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Mechanisms of Thermal Rearrangement of Diarylbis(pyridine)platinum(II) Complexes: Reductive Carbon–Carbon Elimination versus Hydrogen Transfer

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Thermolytic behavior in solution of a series of complexes *cis*-$(py)_2Pt(4\text{-}C_6H_4R)_2$ (R = H, CMe_3, CF_3; py = pyridine) has been examined. When R = CMe_3, thermolytic rearrangement generates biaryl via unimolecular reductive elimination without prerequisite ligand dissociation. Arene elimination is an important, temperature-dependent, competitive reaction, which is suppressed by deuteriation of either aryl or pyridine ligands. Comparison with photolytic rearrangement of $Hg(4\text{-}C_6H_4CMe_3)_2$ indicates that Pt–C homolysis is not a significant contributor. A mechanism is indicated in which successive, reversible H transfers from pyridine and aryl ligands may occur, the latter resulting in a rare example of aryl group isomerization prior to elimination. For R = H, similar mechanistic competition is observed, but when R = CF_3, concerted mononuclear reductive elimination is the only significant pathway. Its activation parameters suggest conformational restriction in the transition state. Metallic Hg alters the rearrangement pattern but not by scavenging heterogeneous byproducts.

Introduction

The controlled reactions of organotransition metals are a fertile source of mechanistic insight into catalytic and stoichiometric, metal-mediated transformations of hydrocarbons. These reactions frequently involve steps in which carbon–hydrogen or carbon–carbon bonds are broken or formed. Predictable control over which of these schemes will operate is still not easy. For example, in the nickel triad alone, carbon–carbon reductive elimination from diorganyl derivatives of Ni(II)[1] and Pd(II)[2] is commonly encountered, although (normally β-) hydrogen transfer is also widespread.[1b,2d,e,3] For Pt(II), in contrast, H-transfer routes are almost universal,[4] and only two types of isolatable diorganylplatinum(II) complexes—diarylmetals[5] and metallacyclobutanes[6] —undergo thermolytic reductive C–C elimination. In further contrast, most alkyl derivatives of related d^8 organogold(III) favor C–C coupling[7] as do many derivatives of tetravalent platinum.[4h,8] Several theoretical discussions have addressed the variations.[1e,9]

Most previous investigations of Pt(II) have featured organophosphines as ancillary ligands. These have emerged as occasional participants in reactions, acting as sources of transferable hydrogen[1i–l,10] and organyl groups.[11] More recently, we have begun investigations on a variety of divalent organoplatinum complexes with nitrogen-donor ligands such as the bidentate 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen), and some of their substituted homologues[12] as well as 2,2′-bipyrimidyl[13] (bipym). These ligands are not always innocent nonparticipants, notably in the case of bpy.[12c] Here we report the first of our studies of diorganoplatinum(II) complexes with the monodentate N-donor, pyridine, as ancillary ligand. The diarylplatinum(II) complexes featured here display some novel and unexpected thermolytic behavior.

Experimental Section

General Data. NMR measurements were performed on Bruker WM 250 (^{1}H 250.13 MHz; ^{13}C 62.9 MHz; ^{31}P 101.3 MHz; FT mode), JEOL FX 90Q (^{1}H 89.55 MHz; ^{13}C 22.13 MHz; ^{19}F 84.27 MHz; ^{31}P 36.21 MHz; ^{195}Pt 19.21 MHz; FT mode) and

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Perkin-Elmer R32 (^{1}H 90 MHz; CW Mode) instruments. IR data were obtained on a Perkin-Elmer 683 spectrophotometer and electronic spectra were measured on a Perkin-Elmer 55 instrument.

HPLC analyses were carried out by using an a Spectra-Physics SP 8100 system. Mass spectra were recorded on a VG 7070 E instrument. Gas chromatography/mass spectrometry (GC/MS) were obtained on VG 7070 E or Finnigan MAT 1020B GC/MS systems. For gas chromatography, a Perkin-Elmer Sigma 1B gas chromatograph was employed.

Elemental analyses were by Imperial College Microanalytical laboratories. Melting points were determined in open capillaries and are uncorrected.

All chemical manipulations were carried out in dry degassed solvents under an atmosphere of argon. Diethyl ether, petroleum ether (40–60 fraction), and THF were distilled under nitrogen from sodium/benzophenone. Benzene, toluene, *p*-xylene, mesitylene, and pyridine were distilled from sodium under argon.

UV irradiations were performed by using the output of a 400-W medium-pressure mercury arc lamp in a water-cooled quartz jacket (Model RB 400, Applied Photophysics Ltd.).

When referred to as "standard recovery", the following manipulations are implied: the organic layer is extracted into ether, dried over $MgSO_4$, decolorized with activated charcoal, and evaporated to dryness.

Preparation of *cis*-Bis(4-*tert*-butylphenyl)bis(pyridine)platinum(II) and Analogues (Modified from Ref 14). An excess of Mg(4-$C_6H_4CMe_3$)Br (6 cm^3 of 0.69 M solution) was added slowly to a suspension of (cod)$PtCl_2$ (560 mg, 1.5 mmol) in ether (15 cm^3) at −78 °C. The reaction temperature was maintained at −20 °C for 12 h and allowed to reach room temperature before hydrolysis. The reaction solution was quenched with cold aqueous ammonium chloride and worked up by standard recovery (vide supra). The colorless crystals of (cod)Pt(4-$C_6H_4CMe_3$)$_2$ are obtained in good yield (71–86%), and further purification is not required.

(cod)Pt(4-$C_6H_4CMe_3$)$_2$ (680 mg, 1.2 mmol) was dissolved in pyridine (10 cm^3) and heated for 4–5 h at 50 °C. The solvent was removed under vacuum at room temperature. Recrystallization from methanol/dichloromethane gave colorless crystals (ovarll yield 66–82%).

py$_2$Pt(4-C_6H_4R)$_2$ (R = H, CF_3) and compounds for deuterium-labeling studies were prepared similarly. Analytical data are collected in Table I.

Preparation of *p*-Bromo-*tert*-butylbenzene-*d*$_4$.[15] To a mixture of *tert*-butylbenzene-*d*$_5$[16] (2.24 g, 16 mmol), bromine (2.56 g, 0.82 cm^3, 16 mmol), concentrated sulfuric acid (14 cm^3), and distilled water (2 cm^3) was added silver sulfate (4.98 g, 16 mmol). The solution was stirred in the dark for 16 h and poured carefully into dilute ice-cooled, aqueous sodium metabisulfite. 4-$BrC_6D_4CMe_3$ was recovered by standard recovery (vide supra) (yield 82%). The resulting yellow oil was distilled under vacuum (56–58 °C at 6 Torr) to give a colorless liquid.

Preparation of Organic Reference Standards (Coupling Products). Method A.[17] Applied for the following compounds: 4,4′-bis-*tert*-butylbiphenyl, 3,4′-bis-*tert*-butylbiphenyl, 3,3′-bis-*tert*-butylbiphenyl, 4-*tert*-butyl-2′-methylbiphenyl, and 4-*tert*-butylbiphenyl. On a 1.2-mM scale a solution of arylmagnesium halide or an equimolar mixture of two different Grignard reagents was cooled to −78 °C. An equimolar amount of anhydrous $CoCl_2$ suspended in diethyl ether was added slowly with vigorous stirring. The solution was stirred for 1 h, allowed to reach 0 °C, and hydrolyzed by filtration into an ice–ammonium chloride mixture. Standard recovery (vide supra) afforded the products.

Method B.[17] Applied for the following compounds: 4-*tert*-butyl-4′-methylbiphenyl, 4-*tert*-butyl-3′-methylbiphenyl, and 4-benzyl-*tert*-butylbenzene. On a 1.2 mM scale Mg(4-$C_6H_4CMe_3$)Br in ether was added slowly to an equimolar amount of haloarene or α-halotoluene in ether in the presence of a catalytic amount (2 mg) of (dppb)$PdCl_2$. The solution was reflued for 5–7 days and hydrolyzed with an ice–ammonium chloride mixture. Standard recovery (vide supra) gave the products.

Preparation of *m*-Bromo-*tert*-butylbenzene.[19] *p*-Amino-*m*-bromo-*tert*-butylbenzene [obtained from Maybridge Chemical Co. and used as supplied] (1 g, 4.3 mmol) was dissolved in a mixture of water, ethanol, and sulfuric acid (20 cm^3/3 cm^3/4 cm^3) and cooled to −5 °C in a salt–ice bath. To the solution was added dropwise $NaNO_2$ (0.6 g, 8.6 mmol), maintaining a temperature below 0 °C. Then over a period of 10 min H_3PO_4 (13 cm^3) was added. The mixture was left to warm slowly to room temperature and stirred for another 14 h. An orange oil separated from the pale solution. Standard recovery (vide supra) gave the product as a pale orange liquid (yield 81%).

The Grignard reagent was obtained in low, but usable yield in diethyl ether. Refluxing in THF might improve reactivity.

Preparation of Bis(4-*tert*-butylphenyl)mercury(II) (Modified from Ref 20). A solution of $HgCl_2$ (570 mg, 2.1 mmol) in THF (20 cm^3) was slowly added to an excess of Mg(4-$C_6H_4CMe_3$)Br in ether. The solution was refluxed for 24 h. The reaction mixture was hydrolyzed with dilute HCl in ice. Standard recovery (vide supra) afforded white crystals of Hg(4-$C_6H_4CMe_3$)$_2$ (yield 78%). ^{1}H NMR data (ppm relative to TMS; acetone-*d*$_6$): 1.34 (s, Me), 7.47 (d, 4 H, H_2 aromatic), 7.56 (d, 4 H, H_3 aromatic, $^3J(H_2{-}H_3)$ = 8.7 Hz).

Thermolytic Reactions. A toluene solution (0.4 cm^3) of known concentration (1.2 × 10^{-3} mol dm^{-3}) of the compound in cleaned and dried tubes (internal diameter 5 mm, external diameter 8 mm, length approximately 150 mm) was freeze–thaw–degassed in three cycles. The tubes were sealed under vacuum. These reaction vessels were kept at a constant and specified temperature by immersion into a thermoregulated (±0.2 °C) silicone oil bath (Haake W13/D8) for a timed period.

To reaction mixtures studied for the effect of mercury on the reaction mixture a drop of mercury (approximately 35 mg, 0.2 mmol) was added. Product analyses were by GC and HPLC.

Deuterium-labeling studies were conducted in the same way. Product distribution was analyzed by GC and deuterium incorporation was measured by GC/MS.

GC Analysis. For *cis*-(py)$_2$Pt(4-$C_6H_4CMe_3$)$_2$. Temperature was held at 130 °C for 5 min, increased at 35 °C/min to 190 °C, maintained for 10 min, and finally increased once more at the same rate to 220 °C. Length of run: 80 min. Flow rate: 1 mL/min (4-m column, 20% SE 30 on Chromosorb D, mesh 80/100).

Quantities are expressed in mole percent of platinum–carbon bonds (see Results and Discussion). Mass balances were 100% (±5%) by reference to the internal standard (4,4′-bitolyl). Molar response factors were 1.0 except for *tert*-butylbenzene (1.03).

For *cis*-(py)$_2$Pt(4-$C_6H_4CF_3$)$_2$ and *cis*-(py)$_2$PtPh$_2$. Temperature was held at 100 °C for 8 min, increased at 40 °C/min to 210 °C, and maintained for 18 min.

HPLC Analysis. Only qualitative analyses were carried out. Reaction products were eluted with a mixture of methanol and water (85/15), and the UV absorption was monitored at 254 nm. Flow rate: 1 cm^3/min. Oven temperature: 45 °C (25-cm column of ODS bonded on 5 μm silica).

NMR: Kinetics. Thick-walled NMR tubes (Wilmad 503 PS, cleaned and dried prior to use) were filled with 0.4 mL of solution of known concentration, freeze–thaw–degassed for three cycles, and sealed under vacuum.

For *cis*-(py)$_2$Pt(4-$C_6H_4CMe_3$)$_2$ in *p*-xylene-*d*$_{10}$ kinetics were measured via ^{1}H NMR on the Bruker WM 250. The *tert*-butyl group provided a convenient peak for kinetic analysis of rearrangements. Kinetics of *cis*-(py)$_2$Pt(4-$C_6H_4CF_3$)$_2$ (in toluene-*d*$_8$) were monitored via ^{19}F NMR on the JEOL FX 90Q.

Photolysis of Hg(4-$C_6H_4CMe_3$)$_2$. A 1.0 mM solution of Hg(4-$C_6H_4CMe_3$)$_2$ in toluene was irradiated under anaerobic con-

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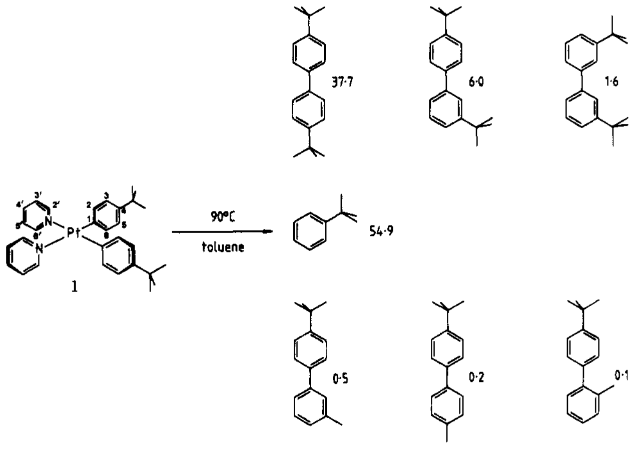
Scheme I



Scheme II

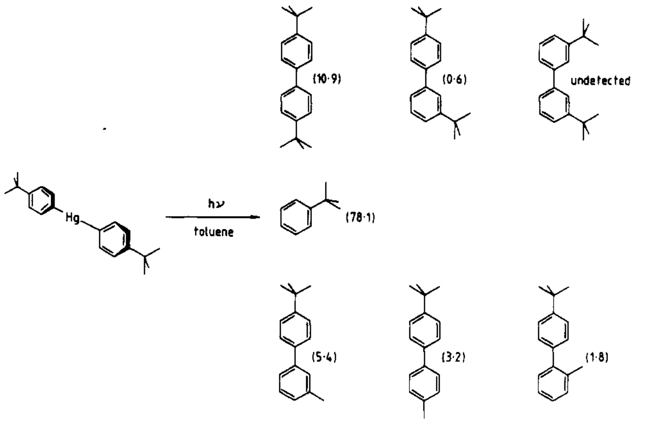


Table I. Analytical Data for *cis*-$(py)_2Pt(4\text{-}C_6H_4R)_2$

		elemental anal.					
		C		H		N	
R	mp (°C)	calcd	found	calcd	found	calcd	found
H	157 dec	52.05	51.84	3.97	3.84	5.52	5.45
CMe_3	175 dec	58.15	58.19	5.81	5.93	4.50	4.50
CF_3	207 dec	44.73	44.86	2.80	2.74	4.35	4.19

ditions for 4 h at 0 °C by using a medium-pressure Hg lamp. The reaction mixture was analysed by GC and HPLC.

Results and Discussion

Synthesis and Spectroscopic Characteristics. Some modifications (see Experimental Section) to reported procedures[14] gave *cis*-$(py)_2Pt(4\text{-}C_6H_4R)_2$ in improved yields (R = H, CMe_3, CF_3). An alternative route[22] gave poorer returns. These complexes were characterized by ^1H (Tables II-IV), ^{13}C (Table V), and, where possible, ^{19}F (Tables II-IV) and ^{195}Pt NMR as well as IR (Table VI) and elemental analysis (Table I). Our ^1H NMR observations accord closely with these on related compounds[23] and *cis*-$(py)_2PtPh_2$ reported previously.[22,24] ^{195}Pt chemical shifts for *cis*-$(py)_2Pt(4\text{-}C_6H_4R)_2$ (−3849, R = H; −3948, R = CMe_3; ppm relative to external $PtCl_6^{2-}$) indicate the presence of one detectable isomer in solution. Comparative data are sparse,[26] but related *cis*-diarylplatinum(II) complexes show similar shifts.[27] The cis configuration is also supported by the IR absorption patterns in the region 500–600 cm^{-1}, associated with Pt–C and Pt–N stretching modes.[28,29]

Thermolytic Behavior of *cis*-$(py)_2Pt(4\text{-}C_6H_4CMe_3)_2$ (1). Product Analysis and Mechanistic Implications. Complex 1 was most suitable for detailed study because of its greater solubility (maximum ca. 4 × 10^{-3} mol·dm^{-3} at ambient temperature) and its distinctive NMR characteristics for the *tert*-butyl group. The product yields in this and subsequent schemes and tables appear in mole percent (mol %), which is defined as

$$\text{mol \%} = \frac{\text{mol of product}}{(\text{mol of Pt–C bonds})} \times 100\%$$

This definition avoids values over 100%, since two aryl groups per platinum can be liberated. Small quantities of dihydrogen would have escaped detection.

Thermolysis of 1 in toluene at 90 °C affords a wide variety of organic products (Scheme I). At this temperature, the main product is *tert*-butylbenzene. In addition, there are three isomeric bis-*tert*-butylbiphenyls (ortho substitution is presumably sterically unfavorable. Small amounts of three isomeric solvent-derived products are also detected. Thermolysis is accompanied by a progressive change in solution color from colorless to yellow. Prolonged heating (>10 half-lives) results in an additional product, 4-benzyl-*tert*-butylbenzene. Variation of concentration ((1–3) × 10^{-3} mol·dm^{-3}) or of solvent had no influence on the product distribution, except for the solvent-derived products. In benzene, 4-*tert*-butylbiphenyl was observed. In *o*- or *p*-xylene and mesitylene, solvent adduct concentrations were too low for identification.

Metal–Carbon Homolysis. Complex product distributions often arise from free radical processes. Duroquinone, added to the thermolysis solution, produced no effect on the product distribution. This experiment, however, only excludes a radical-chain process but not necessarily a homolytic platinum–carbon cleavage.

Diorganylmercury(II) compounds HgR_2 (R = alkyl/aryl) undergo Hg–C homolysis on irradiation.[30] To generate a product distribution authentically derived from aryl radicals, a toluene solution of $Hg(4\text{-}C_6H_4CMe_3)_2$—at the same concentration as for thermolyses of 1—was photolyzed at 0 °C. $Hg(4\text{-}C_6H_4CMe_3)_2$ does not undergo thermolytic reaction up to 90 °C.

Although the same hydrocarbons are formed (Scheme II), a comparison of the product distribution of thermolysis of 1 with that of the photolysis of $Hg(4\text{-}C_6H_4CMe_3)_2$ displays several important disparities (Table VII).

There is a significant increase in formation of $PhCMe_3$ and solvent adducts from the photolytic reaction. Conversely, only 11.5 mol % of aryl groups couple to yield biaryls. A clear difference in yield distribution is evident for the isomeric biaryls and the three solvent-derived isomers. The internal ratios of the latter (parentheses, Table VII) are similar, however. Solvent-derived hydrocarbons, though, comprise less than 1 mol % of organoplatinum thermolysis products. A major contribution from a homolytic pathway can, therefore, be excluded, although the operation of a minor radical route quite possibly ac-

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Table II. ^1H NMR and ^{19}F NMR Characteristics of $(cod)Pt(4\text{-}C_6H_4R)_2$

	aryl[a]			cod[a]	
R	H_2	H_3	H_4/H_R	CH	CH_2
H	7.27 ($^3J(H_2\text{–}H_3)$ = 7.9 Hz, $^4J(H_2\text{–}H_4)$ = 1.2 Hz, $^3J(Pt\text{–}H_2)$ = 70 Hz)	7.02 ($^3J(H_2\text{–}H_3)$ = 7.2 Hz)	6.84	5.12 ($J(Pt\text{–}H)$ = 39 Hz)	2.52 ($J(Pt\text{–}H)$ = 16 Hz)
CMe_3	*b*	*b*	1.18	5.11 ($J(Pt\text{–}H)$ = 38 Hz)	2.50 ($J(Pt\text{–}H)$ = 15 Hz)
CF_3	7.36 ($^3J(Pt\text{–}H_2)$ = 74 Hz, $^3J(H_2\text{–}H_3)$ = 8 Hz)	7.20 ($^4J(H\text{–}F)$ = 3 Hz, $^3J(H_3\text{–}H_2)$ = 8 Hz)	91.7[c]	5.06 ($J(Pt\text{–}H)$ = 39 Hz)	2.53 ($J(Pt\text{–}H)$ = 16 Hz)

[a] $\delta(^1H)$ in ppm relative to internal Me_4Si in chloroform-*d*. [b] Obscured. [c] $\delta(^{19}F)$ in ppm relative to $CFCl_3$.

Table III. ^1H NMR and ^{19}F NMR Characteristics of *cis*-$(DMSO)_2Pt(4\text{-}C_6H_4R)_2$

	aryl[a]			DMSO[a]-
R	H_2	H_3	H_4/H_R	CH_3
H	7.68 ($^3J(H_2\text{–}H_3)$ = 7 Hz, $^4J(H_2\text{–}H_4)$ = 1.8 Hz)	7.05–6.8 (m[b])	7.29 ($^3J(H_3\text{–}H_4)$ = 8 Hz)	2.81 ($^3J(Pt\text{–}H)$ = 15 Hz)
CF_3	7.43 ($^3J(H_2\text{–}H_3)$ = 8 Hz)	7.13 ($^3J(H_3\text{–}H_2)$ = 8 Hz)	87.44[c]	2.85 ($^3J(Pt\text{-}H)$ = 16 Hz)

[a] $\delta(^1H)$ in ppm relative to internal Me_4Si in chloroform-*d*. [b] Obscured. [c] $\delta(^{19}F)$ in ppm relative to $CFCl_3$.

Table IV. ^1H NMR and ^{19}F NMR Characteristics of $(py)_2Pt(4\text{-}C_6H_4R)_2$

	pyridine[a]				aryl[a]			
R	$H_{2,6}'$	$H_{3,5}'$	H_4'	J (Hz)	$H_{2,6}$	$H_{3,5}$	(H_4/H_R)	J (Hz)
H[b]	8.47	7.21	7.75	$^3J(Pt\text{–}H_2')$ = 16 $^3J(H_2'\text{–}H_3')$ = 4.8 $^3J(H_3'\text{–}H_4')$ = 7.6 $^4J(H_2\text{–}H_4)$ = 1.7	7.02	6.80	6.88[d]	$^3J(Pt\text{–}H_2)$[e] $^3J(H_2\text{–}H_3)$ = 6.7 $^3J(H_3\text{–}H_4)$[e] $^4J(H_2\text{–}H_4)$ = 2.8
CMe_3[c]	8.22	6.17	6.62	$^3J(Pt\text{–}H_2')$ = 20 $^3J(H_2'\text{–}H_3')$ = 6.3 $^3J(H_3'\text{–}H_4')$ = 9.2 $^4J(H_2\text{–}H_4)$ = 1.4	7.42	7.02	1.27	$^3J(Pt\text{–}H_2)$ = 64.7 $^3J(H_2\text{–}H_3)$ = 8.3
CF_3[b]	8.45	7.26	7.78	$^3J(Pt\text{–}H_2')$ = 19 $^3J(H_2'\text{–}H_3')$ = 4.8 $^3J(H_3'\text{–}H_4')$ = 7.0 $^4J(H_2'\text{–}H_4')$ = 1.6	7.18	7.03	91.67[f]	$^3J(H_2\text{–}H_3)$ = 8.0 $^3J(Pt\text{–}H_2)$[e]

[a] $\delta(^1H)$ in ppm realtive to internal Me_4Si. [b] In chloroform-*d*. [c] In 2-xylene-d_{10}. [d] Multiplet. [e] Obscured. [f] $\delta(^{19}F)$ in ppm relative to $CFCl_3$.

Table V. ^{13}C NMR Characteristics of $(py)_2Pt(C_6H_4R)_2$

	pyridine[a]			aryl[a]				
R	$C_{2',6'}$	$C_{3',5'}$	$C_{4'}$	C_1	$C_{2,6}$	$C_{3,5}$	C_4	R
H[a]	151.9	123.7	137.0	153.5	135.7	127.2	128.7	
CMe_3[a]	151.7	122.9	136.4	*b*	138.2	125.0	*b*	CMe_3 41.5 CMe_3 31.6

[a] $\delta(^{13}C)$ in ppm relative to internal Me_4Si recorded in chloroform-*d*. [b] Not detected.

Table VI. Infrared Characteristics of $(py)_2Pt(4\text{-}C_6H_4R)_2$[a]

R	IR absorptns (cm^{-1})
H	3045 m, 3030 m, 2990 v, 2970 v, 1640 vw, 1590 vs, 1565 vs, 1475 m, 1460 s, 1440 vs, 1420 s, 1390 m, 1350 m, 1340 w, 1250 w, 1236 m, 1211 s, 1203 m, 1180 w, 1150 w, 1080 m, 1070 s, 1065 vs, 1046 m, 1025 vs, 1014 s, 950 w, 900 s, 880 w, 768 s, 746 vs, 740 vs, 701 vs, 662 m, 641 m, 506 m, 464 w, 400 vw
CMe_3	3060 m, 3000 w, 2955 s, 2900 m, 2860 m, 1600 s, 1582 m, 1571 w, 1480 s, 1448 s, 1390 sh, 1378 m, 1359 m, 1351 m, 1268 m, 1240 w, 1210 m, 1155 w, 1125 s, 1107 m, 1070 m, 1061 m, 1045 m, 1014 m, 945 w, 920 vw, 820 vs, 761 vw, 728 w, 698 vs, 640 m, 580 m, 570 m, 460 vw
CF_3	2980 m, 2920 m, 1625 w, 1590 w, 1560 w, 1495 w, 1392 w, 1325 m, 1261 m, 1195 s, 1180 m, 1165 w, 1125 w, 1072 w, 1052 w, 930 w, 760 vs, 715 sh, 575 vs, 550 vs, 465 vs, 440 vs

[a] Recorded as 4% dispersions in KBr.

counts for the solvent-derived products as well as, in the event, comparable (insignificant) proportions of the biaryls and arene.

Gas-phase generation of *tert*-butylphenyl radicals gives different product distributions, including more extensive isomerization of the 4-*tert*-butylphenyl radical.[31] In parallel with our observations, neither bibenzyl nor diphenylmethane were observed as products of the photolysis of the related compound $HgPh_2$ in toluene.[30b]

Biaryl Formation. Having excluded radicals as main precursors of biaryl, the most plausible alternative is concerted carbon–carbon reductive elimination from platinum. In order to establish the molecularity of the elimination, equimolar amounts of $(py)_2Pt(C_6H_4CMe_3)_2$ (**1**-d_0) and $(py)_2Pt(C_6D_4CMe_3)_2$ (**1**-d_8) were thermolyzed together in toluene. Of the three possible biaryl products—bis-*tert*-butyldiphenyl-d_0, -d_4, and -d_8—only the d_0 and d_8 species are expected from a purely intramolecular reaction. At the other extreme, for random intermolecular coupling, a statistical distribution of all three in which the cross-coupled d_4 product predominates would be predicted. In fact, the relative extent of biaryl production by the two complexes is markedly different (vide infra), but, most significantly, biaryl formation itself emerges as predominantly intramolecular (98.1%); biaryl-d_4 comprised only 1.9% of the total biaryl detected (detailed product distribution, Table VIII).

Thermolysis of equimolar amounts of **1** and $(py)_2PtPh_2$ (**2**) was inconclusive because the rates of decomposition differ so substantially, due to the effects of the 4 substituents. Additionally, the limited solubility of py_2PtPh_2 permitted only low reaction concentrations, and reliable

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(31) Fields, E. K.; Meyerson, S. *J. Org. Chem.* **1978**, *43*, 4705.

Table VII. Product Distributions (mol %) from Photolyzed $Hg(4\text{-}C_6H_4CMe_3)_2$ and Thermolyzed 1-d_0[a]

		$Me_3CC_6H_4{\cdot}C_6H_4CMe_3$				$MeC_6H_4{\cdot}C_6H_4CMe_3$			
			isomer				isomer		
complex	$PhCMe_3$	total	4,4′	3,4′	3,3′	total	3′,4	4′,4	2′,4
$Hg(4\text{-}C_6H_4CMe_3)_2$	78.1	11.5	10.9 (94.8)[b]	0.6 (5.2)[b]		10.4	5.4 (51.7)[b]	3.2 (30.7)[b]	1.8 (17.6)[b]
$(py)_2Pt(4\text{-}C_6H_4CMe_3)_2$	54.9	45.4	37.7 (83.0)[b]	6.0 (13.2)[b]	1.6 (3.8)[b]	0.8	0.5 (52.4)[b]	0.2 (26.8)[b]	0.1 (20.7)[b]

[a] In toluene; photolysis at 0 °C, thermolysis at 90 °C. [b] In parentheses, isomer as percent of total biaryl. [c] Not detected.

Table VIII. Thermolytic Product Distribution (mol %) from *cis*-$(py)_2PtAr_2$ (1-d_n)[a]

		$PhCMe_3$						$Me_3CC_6R_4{\cdot}C_6R_4CMe_3$										
system	solv $-d_n$	total	d_0	d_1	d_3	d_4	d_5	total	4,4′	3,4′	3,3′	d_0	d_1	d_2	d_4	d_7	d_8	solv-derived products
1-d_0	d_0	54.9	54.9					45.4	37.7	6.0	1.6	45.4						0.8
	d_{10}[b]	53.9	48.0	5.9				45.5	38.3	5.6	1.6	39.5	4.4	1.6				1.1
1-d_{10}	d_0	2.4	1.5	0.9				96.8	96.8			96.8						0.8
	d_8	1.2	0.7	0.5				98.8	98.8			88.9	9.9					0
1-d_8	d_0	3.5			0.4	2.2	0.9	96.1	90.2	5.8	0.1						96.1	0.4
	d_8	3.2			0.5	1.8	0.9	96.7	90.2	5.9	0.6					0.1	96.6	0.1
1-d_0 + 1-d_8	d_8	40.6	29.1	1.9	3.3	5.0	1.3	59.2	52.6	5.9	0.8	12.9	1.4		1.1	12.5	31.3	0.2
1-d_0 + Hg	d_8	19.8	*c*	*c*	*c*	*c*	*c*	79.8	72.8	6.1	0.9	*c*	*c*	*c*	*c*	*c*	*c*	0.4

[a] At 90 °C in toluene, unless otherwise noted. [b] 4-Xylene-d_{10}. [c] Not examined.

measurements, therefore, proved impossible.

***tert*-Butylbenzene Formation.** During the thermolysis of 1, a significant amount of *tert*-butylbenzene is produced also (Table VIII and Scheme I). This requires hydrogen abstraction from either the solvent or the parent complex. Deuterium labeling was employed in an effort to locate the source of transferred hydrogen. Such results can be ambiguous. ^2H transfer in a labeled system is a reasonable indication that ^1H *is* transferred in the unlabeled system. If ^2H is *not* transferred, though, it cannot be inferred reliably that ^1H would not migrate because heavy isotope abstraction from that site may be kinetically suppressed.

To offset uncertainties as much as possible, the molecule was systematically deuteriated. The complexes *cis*-$(C_5H_5N)_2Pt(4\text{-}C_6H_4CMe_3)_2$ (1-d_0), *cis*-$(C_5D_5N)_2Pt(4\text{-}C_6H_4CMe_3)_2$ (1-d_{10}), and *cis*-$(C_5H_5N)_2Pt(4\text{-}C_6D_4CMe_3)_2$ (1-d_8) were prepared and characterized. These complexes were thermolyzed in both toluene-d_0 and toluene-d_8 (or 4-xylene-d_{10}) at 90 °C. Organic product distributions appear in Table VIII.

Solvent deuteriation has little effect on the product distribution from 1 except possibly on the solvent-derived products; their low concentrations make reliable distinction difficult. There is, though, detectable deuterium incorporation in biaryl (6.0 mol %, total) and *tert*-butylbenzene (5.9 mol %, d_1) evolved by 1-d_0.

On the other hand, a striking constrast in behavior between undeuteriated and deuteriated organoplatinum complexes is evident. Formation of *tert*-butylbenzene from 1-d_{10} *and* 1-d_8 is suppressed in favor of biaryl elimination. In thermolysis 1-d_{10}, ^2H transfer from pyridine-d_5 ligands is the minor route to the small amount (1–2 mol %) of *tert*-butylbenzene produced.

Reaction of 1-d_8 where ^1H transfer from pyridine is possible, also yields small quantities (3–3.5 mol %) of *tert*-butylbenzene. The bulk of this, however, is arene-d_4, and the close correspondence of the yields in deuteriated and undeuteriated solvent suggests that in this instance the major source of transferred ^1H *is* coordinated pyridine. Significantly, the product distribution from co-thermolysis of mixed 1-d_0 and 1-d_8 is close to that expected from equimolar amounts of the two, reacting independently.

Kinetic Measurements. The thermal rearrangements of 1 were observed by monitoring its disappearance and the appearance of *tert*-butylbenzene and bis-*tert*-butylbiphenyl. Thermolysis was consistently first-order for at least 1 half-life. Rate constants are presented in Figure 1.

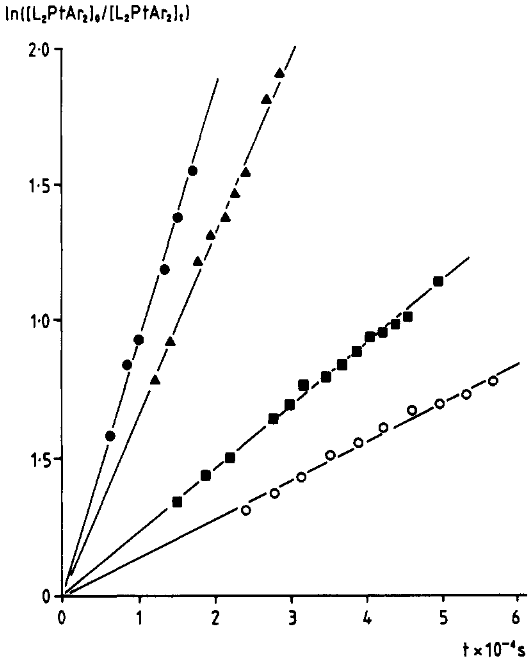

Figure 1. First-order rearrangement of 1-d_0 at the following: 80 °C, $k = 8.79 \times 10^{-5}\ s^{-1}$; 75 °C, $k = 6.04 \times 10^{-5}\ s^{-1}$; 70 °C, $k = 2.23 \times 10^{-5}\ s^{-1}$; 65 °C, $k = 1.33 \times 10^{-5}\ s^{-1}$.

These parameters conform to the Arrhenius relationship from which activation parameters $E_a = +131 \pm 16$ kJ mol^{-1} and $A = 8.98 \times 10^{18}$ were evaluated.[5a] The overall activation entropy was found to be $\Delta S^{\ddagger} = +110 \pm 15$ J K^{-1} mol^{-1}. The apparent activation enthalpy $\Delta H^{\ddagger}$ and free energy of activation $\Delta G^{\ddagger}$ were estimated as 128 and 89 kJ mol^{-1}, respectively.

The presence of free pyridine had no influence on the rate constant or product distribution. Pyridine dissociation (or association), therefore, is not a mechanistic requisite up to and including the rate-controlling transition state(s). This also suggests that isomerization *cis*-1 $\rightleftharpoons$ *trans*-1 is not a control on preferred pathway during thermolysis, since addition of free ligand would, in such an event, be expected to affect isomerization rates[32] and hence the rearrangement

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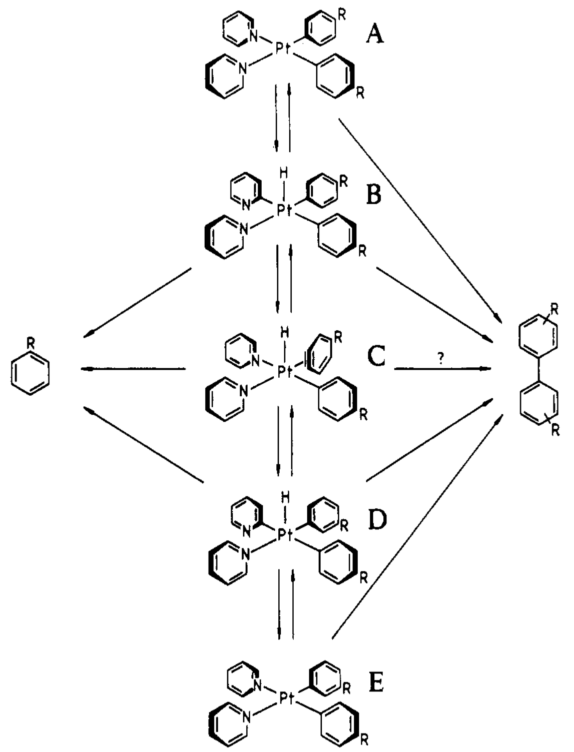
[32] Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, *9*, 185.

Scheme III



rates and/or product distribution.

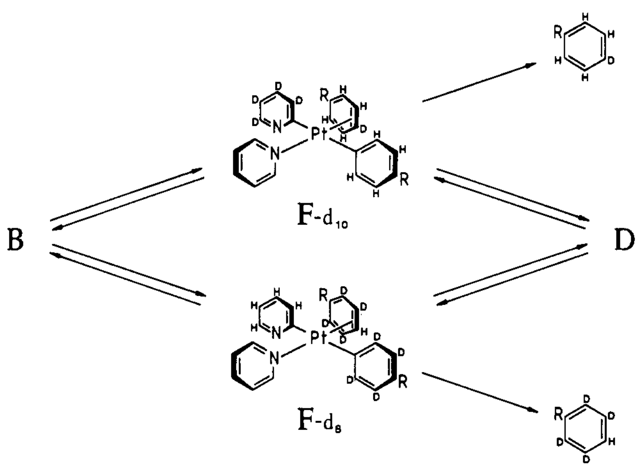
Mechanistic Implications. Leaving aside minor reactions, biaryl and arene generation from 1 clearly represents a finely balanced competition which is severely perturbed by deuteriation. Specifically, 1 must have available a selection of thermolytic intermediates, access to or escape from which may be kinetically inhibited by deuterium substitution. Since all deuterium in these studies is initially carbon-bound, it follows that rearrangement of 1 is controlled by processes in which hydrogen is transferred from (or to) carbon sites on *both* the pyridine and the aryl ligands. A mechanistic regime consistent with our observations is outlined in Scheme III. (Tetragonal-pyramidal geometry is favored for both pentacoordinate d^8 and d^6 configurations on LSFE grounds,[33] especially with π-acid ligands, and the trigonal-bipyramidal configuration for d^6 would be Jahn–Teller unstable.) All isomeric permutations are not shown.

As an initial step, $(py)_2Pt(C_6H_4R)_2$ (A; R = CMe_3, 1-d_0) isomerizes via H transfer to a formally Pt(IV) species, B. Whether this corresponds to a "pyridyne" configuration, B_1 (Figure 2), or the 2-pyridyl structure B_2 is immaterial (zwitterionic B_3 is also possible). Deuteriation on pyridine introduces primary isotope effects that should inhibit this step and any subsequent reductive elimination of arene from B. Consequently, C–C reductive elimination from A or B, if formed, will be prefered, in accord with the product distribution from 1-d_{10} (Table VIII), which eliminates least arene, and no biaryl isomerization is observed.

Besides reversion, B has three available transformations. It could isomerize by aryl H transfer generating Pt(II)-benzyne species C, or it could reductively eliminate biaryl or arene.

For aryl-deuteriated derivative 1-d_8, isomerization A to B will hardly be affected. Rearrangement of B to C, though, will be subject to a primary isotope effect and will be a less attractive option. Accordingly, less biaryl isomerism is observed from 1-d_8. Comparing the proportions of 4- and 3-substituted rings in the biaryl from each of 1-d_0 and 1-d_8 suggests an isomerization ratio, $k^D/k^H \simeq 3$. This presumably reflects mainly the primary isotopic restriction on transformation of B to D.

Scheme IV



Benzyne complex C provides the link between these isomers. Biaryl elimination from C is perhaps less probable as it is a two-step process (benzyne "insertion" into Pt–C prior to reductive C–H elimination). Although C has only one eliminable aryl ligand, the isotopic distribution from 1-d_{10} indicates that some H may be transferred from an aryl group to the one eliminated first, presumably via C-d_{10}. The extent of H/D scrambling between pyridine and aryl ligands prior to hydrocarbon elimination has not been determined. Direct isomerization A to C is also possible. This clearly is more energetic than biaryl elimination from A, however, to account for the absence of isomeic biaryls (and the especially low incidence of arene) from 1-d_{10}.

An η^2-arene complex, F (Scheme IV), might be an intermediate in arene elimination.[34] More crucially, such a species could act as an alternative to C as an isomerization link between B and D, if C–H readdition is facile. Isotope inhibition, however, would lead to isomer distributions that are the reverse of those observed. In particular, F-d_{10} should exhibit preference for remetalation at C_3; 1-d_{10}, though, shows no biaryl isomerism. Conversely F-d_8 would insert preferentially at C_4; 1-d_8, however, does eliminate some isomeric biaryls, which contain little of the d_7 isotopomer expected if F-d_8 mediated the aryl isomerization. Moreover, F cannot explain (the predominant) elimination of arene-d_0 from 1-d_{10}.

The unexplained aspect, however, is the evident reluctance of B-d_8 to release arene; this must also stem from an isotope effect on H-migration. Deuterium isotope effects on reductive elimination from platinum have been observed previously. Methane evolution from *cis*-$(Ph_3P)_2Pt(CH_3)H$ exhibited an appreciable primary isotope effect, $k^H/k^D = 3.3 \pm 0.3$.[35] As noted, such an effect may be an impediment to arene elimination from B-d_{10}. For reductive elimination of ethane from $L_2Pt(I)(CR_3)_3$ (L = PMe_2Ph, R = H or D) a secondary deuterium isotope effect on the rate, $k^H/k^D = 1.10 \pm 0.05$, was reported.[36] In the

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(33) Calculated from: Zuckerman, J. J. *J. Chem. Educ.* **1965**, *42*, 315. Krishnamurthy, R.; Schapp, W. B. *Ibid.* **1969**, *46*, 799 (assuming idealized regular geometries).

(34) (a) Jones, W. D.; Feher, F. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) *Ibid.* **1986**, *108*, 4814.

(35) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

(36) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Organomet. Chem.* **1973**, *49*, C61.

case of 1-d_8, one explanation is that B-d_8 experiences such a large isotope effect on *both* biaryl and arene elimination that it prefers to revert to A (which may then release biaryl). The other possibility is that there is a larger isotope effect on arene liberation from B than on biaryl elimination.

In an effort to evaluate such an effect, an equimolar mixture of 1-d_0 and 1-d_8 in toluene was allowed to react with *1 equiv* of HCl, and the isotope characteristics of the evolved *tert*-butylbenzene were measured. Studies of protolytic scission of Pt–C bonds have established that the reaction course depends on the nature of the cleaved group and the trans effect of the ligand opposite.[37] With ligands of weak trans effect (e.g., Cl) the favored path is oxidative addition of HX, followed by C–H elimination, whereas with stronger trans effects (e.g., alkyl, aryl, PR_3) direct H transfer via a three-center transition state predominates. For the oxidative addition route, elimination from the hexacoordinate platinum(IV) intermediate is proposedly rate-controlling.[37c] In the case of 1, prior oxidative addition to Pt may be anticipated due to the relatively weak trans effect of the pyridine ligand.[38]

Treatment of equimolar 1-d_0 and 1-d_8 afforded *tert*-butylbenzene with d_0/d_4 = 19:1. The Pt(IV) intermediate envisaged does not exactly model the features of B (no biaryl was detected), and the strong preference doubtless derives also from isotope effects on contributory steps in addition to final reductive elimination. Nevertheless, this observation suggests that, for B-d_8, reductive elimination of *tert*-butylbenzene-d_4 may be subject to a substantial, unfavorable isotope effect.

Both 1-d_{10} and 1-d_8 suppress elimination of isomeric biaryls by, we propose, kinetically restricting access to B and C, respectively. Evidence that 1 can, and probably does, eliminate biaryl from A and B (and D and E in the case of 1-d_0) emerges from comparison of the isotope effects on biaryl elimination from 1-d_8 and 1-d_{10}. At 65 °C, 1-d_8 eliminates (mainly) biaryl more slowly ($k_{65} = 7.49 \times 10^{-6}$ s^{-1}) than the rearrangement of 1-d_0 ($k_{65} = 1.33 \times 10^{-5}$ s^{-1}). Biaryl liberation from 1-d_{10}, in contrast, is immeasurably slow at this temperature. If A was the sole source of biaryl, then no more than a secondary kinetic disinction between 1-d_8 and 1-d_{10} would be expected. It must be concluded therefore that 1-d_8 (and presumably 1-d_0) can also eliminate Ar–Ar from the hydridodiarylplatinum species.

We have established that linkage isomerization of aryl ligands does occur prior to biaryl elimination in accordance with Scheme III. Bromine reacts with 1-d_0 in toluene to yield 4-bromo-*tert*-butylbenzene quantitatively and with >98% isomeric purity. A solution of 1-d_0, thermolyzed for 1 half-life, was treated analogously with bromine. Bromo-*tert*-butylbenzene was produced in isomeric ratio 4:3:2 = 81:19:0. This demonstrates an extent of isomerization in the residual *cis*-$(py)_2PtAr_2$ comparable with the ratio of 4-substituted to 3-substituted aryl components in the biaryl eliminated from 1-d_0 (89:11) and establishes the integrity of intermediate E. This appears to be the first reported instance of reversible aromatic β-hydrogen transfer in an arylmetal and is in marked contrast to the behavior of diarylplatinum(II) with monodentate phosphine ligands[5] and of *cis*-$(py)_2Pt(4\text{-}C_6H_4CF_3)_2$ (vide infra), both of which rearrange via predominant, regioretentive reduction elimination of biaryl.

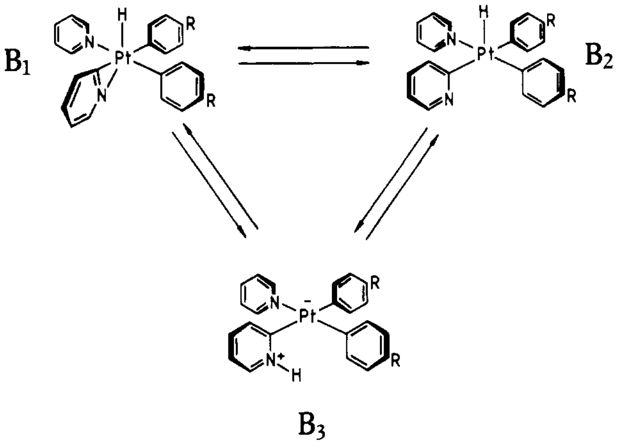

Figure 2. Isomeric options for B.

The product distributions displayed in Table VIII apply at 90 °C, but variation of temperature has a profound effect on the relative extents of biaryl and arene formation from 1-d_0. As temperature increases, biaryl production becomes predominant (Figure 3), ca. 77 mol % at 150 °C. This indicates that biaryl formation is entropically favored, either through control on relative stability of key precursors (more positive ΔS) or on the processes leading to biaryl (more positive $\Delta S^{\ddagger}$).

Although B, C, and D cannot be observed during these rearrangements, complexes with these features do have precedent among organotransition metals. For instance, 2-metalation of pyridine has been observed in several polymetallic[39] and monometallic[40–44] systems. Among the latter, assignments of η^2-pyridyne configurations (cf. B_1, Figure 2) have derived from relatively electron-poor metal complexes, notably those of Ti(III),[40] Sc(III),[41a] Y(III),[41b] Lu(III),[42] and U(V).[43]

There are, though, several structurally well-characterized mononuclear 2-pyridyl complexes of Pd(II)[44] and Pt(II)[44b] with no discernible M–N interaction (cf. B_2), although these were synthesized not via pyridine metalations, but from oxidative addition of 2-halopyridine. Our attempts to isolate 2-pyridylplatinum complexes by reaction of 2-pyridyllithium with L_2PtCl_2 (L_2 = cod, dppe or L = py, Ph_3P) have been fruitless.[45] Corresponding N-protonated (and alkylated) derivatives (cf. B_3) have also been characterized.[44] This isomer maintains the formal oxidation state Pt(II), and its availability as a reservoir site for transferred H could, in principle, affect the relative likelihood of arene or biaryl elimination from B or D.

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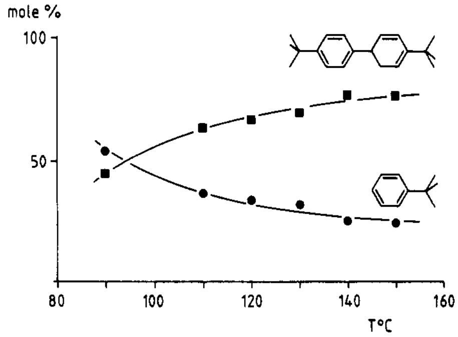
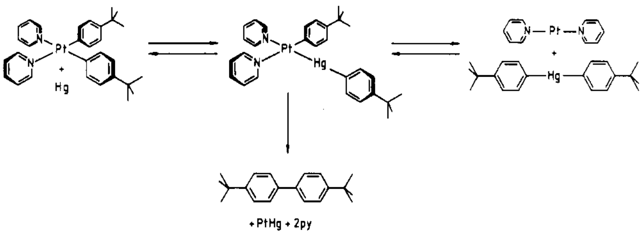


Figure 3. Temperature dependence of product distribution from 1-d_0.

Benzyne coordination to polymetallic[46] and monometallic[47-52] fragments is also well established. In the latter category, the η^2-benzyne ligand may coordinate to metals of widely varying electron availability, including crystallographically characterized Ta(III),[47] Zr(II),[48] Re(II),[49] and Ni(0)[50] complexes as well as others inferred for Ti, Zr,[51] Nb, Ta, Mo, and W.[52,53] Only with electron-poor metals has η^2-benzyne resulted from H-abstraction from an arylmetal, but not via a hydridometal intermediate.[47,48,50-52] The evidence of 4- to 3-isomerization both in biaryls *and* in 1 (after 50% thermolytic decay) reinforces our proposition of an aromatic β-hydrogen transfer to Pt.

During the course of this investigation, another hydridoplatinum(IV) system has emerged in which C–C elimination competes successfully with C–H elimination, which is normally expected to be more facile. This involved the liberation of dimethylcyclopropane from a hydridoplatinacyclobutane.[54] Reductive C–C elimination from Pt(IV) is a favorable option,[8] and, given the ready eliminability of dimethylcyclopropane[6] and of biaryls[5] evident from Pt(II) systems, then it is less surprising that C–H elimination from hydridodialkyl- or hydridodiarylplatinum(IV) intermediates is not necessarily the inevitable outcome. Reductive C–C elimination from B (or D) might also involve the 2-pyridyl ligand. No phenylpyridine (or bipyridyl) was detected, but reluctance of 2-pyridyl to participate in reductive elimination has been noted.[39] In Pt(II) derivatives, the 2-pyridyl–platinum bond is remarkably inert, and treatment with protic acids leads only to the N-protonated species.[43]

Scheme V



Scheme III addresses the mechanistics of the initial arene elimination only. Clearly, a second arene elimination ensues from the resultant organoplatinum fragment as indicated by the mass balances of aryl products (100 ± 5 mol %) and the absence of significant cross-coupling in the biaryls from combined thermolysis of 1-d_0 and 1-d_8. The foregoing proposals, based on arene isotopomer distributions, apply to all arene produced, and so similar conclusions must follow regarding H (D) transfer to the second arene.

No clear explanation has emerged from this study to why the thermolytic behavior of 1 contrasts to such an extent with that of corresponding diarylbis(phosphine) platinum complexes,[5] particularly in respect of the competitive liberation of metal-derived arene and the isomerization of aryl ligands prior to elimination. Relative steric and electronic profiles for heteroaromatic N-donors have not yet emerged for comparison with those of phosphine ligands. Indeed, difficulties in such correlations have been noted.[55] One clear and unexpected facet of complex 1 is the relative lability of coordinated pyridine as a source of transferable hydrogen (qualitatively greater than that of alkyl-[6] or arylphosphines[5] or of bipyridyl[12c]). This rearrangement is apparently the trigger for the related aryl/aryne isomerization; otherwise more isomeric biaryls would be expected from 1-d_{10}. One respect in which pyridine differs from phosphine or bidentate heteroaromatic N-donor ligands is that labile pentacoordinate intermediates can be reached in a single step without (even temporary) decoordination of an ancillary ligand. We are exploring in more detail the mechanistic role of pyridine in organometallic derivatives of platinum and its group.

Influence of Metallic Mercury on Thermolysis. Unwanted heterogeneous reactions catalyzed by metallic products of decomposition are a constant possibility in reactions of organotransition metals. Several methods have been used to detect heterogeneous components in complex mechanisms.[56] In earlier studies of organoplatinum(II) compounds, heterogeneous reactions were suppressed by amalgamation with metallic mercury.[11]

Thermolysis of 1-d_0 in the presence of metallic mercury at 90 °C led to a marked increase in biaryl elimination (79.8 mol %) at the expense of arene liberation (19.8 mol %). The relative incidences of isomeric biaryls (<10% of total; cf. 20%, Table VIII) and of solvent-coupling products (0.4 mol %) were also significantly reduced. Any inference that Hg is scavenging some heterogeneous agent that otherwise contributes to arene formation (and possibly to isomeric biaryls and solvent products) is contradicted by the deuteriation studies and, in particular, the independent behavior of 1-d_0 and 1-d_8 when thermolyzed together. Mercury must take a different role, stimulating coupling

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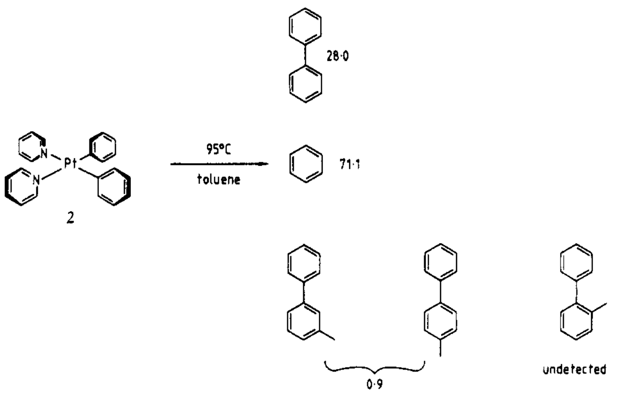
Table IX. Activation Data for Thermolytic Rearrangements of L_2PtR_2

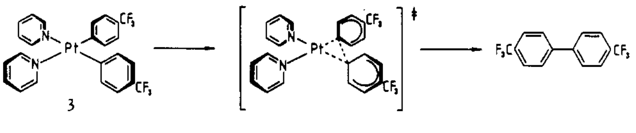
	$(py)_2Pt(4\text{-}C_6H_4CMe_3)_2$	$(py)_2Pt(4\text{-}C_6H_4CF_3)_2$	$(PPh_3)_2Pt(4\text{-}C_6H_4Me)_2$	$(bpy)Pt(C_6H_4CMe_3)_2$	$(bpy)Pt(CH_2CMe_2Ph)_2$
E_a (kJ/mol)	131	59	76	150	129
A	9.0×10^{18}	8.5×10^7	1.1×10^8	9.7×10^{14}	2.8×10^{15}
log A	18.95	7.9	8.0	14.99	15.44
$\Delta S^\ddagger$ ($J \cdot K^{-1} \cdot mol^{-1}$)	+109	−102	−99	+34	+43
$\Delta H^\ddagger$ (90 °C) ($kJ \cdot mol^{-1}$)	128	56	74	147	127
ref	*a*	*a*	5a	44b	12b

[a] This work.

Scheme VI



Scheme VII



and improving its regioretention. The nature of interaction is not yet obvious but might, for example, involve Pt(I)–Hg(I) aryl intermediates such as cis-$(py)_2Pt(HgAr)Ar$. Related species have been characterized for the obverse reaction—that of HgR_2 with zerovalent platinum phosphine complexes PtL_3[57] and are isolable when R is an electronegative alkyl or aryl group[58] or an aryl ligand with bulky ortho substituents.[59] The usual thermolytic reaction of *cis*-$L_2Pt(HgR)R'$ is formation of *cis*-L_2PtRR' and metallic Hg—the reverse of that proposed here. The notable reductive eliminability of biaryls[5] (without strongly electronegative or bulky substituents), the differing coordinative properties of pyridine (cf. phosphines), and the stability of platinum amalgams[55] may, however, combine to (a) increase the accessibility of $L_2Pt(HgAr)Ar$ and/or (b) raise the favorability of coupling, which provides an irreversible escape from equilibria which may operate on 1 in the presence of Hg (Scheme V). $Hg(4\text{-}C_6H_4CMe_3)_2$ was not detected. Other residual products were not exhaustively studied. We are studying other reactions of Hg with related organoplatinum species, but this is further indication that this type of experiment must be interpreted cautiously.

Thermolytic Behavior of *cis*-$(py)_2PtPh_2$ (2). Rearrangement of 2 in toluene is similar to 1-d_0, as shown in Scheme VI. At 95 °C the major product is benzene (71.1 mol %). Some biphenyl (28.0 mol %) is also eliminated, and minor amounts of isomeric solvent products (4- and 3-methylbiphenyl; 0.9 mol % total) are also eliminated. The extent of isomerization could not be estimated at such low levels. The general similarity of the product distribution to that of 1-d_0 suggests that the same two competing reactions afford biphenyl and benzene.

At comparable temperatures, more benzene is formed from 2 than *tert*-butylbenzene from 1. The *tert*-butyl group is electron donating and should favor reductive elimination.[5] The substituent effect clearly acts more powerfully on the C–C elimination than on C–H coupling. This might be due to the cooperative effect of two such substituents during biaryl formation. Comprehensive kinetic investigations on 2 were not pursued due to its inconveniently low solubility.

Thermolytic Behavior of *cis*-$(py)_2Pt(4\text{-}C_6H_4CF_3)_2$ (3). Product Analysis and Reaction Mechanism. In contrast to the thermal rearrangements of *cis*-$(py)_2Pt(4\text{-}C_6H_4R)_2$ (R = H, 2; R = CMe_3, 1-d_0) where complex product mixtures are obtained, thermolysis of 3 gives mainly 4,4′-bis(trifluoromethyl)biphenyl. A minor amount of (trifluoromethyl)benzene (5.6 mol %) is formed. There is no temperature dependence on the product distribution in the range 80–110 °C. No isomeric biaryls or solvent-derived products are observed.

The absence of radical thermolysis products, such as solvent adducts or (trifluoromethyl)benzene, in significant quantities and the regiospecificity of biaryl formation imply that intramolecular reductive elimination is the main thermolytic pathway (Scheme VII). Overall rearrangement of 3 is slowest (vide infra) in accordance with an expected retarding effect on reductive elimination by an electron-withdrawing substituent. Nevertheless, C–C elimination predominates, which seems to indicate that C–H elimination is more susceptible to a decelerating substituent (recall its lesser sensitivity to an accelerating group, vide supra). An alternative explanation is tht CF_3 inhibits the hydrogen-transfer steps which form B or C (Scheme III).

Kinetic Measurements and Comparisons. Thermolytic decay of 3 and appearance of biaryl were first-order over at least 3 half-lives. First-order plots and rate constants with varying temperature appear in Figure 4. These data conform to the Arrhenius relationship, from which it was deduced that $E_a = 59 \pm 2$ kJ mol^{-1} and $A = 8.5 \times 10^7$. These data imply that $\Delta H^\ddagger_{90} = 56 \pm 2$ kJ mol^{-1} and $\Delta S^\ddagger = -102 \pm 11$ J mol^{-1} K^{-1}. Since these derive, we propose, from a single-step process, their relative sizes and implications are more meaningful.

The values are compared with those from thermolytic reaction of a variety of related organoplatinum systems in Table IX. Most striking is the similarity between 3 and *cis*-$(Ph_3P)_2Pt(4\text{-}C_6H_4CH_3)_2$.[5] In particular, the negative values for $\Delta S^\ddagger$ correspond closely. For the phosphine homologue, this feature was attributed to a loss of conformational freedom on approaching the transition state due to extensive C–C interaction (initially through π-orbitals) before Pt–C scission was accomplished (Scheme VII).[5] This comparability underlines the contention that

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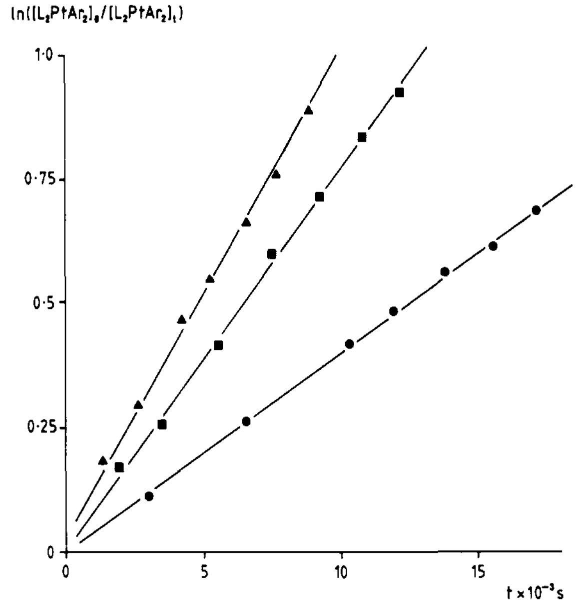

Figure 4. First-order rearrangement of **3** at the following: 95 °C, $k = 8.96 \times 10^{-5}$ s^{-1}; 90 °C, $k = 7.64 \times 10^{-5}$ s^{-1}; 80 °C, $k = 4.02 \times 10^{-5}$ s^{-1}.

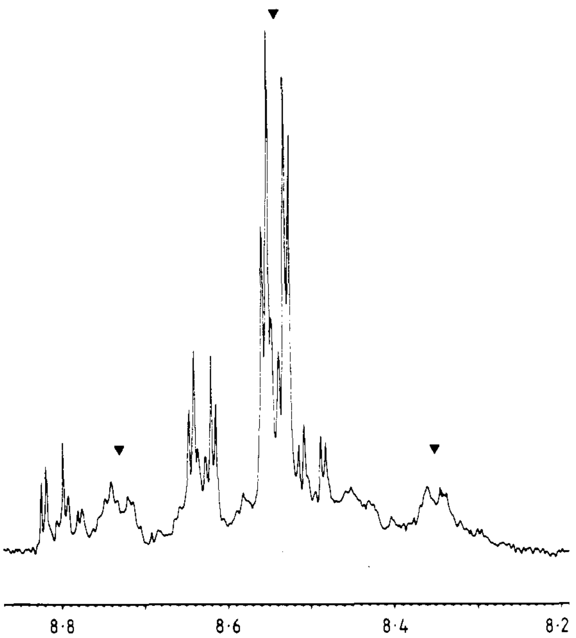

Figure 5. ^{1}H NMR characteristics of solution after complete thermolysis of **3**: $\delta(^1H)$ 8.54 (^3J(H–H) = 6.6 Hz, ^3J(Pt–H) = 99 Hz).

3 rearranges via an uncomplicated unimolecular concerted reductive elimination from the 4-coordinate parent. More surprising is the slight enthalpy advantage displayed by **3** in spite of its electron-withdrawing 4-substituents. It appears that pyridine and triphenylphosphine exert opposing influences on C–C elimination, approximately counter-balancing the electronically opposed effects of the 4-substituents. The source of this influence is not clear, since pyridine exerts a weaker kinetic trans labilizing effect[38] and (on NMR evidence) a weaker thermodynamic trans weakening influence than PPh_3.[60] Nevertheless, attainment of the elimination transition state (Scheme VII) is unexpectedly easy for **3**.

Parameters for the roll-over 3-metalation mechanism of the structurally related (bpy)Pt(4-$C_6H_4CMe_3)_2$ and cyclometalation of (bpy)Pt($CH_2CMe_2Ph)_2$ show no similarity to any of the previously discussed compounds. The positive entropy of activation was proposed in both cases as consistent with molecular freedom associated with prerequisite Pt–N scission steps, already excluded here on independent grounds. The C–C elimination preference exhibited by **3** and, to lesser extents, **1** and **2** while alternative (H transfer) routes are favored by its bidentate-ligand counterparts (biL)Pt(4-$C_6H_4R)_2$ (biL = bpy, bipym, phen; R = H, CH_3, CMe_3, CF_3)[12c,45b] accords well with theoretical proposals on the controls on reductive elimination.[9b,c]

Residual Platinum Species. Although we have discussed in detail the organic product distributions from $(py)_2Pt(C_6H_4R)_2$, we have not addressed the fate of the metal after hydrocarbon elimination. This question is not wholly resolved, but the available evidence is presented here.

Reductive elimination of biaryl should generate the zerovalent species $Pt(py)_2$ as the primary product. During rearrangement of **3**, the ^{1}H NMR signals characteristic of $H_{2,6}'$ (at 8.45 ppm) progressively gave way to a similar new doubled doublet at 8.54 ppm which also had broadened ^{195}Pt satellites, J(Pt–H) = 99 Hz (Figure 5). Such broadening is characteristic of Pt complexes with N-donor ligands.[60] Overall, though, only 40–50 mol % of original pyridine remains detectable by ^{1}H NMR (using the total *tert*-butyl signal as internal standard) in solution after thermolysis. The remainder is ultimately precipitated as a component of a brown microcrystalline solid whose IR spectrum confirmed the incorporation of pyridine. Its insolubility suggests a polymeric nature. On the basis of the elemental analysis of the latter [C, 27.11; H, 2.21; N, 5.49; py:Pt ≈ 3:2) and the amount of pyridine in soluble form, it can be estimated that the ratio py:Pt ≈ 3:1 in solution. It was established by HPLC that there was no free pyridine present in the residual solutions, and so the (major) soluble Pt-containing component has approximate stoichiometry $Pt(py)_3$. While zerovalent platinum derivatives of this type with P-donor ligands are well-known,[51] corresponding N-donor complexes have no precedent. The observed coupling to ^{195}Pt is, however, abnormally large for a Pt(II) complex and must be attributable to greater S character in the bonds transmitting the effect. Larger ^1J(Pt–P) values are, for this reason, associated with Pt(0) complexes.[62]

Although secondary formation of $Pt(py)_3$ is an attractive proposition, we cannot yet claim to have demonstrated its presence unambiguously. Attempts to isolate the product by concentration of its solutions led to precipitation of subsequently insoluble solid with IR characteristics similar to those of the initially deposited polymer. Addition of excess PPh_3 or dppe to filtered solutions of thermolyzed **3** in endeavor to trap Pt(0) also deposited intractable materials. Addition of bromine, though, did yield orange $(py)_2PtBr_4$ as a major product.

The same species was evident to a more limited extent in ^{1}H NMR spectra as **1** rearranged. Similar attempts at characterization were also inconclusive. Moreover other pyridine-containing complexes may also be present. Additional signals are evident at lower field (8.63 and 8.88 ppm; Figure 5). Coupling to ^{195}Pt is not observable but

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is probably obscured. We are exploring alternative routes to pyridine complexes of low-valent platinum.

Acknowledgment. We thank Imperial College (ORS Awards) and Austausch-Stipendium, ETH, Zürich, Switzerland, for financial support (to S.E.H.). We are also grateful to Dr. Judith Challis and John Bilton of this Department and to Drs. Graham Taylor, John Williams, and David Watson of the Royal Postgraduate Medical School, Hammersmith Hospital, for GC–MS measurements. We are additionally indebted to Dick Sheppard and Sue Johnson for high-field NMR and to Johnson-Matthey Ltd. for continued support through generous loans of platinum. Equipment grants by the University of London Central Research Fund and the Royal Society, in partial support of this work, are also gratefully acknowledged.

Registry No. 1, 116840-52-9; 2, 64827-25-4; 3, 116840-53-0; Mg(4-$C_6H_4CMe_3$)Br, 63488-10-8; (cod)$PtCl_2$, 12080-32-9; (cod)Pt(4-$C_6H_4CMe_3$)$_2$, 57110-64-2; Hg(4-$C_6H_4CMe_3$)$_2$, 20657-25-4; *m*-bromo-*tert*-butylbenzene, 3972-64-3; *p*-amino-*m*-bromo-*tert*-butylbenzene, 103273-01-4.

Chemistry of the Complexes NiM(CO)$_4$(η^5-C_5H_5)(η^5-C_5H_4Me) (M = Mo, W): Evidence for an Associative Pathway in Their Reactions with Alkynes

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Received February 2, 1988

Mechanistic aspects of reactions of the complexes NiM(CO)$_4$CpCp′ (M = Mo, W; Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me) with alkynes are presented. The nickel–tungsten complexes react with alkynes to yield bridging alkyne species; nickel–molybdenum complexes in addition afford nickelacyclobutenone species (Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* 1987, *6*, 2298–2306). Benzene solutions of the complexes (η^5-C_5H_5)(CO)Ni–W(CO)$_3$(η^5-C_5H_4Me) (**1**) and (η^5-C_5H_4Me)(CO)Ni–W(CO)$_3$(η^5-C_5H_5) (**2**) undergo metal–metal bond cleavage, forming a statistical equilibrium mixture of the four heterodinuclear complexes **1**, **2**, (η^5-C_5H_5)(CO)Ni–W(CO)$_3$(η^5-C_5H_5) (**3**), and (η^5-C_5H_4Me)(CO)Ni–W(CO)$_3$(η^5-C_5H_4Me) (**4**) when trace impurities are present. High-purity samples of **1** and **2** do not undergo metal–metal bond metathesis. Crossover experiments demonstrate that phenylacetylene reacts with a heterodinuclear species. The reaction rate of **1** with alkynes decreases in the order phenylacetylene > 2-butyne ≫ diphenylacetylene. Competition studies indicate rate-determining alkyne attack is at the nickel atom. Kinetic studies of the reactions of **1** and **3** with phenylacetylene exhibited a first-order rate dependence on both the mixed-metal complex *and* the phenylacetylene concentrations for moderate concentrations of alkyne and metal complex. The reaction of **1** with phenylacetylene was also monitored under high phenylacetylene concentrations. Pseudo-first-order behavior was observed, suggesting the formation of a transient intermediate, possibly the η^3 species (η^3-C_5H_5)(CO)Ni–W(CO)$_3$(η^5-C_5H_4Me). The nickel–molybdenum complexes (η^5-C_5H_5)(CO)Ni–Mo(CO)$_3$(η^5-C_5H_4R) (**5**, R = Me; **6**, R = H) form bridging alkyne complexes primarily via the pathway observed in the nickel–tungsten case. Kinetic and mechanistic experiments indicate that alkyne-bridged and nickelacyclobutenone species are formed from common intermediates. Decarbonylation of the nickelacyclobutenone complex (η^5-C_5H_5)Ni{μ-C(O)C(H)C(Ph)}Mo(CO)$_2$(η^5-C_5H_4Me) (**9**) to (η^5-C_5H_5)Ni(μ-PhC_2H)Mo(CO)$_2$(η^5-C_5H_4Me) (**5a**) produces less than 5% of **5a** over a 3-h period, indicating that decomposition of intermediate metallacyclic species is not the major pathway to the nickel–molybdenum alkyne-bridged complexes.

Introduction

Heterodimetallic complexes have been implicated in catalysis and studies of their syntheses and reactivity are underway in several laboratories.[1] In comparison to their homonuclear analogues, mixed-metal species frequently exhibit enhanced reactivity and distinctly different chemistry;[2] synergistic effects may be partly explained by the polarity of many heteronuclear metal–metal bonds. Despite current attention focused on these complexes, their kinetic and mechanistic behavior has been a relatively neglected area. Most mechanistic work on heterodimetallic species has centered on simple metal carbonyl complexes, in which the metals are closely related and has been undertaken in conjunction with homometallic studies. The mixed-metal complex MnRe(CO)$_{10}$,[3] for example, has

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