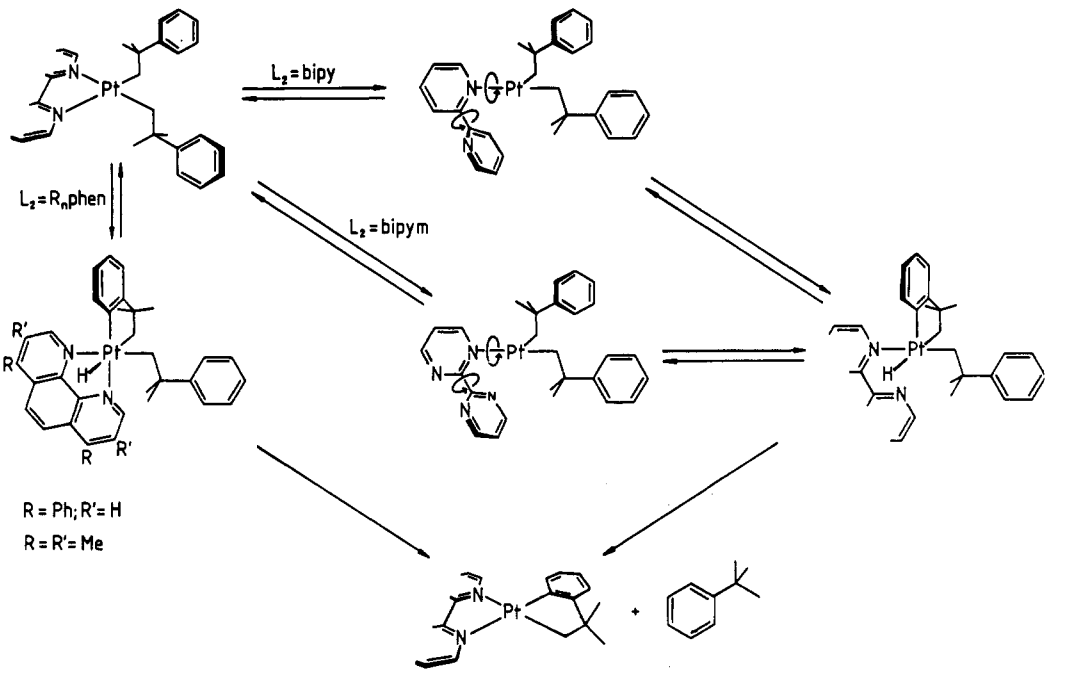
Phenanthroline, on the other hand, lacks C–C rotational flexibility should a Pt–N bond dissociate. Consequently, k_{-1} increases in significance and the contribution of a H-transfer step (k_2 in the simple model) to k_{obsd} rises correspondingly. Preliminary Pt–N dissociation may not be a prerequisite for this more rigid ligand, of course. Hydrogen transfer to four-coordinate Pd(II) and Pt(II) has been noted,[15g,h,19] usually where ligand loss is suitably inhibited. This eventuality is depicted in Scheme III. Although the composite nature of k_{obsd} makes definite conclusions difficult, the positive entropy of activation ($\Delta S^\ddagger = +44$ J mol^{-1} K^{-1}) apparent here may originate from an activated state with appreciable Pt–C and Pt–H scission accomplished. Comparable positive activation entropies have emerged for aryl C–H elimination from Rh(η^5-C_5Me_5)(Ar)(H)(PMe_3)[1c] and can be correlated with the formation of two particles from one.[20] By contrast, C–C elimination from diarylplatinum(II) reveals a negative $\Delta S^\ddagger$.[16a]

While primary isotope effects of magnitude 2–4 have been suggested[1a] as more characteristic of reductive elimination than of oxidative addition, the experimental basis for this assertion is still limited to few examples and even

(19) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457. Ozawa, F.; Kurihara, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 399.

(20) See, e.g.: Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1986; Chapter 3. See also: DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.*, **1982**, *104*, 3601 and ref 2c and references therein.

Scheme III



inverse isotope effects can arise from reductive C–H elimination under certain conditions.[1i]

A two-step view of hydrogen transfer (rather than a direct migration from carbon to carbon) is favored in view of precedent. There is a notable example of an isolable hydridoiridium(III) product of oxidative addition of the same C–H bond in a neophyliridium system.[2d] There are now also numerous examples of intermolecular additions of aromatic (and aliphatic) C–H bonds to metal centers, affording isolable or detectable derivatives,[1] and recent related studies on intramolecular aliphatic C–H activation at Pt(II) have adopted an oxidative addition/reductive elimination sequence as most plausible.[2a–c]

As noted, there was no detectable transfer of the (more plentiful) aliphatic γ-hydrogens of the neophyl group. Given a choice of attack on γ- or δ-aliphatic sites, Pt(II) has displayed a preference for 5-membered ring formation, although not to the complete exclusion of the metallacyclobutane.[2b] The product distribution from these neophylplatinum complexes, therefore, may reflect some degree of site preference for aromatic C–H attack.[7] This has been ascribed elsewhere to the ability of sp^2 carbon to form η^2-hydrocarbon–metal complexes as presursors to C–H activation;[1e,f] the dangers in such presuppositions have also been noted.[1m]

B. P-Donors: *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$. (i) Thermolytic Kinetics. In the absence of added Et_3P, cyclizations generally conformed to first-order rates although the plots occasionally showed curvature and were inclined to poor reproducibility. Similar inconsistencies emerged from studies of *cis*-$Pt(CH_2CMe_3)_2(PEt_3)_2$ and were attributed to the presence of traces of dioxygen.[2a] The majority of kinetic experiments were therefore carried out by using toluene-d_8 solutions of *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$ containing added Et_3P, which showed excellent reproducibility.

These results are summarized in Table VII which also includes measurements on the deuterated analogue *cis*-$Pt(CH_2CMe_2C_6D_5)_2(PEt_3)_2$. Several conclusions may be drawn from these data. Experiments 1, 3, 4, and 8–11 (and Figure 4) show the temperature dependence of the observed first-order rate constant k_{obsd}, in both the presence and the absence of Et_3P. The data display Arrhenius linearity (Figure 5). Although the results in the presence

Table VII. First-Order Metallacyclization Rates for *cis*-$Pt(CH_2CMe_2C_6R_5)_2(PEt_3)_2$ under Various Conditions[a]

expt	R	[Pt], mol L^{-1}	[L], mol/L^{-1}	temp, °C	$10^5\ k_{obsd}$, s^{-1}
1	H	0.04	0	35	18.00[b]
2	D	0.04	0	35	6.40[b,d]
3	H	0.036	0	29.5	4.30[b]
4	H	0.036	0	25	1.80[b,d]
5	H	0.08	0	29.5	4.00[b,d]
6	H	0.04	0.07	65	0.59[b]
7	D	0.04	0.07	65	0.17[b]
8	H	0.037	0.04	60	1.31[c]
9	H	0.037	0.04	62.5	2.47[c]
10	H	0.037	0.04	64.9	3.84[c]
11	H	0.037	0.04	70	10.50[c]
12	H	0.073	0.68	80	3.73[c]
13	H	0.073	0.40	80	6.40[c]
14	H	0.073	0.25	80	8.44[c]
15	H	0.06	0	35	0.67[c,e]
16	H	0.06	0	40	2.98[c,e]

[a] Measured in toluene-d_8 under argon or dinitrogen atmosphere. [b] Obtained by method 1—see Experimental Section. [c] Obtained by Method 2—see Experimental Section. [d] k_{obsd}(initial) calculated from the initial three points on the plot.

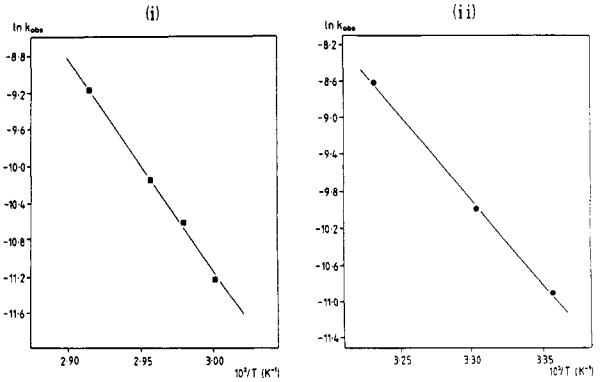


Figure 5. Arrhenius plots for metallacyclizations of *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)_2$: (i) in presence of 0.037 M PEt_3, (ii) in absence of PEt_3.

Scheme IV

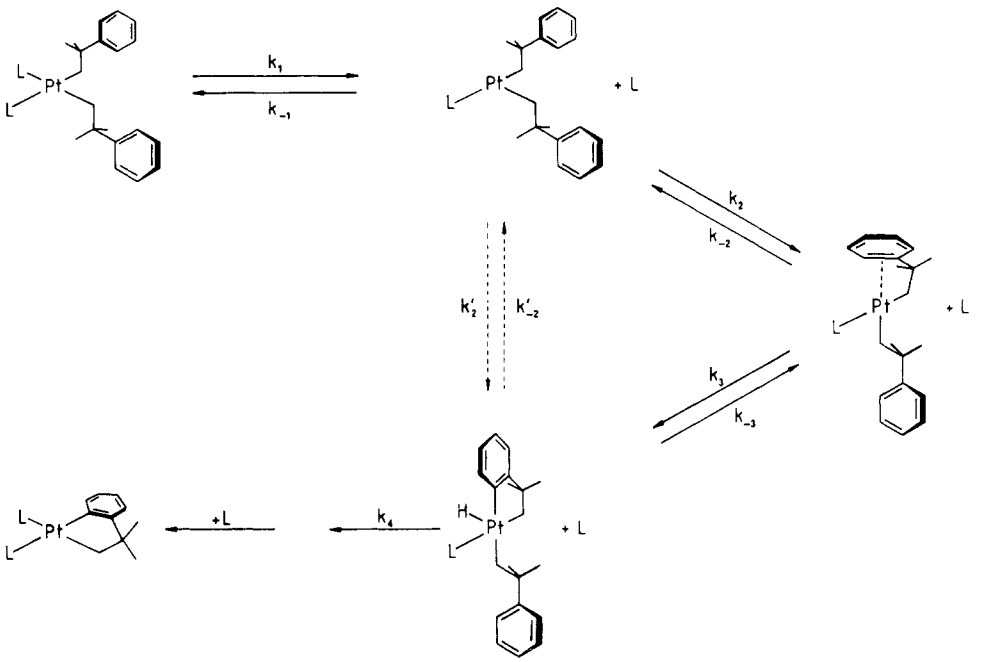


Table VIII. Arrhenius Activation Parameters for Metallacyclization of *cis*-Pt(CH_2CMe_2Ph)$_2$(PEt_3)$_2$

concn of added PEt_3, mol dm^{-3}	E_a, kJ mol^{-1}	ln A	$\Delta H^{\ddagger}$,[a] kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}
0.037	194 ± 10	59	192 ± 10	+239 ± 20
0	176 ± 30	60	174 ± 30	+248 ± 50

[a] At 80 °C.

of Et_3P show better correspondence, the two afford similar activation parameters (Table VIII).

Comparing experiments 1 with 2 and 6 with 7 (Table VII) demonstrates a substantial kinetic isotope effect for the cyclization; in both the absence and the presence of Et_3P, k^H/k^D = 3.40 ± 0.10 (Figure 6). Again, the results in presence of free phosphine are more reproducible, but the two are reassuringly similar.

Experiments 3 and 5 show that the rate constant is unaffected by the initial concentration of *cis*-Pt(CH_2CMe_2Ph)$_2$(PEt_3)$_2$ and confirm the strictly first-order kinetics of the rearrangement. The dependence of k_{obsd} on the concentration of added Et_3P at 80 °C appears from results 12–14. A plot of the reciprocal of the rate constant against the phosphine concentration is linear with a nonzero intercept (Figure 7).

(ii) Mechanistics. The inhibiting effect of added phosphine could arise in either of two ways. Association of PEt_3 could afford a species PtR_2L_3 which is inert compared with PtR_2L_2. Alternatively, ligand dissociation forming PtR_2L—which would be retarded by excess L—may be a prerequisite to C–H activation. Our observations suggest that the latter is more likely. Metallacyclization of PtR_2L_2 at 80 °C in presence of 0.68 M PEt_3 has k^{80}_{obsd} = 3.7 × 10^{-5} s^{-1} while with 0.04 M added phosphine k^{80}_{obsd} = 7.4 × 10^{-4} s^{-1} [from Figure 4(i)]. In the absence of excess phosphine when, presumably, PtR_2L_3 is *not* involved in cyclometalation, we estimate [from Figure 4(ii)] $k^{80}_{obsd} \simeq 1.0$ s^{-1}, some 4–5 orders of magnitude greater than in presence of phosphine. If metallacyclization of PtR_2L_3 was responsible for the slower rates, then at least 95% of dialkylplatinum would need to be in

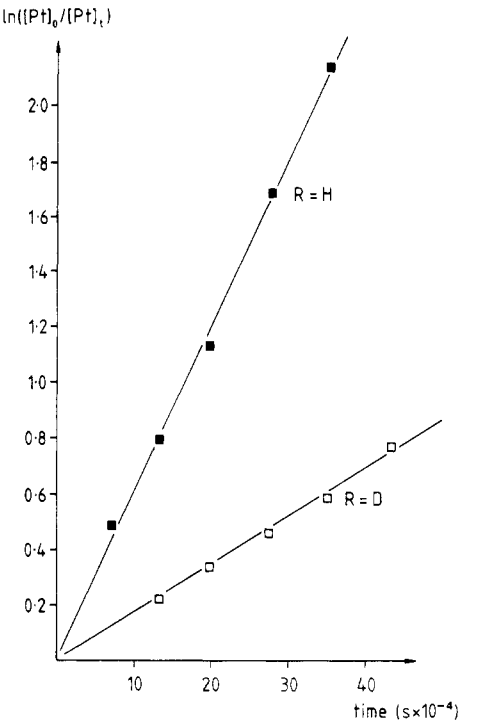


Figure 6. Deuterium isotope effect on metallacyclization rate for *cis*-(Et_3P)$_2$Pt($CH_2CMe_2C_6R_5$)$_2$ at 65 °C with 0.037 M PEt_3 present.

this form at 0.68 M added L to account for the fact that the rate at 0.04 M phosphine is 5% of that at the higher concentration. In the event, no species other than PtR_2L_2, metallacycle, and free PEt_3 (at the expected intensities) were detected during continuous monitoring of reaction by ^{31}P NMR.

A mechanistic scheme consistent with our observations and based on equilibrium dissociation of PEt_3 appears in Scheme IV. Assuming that steady-state concentrations develop for all of the intermediates, the form of the rate law will be that of eq 1; a first-order rate law is predicted with an observed rate constant k_{obsd} (eq 2), in agreement with experiment. Moreover, at constant temperature (80

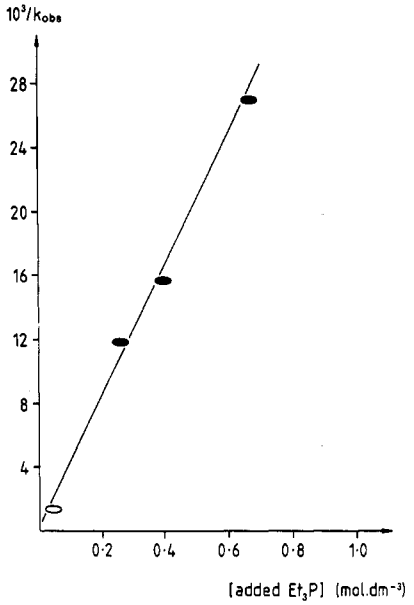


Figure 7. Effect of added Et_3P on metallacyclization rate for *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)_2$ at 80 °C.

°C) k_{obsd} varies inversely with phosphine concentration (Figure 7) in accordance with eq 3 (from eq 2). The

$$-\frac{d[1]}{dt} = \left\{\frac{k_1k_2k_3k_4}{k_{-1}[k_4(k_{-2} + k_3) + k_{-2}k_{-3}][L] + k_2k_3k_4}\right\}[1] \quad (1)$$

$$k_{obsd} = \frac{k_1k_2k_3k_4}{k_{-1}[k_4(k_{-2} + k_3) + k_{-2}k_{-3}][L] + k_2k_3k_4} \quad (2)$$

$$\frac{1}{k_{obsd}} = \left\{\frac{k_{-1}[k_4(k_{-2} + k_3) + k_{-2}k_{-3}]}{k_2k_3k_4}\right\}[L] + \frac{1}{k_1} \quad (3)$$

$$-\frac{d[1]}{dt} = \left\{\frac{k_1k'_2k_4}{k_{-1}(k'_{-2} + k_4)[L] + k'_2k_4}\right\}[1] \quad (4)$$

experimental uncertainty in determining the intercept allows an estimate of k_1 only within broad limits: $10\ s^{-1} > k_1 \geq 10^{-3}\ s^{-1}$. Nevertheless, this excludes phosphine dissociation as the rate-limiting process, at least in presence of added L, since k_1 is more than an order of magnitude greater than any rate observed under these conditions (Table VII). This contention is supported by the considerable deuterium isotope effect ($k^H/k^D = 3.40$) which would not be expected if preliminary ligand loss was rate-determining [see section A(ii)].

The fact that the isotope effects are unaffected by the presence of excess PEt_3 suggests that phosphine dissociation is also not rate limiting in its absence. That there is no major mechanistic change upon addition of excess L is further borne out by the correspondence in activation parameters under the two sets of conditions (Figure 5 and Table VIII).

Cyclization lends itself well to comparison with that of the neopentyl analogue *cis*-$Pt(CH_2CMe_3)_2(PEt_3)_2$, whose cyclization via γ-C–H activation recently has been exhaustively studied by Whitesides and co-workers.[2a] The neophyl complex shows broad parallels to the aliphatic system (including closely comparable isotope effects), and the authors have drawn similar conclusions regarding the kinetic role of phosphine loss.[2a,b]

The neophylplatinum derivative is considerably more labile than its neopentyl analogue. Thus *cis*-$Pt(CH_2CMe_3)_2(PEt_3)_2$ cyclizes in the absence of added PEt_3 with $k_{obsd} = 1.5 \times 10^{-5}\ s^{-1}$ at 118 °C,[2a] while *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$ reacts at comparable rate ($k_{obsd} = 1.8 \times 10^{-5}\ s^{-1}$) at only 25 °C. Activation of aromatic C–H bonds is often more facile than corresponding aliphatic reactions, and, as noted [section A(ii)] this may be due to the availability of (η^2-arene)metal complexation, which gives aromatic sites an activation enthalpy advantage over aliphatic competitors.[1c,d,i] If this is the case here, it is not clear within the limits of experimental error. The inclusion of such an η^2-arene intermediate in Scheme I is, therefore, conjectural. Its omission would not compromise previous arguments based on the theoretical rate law, which would have the form of eq 4. We do have some preliminary spectroscopic evidence for formation of an intramolecular η^2-arene cationic complex when $Pt(CH_2CMe_2Ph)I(dppe)$ is treated in $CDCl_3$ with $AgBF_4$,[21] although this would not guarantee a role in metallacyclization.[1b] Such details of the mechanism are the basis for our current further studies of aromatic C–H activation.

As with N-donors, aromatic cyclometalation is favored exclusively over γ-C–H abstraction from the neophyl ligands as well as δ-C–H abstraction from phosphine ligands or carbon–carbon reductive elimination of the neophyl ligands. The last two reactions compete to a minor extent with metallacyclization of the neopentyl analogue, but we have detected no such competition even when attack on the phenyl ring is rendered less favorable by ring deuteration. We have already excluded *cis*-$Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)(PEt_3)_2$—formed by an alternative C–H addition/elimination cycle—as a participant in these reactions.[7]

Metallacyclization of *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$ displays a substantial overall activation enthalpy [closely comparable to that of *cis*-$Pt(CH_2CMe_3)_2(PEt_3)_2$] which is apparently offset by a favorably large positive entropy of activation. Given the composite nature of k_{obsd}, quantitative comparisons of activation entropies may be ill-advised. $\Delta S^{\ddagger}_{obsd}$ is inherently approximate and contains entropies of formation of precursors as well as the activation entropy leading to the most energetic transition state. It is, perhaps, best explained if reductive elimination (k_4) makes a high contribution to k_{obsd}. As well as the additional molecular freedom arising from phosphine expulsion, there may be extensive dislocation of M–C and M–H (with concomitant C–H formation) upon attainment of the final transition state. Entropy increases of this magnitude have been correlated with the generation of three particles from one.[20] The neophyl group may be sufficiently bulky that the relaxation of steric congestion associated with both k_1 and k_4 is proportionately greater than for the neopentyl system. There also may be some advantage associated with the size and type of metallacycle formed which partially offsets the entropic disadvantages of ring closure. These are other facets currently under investigation. We are also studying complexes which will cast a more reliable light on metal discrimination between aromatic and aliphatic sites than do the dineophyl systems.

Conclusions

(1) Metallacyclization of *cis*-$Pt(CH_2CMe_2Ph)_2L_2$ is facile and occurs exclusively at an aromatic 2-carbon site.

(2) Where L_2 is 2,2′-bipyridyl or 2,2′-bipyrimidyl, the kinetic data are consistent with a close approach to a rate-limiting Pt–N scission.

(21) Griffiths, D. C.; Young, G. B., unpublished work.

(3) Where L_2 has the conformationally rigid 1,10-phenanthroline skeleton, hydrogen transfer—plausibly reductive C–H elimination—contributes substantially to rate control.

(4) Where L is PEt_3, Pt–P dissociation is a prerequisite, but not the rate-limiting, process. Reductive C–H elimination, again, plausibly makes the most energetic contribution to rate control.

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Synthesis, Oxidative Addition, and Structural Studies of the Metal–Metal Bonded Bimetallic Complexes $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PC_5H_4N)M(CO)Cl]$ (M = Rh, Ir)

Giuseppe Bruno, Sandra Lo Schiavo, Enrico Rotondo, Carmela Grazia Arena, and Felice Faraone*

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Salita Sperone 31, Villaggio S. Agata, 98010 Messina, Italy

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Reaction of $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ or $[Rh_2(\eta^5\text{-}C_5H_5)_2(CO)_3]$ with 2-(diphenylphosphino)pyridine (Ph_2PPy) gave $[Rh(\eta^5\text{-}C_5H_5)(CO)(Ph_2PPy)]$ (1) in which Ph_2PPy acts as monodentate P-bonded ligand. Compound 1 reacted with $[Rh(CO)_2Cl]_2$ and $[Ir(CO)_2(p\text{-toluidine})Cl]$ to give the Ph_2PPy-bridged complexes $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Rh(CO)Cl]$ (2) and $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)Ir(CO)Cl]$ (3), respectively, in which a metal–metal bond is present. The structure of the unsymmetrical bimetallic compound 2 has been determined by X-ray crystallography. The crystal is monoclinic with space group $P2_1/c$, and the cell constants are a = 15.928 (2) Å, b = 11.322 (2) Å, c = 26.646 (4) Å, β = 104.2 (2)°, and Z = 8. The structure has been refined to a final R value of 0.042. The unit cell contains two crystallographically independent molecules that have very similar structures. The structure is characterized by the short Rh(1)–Rh(2) bond distance of 2.648 (1) Å, by the different coordination geometry of the two rhodium atoms, and by the presence of an asymmetric CO bridging ligand. The ligands about Rh(1) are disposed in an approximately tetrahedral environment, and the Rh(2) coordination geometry is that of a distorted square pyramid with the vertex shifted toward the Rh(1)–Rh(2) vector. The Ph_2PPy is twisted about the Rh(1)–Rh(2) bond to avoid unfavorable contacts. 2 reacts with SO_2 to produce $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}Ph_2PPy)(\mu\text{-}SO_2)Rh(CO)Cl]$ (4). The addition of Cl_2 or Br_2 to 2 gave the rhodium(III) complexes $[(\eta^5\text{-}C_5H_5)X_2Rh(\mu\text{-}Ph_2PPy)Rh(CO)X_3]$ (5, X = Cl; 6, X = Br); the same reaction with I_2 occurred with formation of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}I)(\mu\text{-}Ph_2PPy)Rh(CO)I_2]$ (7) and $[(\eta^5\text{-}C_5H_5)I_2Rh(\mu\text{-}Ph_2PPy)Rh(CO)I_3]$ (8). Spectroscopic data indicated that 7 is a Rh^{II}–Rh^{II} species. It crystallizes in the monoclinic system, space group $P2_1/c$, with a = 7.847 (1) Å, b = 16.995 (2) Å, c = 19.446 (3) Å, β = 96.4 (1)°, and Z = 4. The structure has been refined to a final R value of 0.026. The rhodium atoms are bridged by the Ph_2PPy and I(1) ligands. The Rh(1)–Rh(2) bond distance of 2.686 (1) Å is very close to that of the precursor 2. The bond angles at Rh(1) atom reflect a large deviation from the tetrahedral coordination geometry. The Rh(2) atom displays a distorted octahedral geometry; significant deviations are with the terminal I(3) and bridging I(1) atoms. The geometry of the bridging iodo ligand appears normal. The structural features of the bridging Ph_2PPy and of the cyclopentadienyl ring are essentially the same as in the precursor 2. Compounds 7 and 8 have been the only products obtained from the reaction of 2 with CH_2I_2.

Introduction

In recent years there has been considerable interest in the synthesis, structural characterization, and reactivity of binuclear complexes in which two metals are held in close proximity by bridging ligands.[1,2] Interest in such bimetallic systems rises from their potential to activate small molecules through cooperative interactions with the metal centers and to act as homogeneous catalysts.[1-3]

Although there are exceptions,[4] bridging ligands such as bis(diphenylphosphino)methane[1,2] (dppm), bis(diphenylarsino)methane[5] (dpam), 2-(diphenylphosphino)-

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