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Mechanistic Studies of the Thermolytic and Photolytic Rearrangement of [Bis(diphenylphosphino)ethane]bis(neophyl)platinum(II)

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Comparative mechanistic studies are presented of the thermolytic and photolytic behavior of the bis(neophyl)platinum(II) derivative $Pt(CH_2CMe_2Ph)_2(dppe)$ (neophyl = 2-methyl-2-phenylpropyl; dppe = 1,2-bis(diphenylphosphino)ethane). Thermolytic rearrangement is less facile than for monodentate P-donor analogues and affords the platinaindan $\overline{Pt(2\text{-}C_6H_4CMe_2CH_2})(dppe)$ by intramolecular aromatic C–H activation and H-transfer to eliminated *tert*-butylbenzene. The kinetic isotope effect on metallacyclization ($k_{obs}{}^{H}/k_{obs}{}^{D} = 2.40$) and the negative activation entropy ($\Delta S^{\ddagger}_{obs} = -13\ (\pm 4)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$) suggest a pathway in which scission of one Pt–P is mechanistically significant but C–H addition to Pt has the most energetic transition state. Photolytic rearrangement in toluene-d_0 proceeds by two major paths, both of which involve primary Pt–C homolysis. The resultant neophyl radical may then provide a destination for migrating hydrogen in a cyclometalation of the residual 17-electron organoplatinum species, leading to $\overline{Pt(2\text{-}C_6H_4CMe_2CH_2})(dppe)$. Alternatively, H-abstraction by the neophyl fragment within the solvent cage produces a benzyl radical which recombines with the metal moiety to give $Pt(CH_2Ph)(CH_2Me_2Ph)(dppe)$. This benzylplatinum complex is also photolabile, giving ultimately platinaindan via benzyl radical expulsion. This "indirect" solvent metalation is not evident during photolysis in toluene-d_8 and in benzene.

Introduction

Direct, intermolecular activation of C–H bonds by d-block organometallic fragments continues to generate considerable interest. These organometallic reactions may be induced photolytically[2] or thermolytically.[2a–d,f,3] Intramolecular C–H activation and transfer reactions (usually resulting in cyclometalations) are particularly attractive to those interested in quantifying the intimate nature of such processes, since major complications—unfavorable entropic contributions and solvent limitations—can be minimized.[4] Aromatic substrates, moreover, offer (in principle) wide, controllable variations in ring substituent whose effects on reactivity are already some of the best understood in mechanistic chemistry. Our recent studies of intramolecular aromatic C–H activation and transfer in bis(neophyl)platinum(II) complexes *cis*-$Pt(CH_2CMe_2Ph)_2L_2$ have demonstrated that the nature of the ancillary ligand(s) also may have profound effects on rearrangement of the (neophyl)platinum skeleton to the product platinaindans. For example, where L_2 is a rotationally flexible, bidentate heteroaromatic N-donor—such as 2,2′-bipyridyl or 2,2′-bipyrimidyl—preliminary Pt–N scission is rate-controlling. On the other hand, where L is the monodentate PEt_3, although H-migration is prefaced by phosphine dissociation, the latter is not rate-limiting.[5] We now report investigation of the thermolytic rearrangement of the analogous system with a bidentate P-donor, 1,2-bis(diphenylphosphino)ethane (dppe).

Though increasing information is emerging regarding the photochemical reactivity of transition-metal–alkyl complexes,[6] comparative thermolytic and photolytic studies of organometallic derivatives of the platinum group, in particular, are still relatively rare.[7] Here we also describe a mechanistic evaluation of the photochemistry of $Pt(CH_2CMe_2Ph)_2(dppe)$ in toluene. A report of the photolytic behavior of $PtR_2(dppe)$ (R = Me, Et, CH_2Ph), primarily in chlorocarbon solvents, has appeared previously.[8]

Experimental Section

General and Instrumental Considerations. Elemental analyses were performed by the Imperial College microanalytical laboratories. NMR spectra were recorded on Bruker WM 250 (^1H, 250.13 MHz; ^{13}C, 62.9 MHz) and JEOL FX 90Q (^1H, 89.55 MHz; ^{31}P, 36.21 MHz) spectrometers. HPLC analyses were performed using a Spectra-Physics automated high-pressure liquid chromatograph comprising an SP8100 solvent delivery module,

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SP8440 spectrometric detector, and SP4200 computing integrator. Separations were carried out on a 25-cm ODS/5 μm silica column at 45 °C, with 80:20 methanol/water as eluent. GCMS analyses were conducted using a VG 7070E system.

All reactions were carried out under argon, using standard anaerobic techniques.[9] The apparatus was thoroughly flame-dried prior to use, and solvents were distilled from sodium under nitrogen. Diethyl ether and *n*-hexane were distilled from sodium/benzophenone. 2-Methyl-3-phenylpropan-2-ol, cycloocta-1,5-diene (cod), 1,2-bis(diphenylphosphino)ethane (dppe), toluene-d_8 and benzene-d_6 were all supplied by Aldrich Chemical Co. Dichloro(cycloocta-1,5-diene)platinum(II) was prepared according to a published method.[10] ^{1}H, ^{13}C, and ^{31}P NMR characteristics for bis(neophyl)platinum complexes have been reported elsewhere.[5]

Syntheses. Preparation of (Cycloocta-1,5-diene)bis(neophyl)platinum(II). This procedure is a modification to that published previously[5] and affords superior yields. To a stirred suspension of magnesium shot (8.0 g, 0.33 mol) activated with 1,2-dibromomethane (0.1 mL) in dry Et_2O (50 mL) was added dropwise a solution of neophyl chloride (8.0 g, 0.06 mmol) in Et_2O (50 mL). The mixture was then brought to reflux for 24 h (yield 100%). This solution (68.0 mL of a 0.6 M solution, 41 mmol) was added dropwise to a stirred suspension of $PtCl_2$(cod) (5.15 g, 13.77 mmol) in Et_2O (50 mL), maintained at −78 °C. The mixture was allowed to reach ambient temperature and stirred for 5 h. After the mixture was cooled to −20 °C, saturated aqueous ammonium chloride (20 mL) was added dropwise. The mixture was then filtered and the ethereal layer decolorized with activated charcoal and dried over $MgSO_4$. The solution was finally concentrated in vacuo and cooled to −25 °C to yield large colorless crystals of the product, which were filtered and washed with cold hexane (yield 6.22 g, 79%). Anal. Calcd: C, 59.03; H, 6.72. Found: C, 58.93; H, 6.80.

(Cycloocta-1,5-diene)bis(neophyl-d_5)platinum(II) was prepared in an analogous fashion (yield 70%). Anal. Calcd: C, 59.24; H, 4.62. Found: C, 59.35; H, 4.71.

Preparation of Chloro(cycloocta-1,5-diene)(neophyl)platinum(II). To a stirred solution of $Pt(CH_2CMe_2Ph)_2$(cod) (3.0 g, 5.27 mmol) in Et_2O (25 mL) was added dropwise at −78 °C a solution of dry HCl in ether (19.3 mL of a 0.3 M solution, 5.79 mmol). The solution was warmed to ambient temperature and stirred for 12 h. The ether was then removed in vacuo to yield a colorless crystalline product (yield 2.48 g, 100%). Anal. Calcd: C, 45.80; H, 5.30. Found: C, 45.86; H, 5.33.

Preparation of [Bis(1,2-diphenylphosphino)ethane]bis(neophyl)platinum(II). $Pt(CH_2CMe_2Ph)_2$(cod) (2.0 g, 3.51 mmol) and dppe (1.40 g, 3.51 mmol) were dissolved together in toluene (20 mL), and the solution was stirred for 24 h at ambient temperature. The toluene was then removed in vacuo and the white solid recrystallized from CH_2Cl_2/MeOH to yield colorless crystals (yield 2.87 g, 95%). Anal. Calcd: C, 64.25; H, 5.86; P, 7.20. Found: C, 64.86; H, 5.96; P, 6.80.

[Bis(1,2-diphenylphosphino)ethane]bis(neophyl-d_5)platinum(II) was prepared in an analogous fashion (yield 84%). Anal. Calcd: C, 63.50; H, 5.79. Found: C, 63.76; H, 5.91.

Preparation of Chloro[bis(1,2-diphenylphosphino)ethane](neophyl)platinum(II). $PtCl(CH_2CMe_2Ph)$(cod) (0.06 g, 0.13 mmol) and dppe (0.06 g, 0.14 mmol) were dissolved together in toluene (20 mL), and the mixture was stirred for 24 h. The toluene was removed in vacuo and the product recrystallized as colorless crystals from CH_2Cl_2/MeOH.(yield 0.07 g, 72%). Anal. Calcd: C, 56.73; H, 4.89. Found: C, 56.59; H, 4.88.

Preparation of Benzylmagnesium Bromide. To a stirred suspension of magnesium shot (4.0 g, 0.16 mol) activated with 1,2-dibromoethane in Et_2O (50 mL) was added dropwise benzyl bromide (5.5 g, 29.2 mmol), and the mixture was stirred at ambient temperature for 4 h. The solution was then filtered (yield 0.58 M, 100%).

Preparation of Benzyl(cycloocta-1,5-diene)(neophyl)platinum(II). To a stirred suspension of $PtCl(CH_2CMe_2Ph)$(cod) (0.86 g, 1.82 mmol) in Et_2O (40 mL) was added dropwise a solution of benzylmagnesium bromide (5.34 mL of a 0.58 M solution, 3.1 mmol) at −78 °C. The mixture was then warmed to ambient temperature and stirred for 7 h. When the mixture was cooled to −20 °C, saturated aqueous ammonium chloride (5 mL) was added dropwise. The organic layer was separated, decolorized over activated charcoal, and dried over $MgSO_4$. The solution was then concentrated in vacuo to yield pale yellow crystals (yield 0.75 g, 78%). Anal. Calcd: C, 56.91; H, 6.11. Found: C, 56.87; H, 6.06.

Preparation of Benzyl[bis(1,2-diphenylphosphino)ethane](neophyl)platinum(II). $Pt(CH_2Ph)(CH_2CMe_2Ph)$(cod) (0.40 g, 0.76 mmol) was dissolved with dppe (0.31 g, 0.76 mmol) in toluene (15 mL) and the mixture stirred at ambient temperature for 24 h. The solvent was then removed in vacuo and the product recrystallized as colorless crystals from CH_2Cl_2/MeOH (yield 0.55 g, 89%). Anal. Calcd: C, 63.10; H, 5.42. Found: C, 62.98; H, 5.48.

Preparation of 2-Chloro-2-methyl-3-phenylpropane.[11] To a solution of thionyl chloride (7.5 mL) in toluene (75 mL) was added a solution of 2-methyl-3-phenylpropan-2-ol (10.0 g, 70.0 mmol) in toluene (20 mL) at −5 °C. The solution was stirred at ambient temperature for 12 h, and the solvent and any residual HCl and SO_2 were removed in vacuo. The crude product was then distilled under reduced pressure (bp 63–64 °C, 10^{-2} mmHg) to give a colorless liquid (yield 8.14 g, 69%).

Preparation of 2-(Chloromagnesio)-2-methyl-3-phenylpropane. To a suspension of magnesium shot (1.4 g, 60 mmol) activated with 1,2-dibromoethane in Et_2O (50 mL) was added dropwise benzyldimethylcarbinyl chloride (0.20 g, 12.2 mmol) and the mixture stirred for 48 h and then filtered (yield 0.13 M, 55%).

Attempted Preparation of (Cycloocta-1,5-diene)(2-methyl-3-phenylpropyl)(neophyl)platinum(II). To a stirred solution of $PtCl(CH_2CMe_2Ph)$(cod) (0.03 g, 0.09 mmol) in Et_2O (15 mL) at −78 °C was added dropwise a solution of $Mg(CMe_2CH_2Ph)Cl$ (3.0 mL of a 0.05 M solution, 0.15 mmol). The mixture was warmed to 0 °C and stirred for 24 h. Workup was achieved by eluting the solution on a silica gel column with Et_2O, the temperature being maintained at 0 °C by means of an ice/water jacket. The resultant solution was concentrated in vacuo. The colorless crystals recovered proved to be $PtCl(CH_2CMe_2Ph)$(cod), and there was no evidence for the desired product in the ^{1}H NMR spectrum.

Analogous reactions of $Mg(CMe_2CH_2Ph)Cl$ with $PtCl_2$(cod) and $PtCl(CH_2CMe_2Ph)$(dppe) were attempted and proved to be equally unsuccessful.

Preparation of Silver Oxalate.[12] To a saturated aqueous solution of $K_2C_2O_4{\cdot}H_2O$ (0.48 g, 2.7 mmol) was added slowly a solution of $AgNO_3$ (1.02 g, 6.0 mmol). The white precipitate that immediately formed was filtered, washed with cold water and ether, and then dried in vacuo for 24 h, with light being excluded from the flask (yield 0.80 g, 98%).

Preparation of [Bis(1,2-diphenylphosphino)ethane](oxalato)platinum(II).[13] $PtCl_2$(dppe) (0.36 g, 0.54 mmol) was dissolved in dichloromethane (20 mL) and silver oxalate (0.20 g, 0.66 mmol) added. The mixture was stirred for several days, with exclusion of light. The solution was filtered and then concentrated in vacuo to yield white crystals of the product (yield 0.34 g, 92%). ^{31}P NMR ($CDCl_3$): δ 30.97 ppm, $^1J_{Pt-P}$ = 3627 Hz.

Preparation of (η^2-Ethene)[1,2-bis(diphenylphosphino)ethane]platinum(0).[12] A suspension of $Pt(C_2O_4)$(dppe) (0.34 g, 0.50 mmol) in deoxygenated acetonitrile (8 mL) and benzene (4 mL) was saturated with ethene by bubbling the gas through the solvents for 10 min. The mixture was irradiated (see Photolyses, below) for 24 h at −5 °C, under an ethene atmosphere. The product was recovered as a brown oil. ^{31}P NMR (benzene-d_6): δ 31.40 ppm, $^1J_{Pt-P}$ = 3460 Hz.

Attempted Preparation of (2-Methyl-1-phenylprop-1-ene)[bis(1,2-diphenylphosphino)ethane]platinum(II). To

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a solution of $Pt(C_2H_4)(dppe)$ (ca. 0.05 mmol) in acetonitrile/benzene-d_6 in a 5-mm NMR tube was added 2-methyl-1-phenyl-1-propene (0.01 g, 0.08 mmol). The ^{31}P NMR spectrum was then recorded. As no reaction had occurred, the solution was heated to 40 °C for 3 h. The ^{31}P NMR spectrum showed no evidence of any change.

Preparation of Bis[bis(1,2-diphenylphosphino)ethane]platinum(0).[14] $PtCl_2(dppe)$ (0.82 g, 1.23 mmol) was added to a stirred suspension of dppe (1.10 g, 2.75 mmol) in a 2:1 ethanol/water (50 mL) mixture. This mixture was then brought to reflux and stirred for 1 h, yielding a pale yellow solution. A saturated aqueous solution of $NaBH_4$ (10 mL) was added dropwise, with immediate precipitation of a dense lemon yellow solid. This was filtered off, dried in vacuo for 12 h, and recrystallized by dissolving in benzene (ca. 10 g in 50 mL), warming to 60 °C, and then adding methanol (37 cm^3) and cooling to −20 °C (yield 1.00 g, 82%). ^{31}P NMR: δ 28.87 ppm, $^1J_{Pt-P}$ = 3730 Hz.

Thermolyses. These were performed in 5-mm medium-walled NMR tubes equipped with coaxial Teflon valves (J. Young Scientific Glassware, London W3 8BS) using solutions (2.00×10^{-2} mol·L^{-1}) of $Pt(CH_2CMe_2Ph)_2(dppe)$ in toluene-d_8, previously distilled from sodium. These solutions were degassed through five freeze–thaw cycles and then sealed under argon. The required reaction temperature was maintained by immersion in a Haake W13 thermoregulated silicone oil bath. Progress of the rearrangement was monitored by ^{31}P and ^1H NMR spectroscopy, and quantification was corroborated by HPLC.

Photolyses. Solutions (5.00 mL) of 1 (2.00×10^{-2} mol·L^{-1}) in toluene, toluene-d_8, or benzene, distilled from sodium, were prepared in dry, Teflon-sealed vessels and degassed through five freeze–thaw cycles. They were then transferred via steel tubing to the immersion well of an Applied Photophysics RQ 400 immersion-well photolysis unit equipped with a 400-W medium-pressure water-cooled mercury-vapor lamp. The average photon flux at 334 nm was measured to be 4.28×10^{-3} einstein·L^{-1}·s^{-1}, using 5.0 mL of ferrioxalate actinometer solution (6.00×10^{-3} mol·L^{-1})[15] with toluene in the cooling jacket (the lamp required 4–5 min of operation to reach this efficiency). This figure represents a realistic (lower limit) estimate of the absorbed intensity (I_a) during photolytic experiments, with water in the jacket but toluene (or benzene) as the reaction solvent. The reaction vessel was oven-dried, assembled while hot, and flushed with argon for 2 h prior to use. During the photolysis, it was immersed in a Fryka-Kaltetechnic KB 300 cryogenic bath (2-propanol), usually at −5 °C (for benzene as solvent, the temperature was maintained at 8 °C). Solutions were stirred vigorously during photolysis. After measured irradiation times, portions of the solution were transferred to argon-filled NMR tubes via Teflon-lined steel tubing and a stainless steel exit valve. (Where the reaction solvent was toluene-d_0 or benzene-d_0, the NMR tubes contained benzene-d_6 or acetone-d_6). The progress of the reaction was investigated by both ^1H and ^{31}P NMR spectroscopy.

Results and Discussion

Thermolysis. Studies of the rearrangement of $Pt(CH_2CMe_2Ph)_2(dppe)$ (1) were carried out over the temperature range 110–130 °C. The complex reacted quantitatively via intramolecular δ-C–H activation, yielding the platinacycle $\overline{Pt(2\text{-}C_6H_4CMe_2CH_2})(dppe)$ (2) and 1 equiv of *tert*-butylbenzene. ^{31}P NMR spectroscopy was the ideal monitor, since resonances due to product and substrate were clearly separated. The appearance of the organic product could be quantified by ^1H NMR spectroscopy—absorption due to the methyl protons appears at δ 1.16 ppm—or by HPLC methods. The reaction was kinetically first order for at least 3 half-lives. The temperature dependence of k_{obs}, the first-order rate constant, conformed linearly to the Arrhenius relationship (Table I and Figure 1), from which values of $\Delta H^{\ddagger}_{obs}$ = 133 (±3) kJ·mol^{-1} (at 298 K) and $\Delta S^{\ddagger}_{obs}$ = −13 (±4) J·K^{-1}·mol^{-1} were calculated.[16]

Table I. Kinetic Data for Thermolyses of $Pt(CH_2CMe_2C_6R_5)_2(dppe)$[a]

temp, °C	R	10^3[dppe], mol·dm^{-3}	10^6k_{obs}, s^{-1}
105	H	0	0.89
110	H	0	1.67
115	H	0	2.72
115	D	0	1.14
115	H	10.0	2.68
115	H	20.0	2.66
120	H	0	4.54
125	H	0	8.37
130	H	0	14.00
135	H	0	22.90

[a] Recorded in toluene-d_8.

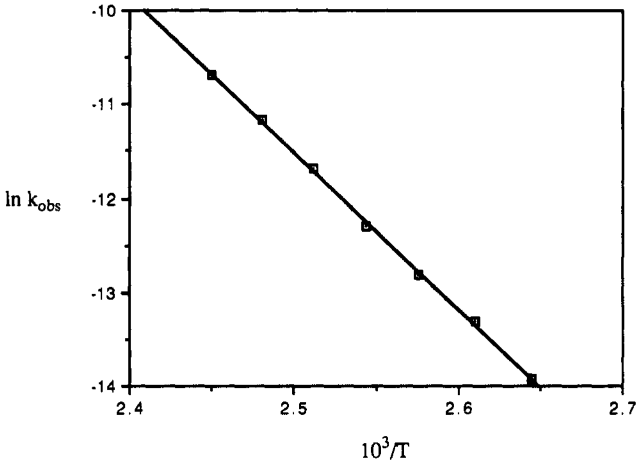

Figure 1. Arrhenius correlation for thermolytic rearrangement of $Pt(CH_2CMe_2Ph)_2(dppe)$.

Scheme I

$$L_2PtR_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} LPtR_2 \xrightarrow[\text{H-transfer}]{k_2} \text{products}$$

Addition of free dppe to reaction solutions had no significant effect on the observed rate constant—values of k_{obs} at 115 °C were 2.72×10^6 and 2.68×10^6 s^{-1} in the absence and presence, respectively, of added dppe (Table I)—indicating that complete dissociation of dppe is not a mechanistic prerequisite for metallacyclization. Similar results emerged previously with bidentate N-donor ligands.[5]

The relative importance of steps in the reaction pathway involving C–H scission or formation often can be deduced by replacement of the migrating hydrogen with deuterium. Thermolysis of $Pt(CH_2CMe_2C_6D_5)_2(dppe)$ gave $C_6D_5CMe_2CH_2D$—confirming the quantitative nature of δ-C–H transfer—and revealed a normal kinetic isotope effect (k^H_{obs}/k^D_{obs}) with a value of 2.40. This effect is larger than that observed for the corresponding N-donor complex $Pt(CH_2CMe_2Ph)_2(bpy)$ (k^H_{obs}/k^D_{obs} = 1.26) but appreciably smaller than that from the monodentate phosphine analogue *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$ (k^H_{obs}/k^D_{obs} = 3.40). Assuming that steady-state concentrations of (nominally) tricoordinate, 14-electron intermediates develop prior to H-transfer (Scheme I), we have argued elsewhere[5] that these two systems resemble limiting cases in which, respectively, Pt–L scission is rate-limiting ($k_2 \gg k_{-1}$ and

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Table II. Organoplatinum Distributions and Rate Constants from Photolyses of PtRR′(dppe)

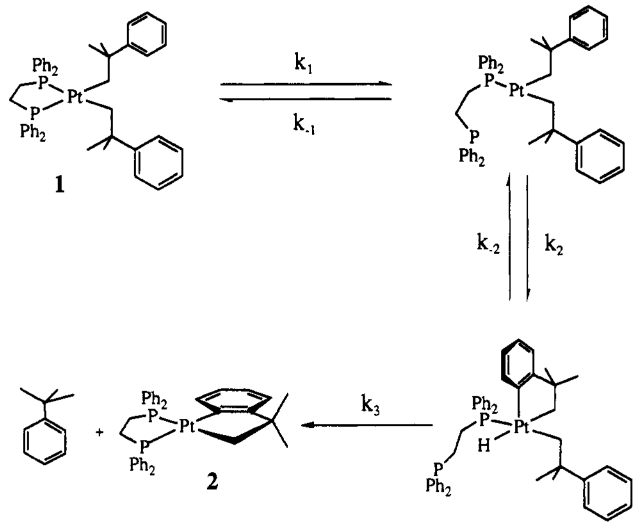
solvent	substrate	irradiation time, h	amt of organoplatinum species, mol %				k_{obs},[a] s^{-1}
			$Pt(CH_2CMe_2Ph)_2L$	A	$\overline{Pt(2\text{-}C_6H_4CMe_2C}H_2)L$	B	
toluene-d_0	$Pt(CH_2CMe_2Ph)_2L$	12	25	28	41	6	3.22×10^{-4}
		30			92	8	
toluene-d_8 or benzene	$Pt(CH_2CMe_2Ph)_2L$	12	35		59	6	2.40×10^{-5}
		30			91	9	$[2.36 \times 10^{-5}]^b$
toluene-d_8 or -d_0 or benzene	$Pt(CH_2CMe_2Ph)(CH_2Ph)L$	12		31	62	7	2.71×10^{-5}
		30			91	9	
toluene-d_8 or -d_0 or benzene	$\overline{Pt(2\text{-}C_6H_4CMe_2C}H_2)L$	20			100		

[a] First-order rate constant for (initial) disappearance of PtRR′(dppe); measured in toluene. [b] k^D_{obs} for $Pt(CH_2CMe_2C_6D_5)L$; measured in benzene-d_0.

$k^H_{obs}/k^D_{obs} = k^H_{-1}/k^D_{-1} \approx 1$) or, alternatively, H-migration is the most energetic requirement ($k_2 \ll k_{-1}$ and $k^H_{obs}/k^D_{obs} = k^H_2/k^D_2$).[17] Between these limits, however, the isotope effect will vary in the range $k^H_2/k^D_2 \geq k^H_{obs}/k^D_{obs} \geq 1$. For example, in the (unlikely) event that $k^H_2 = k^H_{-1}$ (and $k^D_2 = k^D_{-1}$) and on the assumption—based on established results[2-4,18]—that a reasonable *lower* limit for k^H_2/k^D_2 is 3.00, then the corresponding lower limit for k^H_{obs}/k^D_{obs} is 2.00.[19] The intermediate isotopic inhibition for $Pt(CH_2CMe_2Ph)_2(dppe)$ ($k^H_{obs}/k^D_{obs} = 2.40$) can be ascribed to a significant—but clearly not rate-limiting—kinetic contribution from reversible dissociation of one Pt–P bond; C–H scission or formation is also kinetically influential up to and including the most energetic transition state.

The net negativitiy of $\Delta S^{\ddagger}_{obs}$ (-13 J·K^{-1}·mol^{-1}) suggests overall loss of molecular freedom on the approach to the most energetic transition state and further supports the conclusion that complete dissociation of dppe is not required. The plausible implication is that oxidative addition of the neophyl C–H bond—which clearly requires conformational restriction—may be a major contributor to the energetics of reaction. Moreover, in previously studied cases where reductive C–H elimination was adjudged the most energetic step ($k_3 \ll k_{-1}, k_2$), the propositions were supported by large, *positive* $\Delta S^{\ddagger}_{obs}$ values, which is commensurate with the formation of two or more particles from one[20] and can be attributed to a dissociative, product-like transition state.[4a,18,21]

Scheme II



On the basis of these observations, the major thermolytic pathway for $Pt(CH_2CMe_2Ph)_2(dppe)$ is proposed (Scheme II) to involve initial, reversible Pt–P dissociation (k_1, k_{-1}), followed by oxidative addition of the ortho phenyl C–H bond to the tricoordinate intermediate (k_2), the step which, we propose, features the most energetic transition state. The phosphine reassociation rate (k_{-1}) is significant enough (relative to k_2) to dilute the overall deuterium isotope effect. Rapid reductive elimination of *tert*-butylbenzene then occurs from the hydridoalkylplatinum(IV) intermediate (k_3), prior to (or concomitant with) phosphine reassociation.

Photolysis. The parent complex $Pt(CH_2CMe_2Ph)_2(dppe)$ (1) shows a weak absorption centered at 328 nm in its electronic spectrum as the lowest energy transition. The low intensity of this band and its insensitvity to solvent variation are both consistent with d–d character. Any other electronic transitions at higher energies are masked by those arising from the phosphine ligand. A medium-pressure mercury lamp was used to provide continuous irradiation at 334 nm (see Experimental Section). Photolytic decay of $Pt(CH_2CMe_2Ph)_2(dppe)$ in toluene or benzene was apparently first order for 1–2 half-lives,[22] as

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[17] Assuming a steady-state concentration of "tricoordinate" intermediate, then $k_{obs} = k_1k_2/k_2 + k_{-1}$ and the isotope effect on k_{obs} is

$$\frac{k_{obs}{}^H}{k_{obs}{}^D} = \frac{k_1{}^H k_2{}^H (k_2{}^D + k_{-1}{}^D)}{k_1{}^D k_2{}^D (k_2{}^H + k_{-1}{}^H)}$$

The isotope effects on k_1 and k_{-1} are negligible, as the relaxation mode for the transition state is a Pt–P vibration; $k_1{}^H/k_1{}^D = k_{-1}{}^H/k_{-1}{}^D = 1$. Hence

$$\frac{k_{obs}{}^H}{k_{obs}{}^D} = \frac{k_2{}^H}{k_2{}^D}\,\frac{1 + \dfrac{k_2{}^D}{k_{-1}{}^D}}{1 + \dfrac{k_2{}^H}{k_{-1}{}^H}}$$

Please note that this equation appeared with a typographical error ("–" for "+" in the numerator) in ref 5.

[18] Foley, P. F.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* 1980, *102*, 6713.

[19] Where $k_2{}^H = k_{-1}{}^H$ (and $k_2{}^D = k_{-1}{}^D$), then

$$\frac{k_{obs}{}^H}{k_{obs}{}^D} = \frac{k_2{}^H}{k_2{}^D}\,\frac{1 + \dfrac{k_2{}^D}{k_{-1}{}^D}}{2} = \frac{1}{2}\left[1 + \frac{k_2{}^H}{k_2{}^D}\right]$$

[20] See, for example: Benson, S. W. In *Thermochemical Kinetics*; Wiley: New York, 1986; Chapter 3.

[21] Reductive C–C elimination can also proceed via an ordered transition state; formation of biaryl from *cis*-$Pt(C_6H_4R)_2L_2$ ($R = CH_3$, $L = Ph_3P$; $R = CF_3$, $L = py$) is characterized by a negative activation entropy ($\Delta S^{\ddagger} = -100 \pm 1$ J·K^{-1}·mol^{-1}). This was ascribed to conformational effects peculiar to the *cis*-diarylmetal: (a) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* 1977, 1892. (b) Himmel, S. E.; Young, G. B. *Organometallics* 1988, *7*, 2440.

[22] For practical reasons—principally, the appearance of an insoluble product (vide infra)—reactions were not followed continuously beyond this stage.

Table III. ^{1}H NMR Characteristics of $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$[a]

	$\delta(^1H)$ (J_{Pt-H}, assignt)		
L_2	neophyl	benzyl	L_2
cod	1.44 (CH_3), 1.94 (89 Hz, CH_2), 6.81–6.87 (p-H), 7.19–7.23 (m-H), 7.45–7.49 (o-H)	2.95 (115 Hz, CH_2), 7.00–7.18 (m,p-H), 7.25–7.38 (o-H)	1.84–2.17 (CH_2), 4.02 (43 Hz, CH trans to neoph), 4.41 (39 Hz, CH trans to benzyl)
dppe	1.56 (CH_3), 2.65 (81 Hz, CH_2), 6.97–7.01 (p-H) m obsc,[b] 7.70 (o-H)	3.56 (96 Hz, CH_2), 7.08–7.67 (phenyl obsc)	1.70–1.94 (CH_2), 7.08–7.16 ($H_{3,4}$), 7.56–7.67 (H_2)

[a] Recorded in chloroform-d_1. [b] obsc = obscured.

Table IV. ^{13}C NMR Characteristics of $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$[a]

	$\delta(^{13}C)$ (J_{Pt-C}, assignt)		
L_2	neophyl	benzyl	L_2
cod	33.93 (58 Hz, CH_3), 42.17 (875 Hz, CH_2), 42.97 (13 Hz, CMe_3), 124.90 (C_4), 126.08 ($C_{3,5}$), 126.67 ($C_{2,6}$), 154.09 (20 Hz, C_1)	31.07 (756 Hz, CH_2), 122.61 (20 Hz, C_4), 127.52 (33 Hz, $C_{2,6}$), 128.37 ($C_{3,5}$), 150.50 (57 Hz, C_1)	28.77, 33.03 (CH_2), 98.41 (59 Hz, CH trans to benzyl), 102.06 (53 Hz, CH trans to neophyl)
dppe	23.44 (J_{P-C} cis 5 Hz, trans 91 Hz, CH_2), 32.85 (37 Hz, CH_3), 43.49 (CMe_3), 123.97 (C_4), 126.77 ($C_{3,5}$), 128.23 ($C_{2,6}$), 156.50 (C_1)	36.65 (J_{P-C} cis 6 Hz, trans 97 Hz, CH_2), 120.88 (C_4), 125.84 ($C_{3,5}$), 127.22 ($C_{2,6}$), 151.24 (C_1)	28.35 (CH_2), 128.37 ($C_{3,5}$), 130.07 (C_4), 132.55 (C_1), 133.60 ($C_{2,6}$)

[a] Recorded in benzene-d_6.

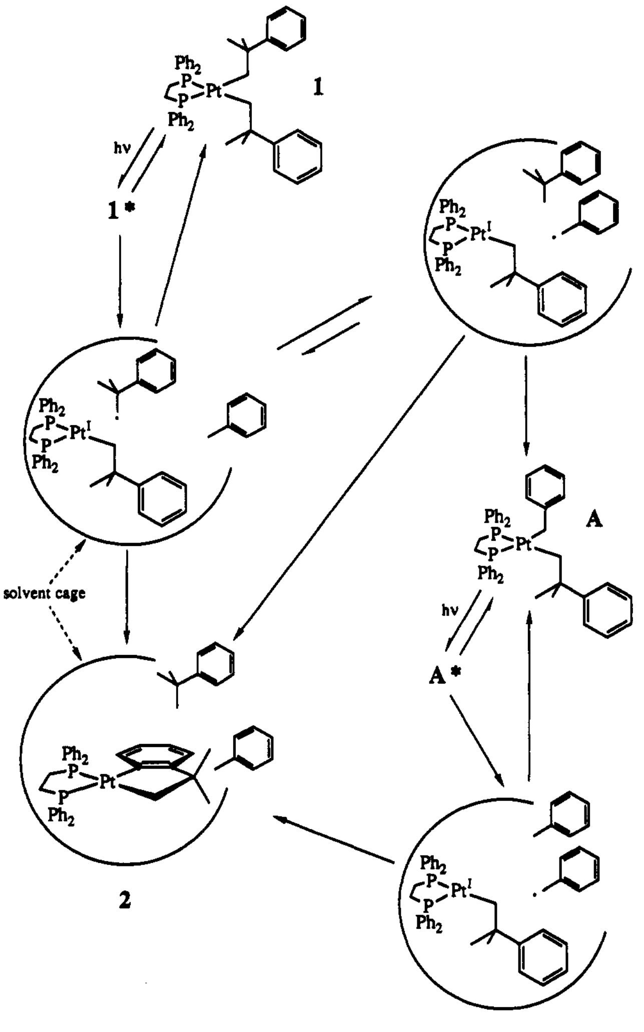
might be expected for an opticially dilute absorbent.[23] The overall rates and, more notably, the product distributions displayed unusual solvent dependence (Table II). Photolysis of toluene-d_0 solutions of $Pt(CH_2CMe_2Ph)_2(dppe)$ for 12 h generated two toluene-soluble products. The first of these is the 3,3-dimethyl-1-platinaindan species $\overline{Pt(2\text{-}C_6H_4CMe_2C}H_2)(dppe)$ (2), formed in the thermolytic reaction. The second species (A) displayed ^{31}P NMR characteristics consistent with an asymmetric dialkylplatinum(II) species. In addition, a small quantity (ca. 6 mol %) of an insoluble, pale yellow material (B) was generated. On further photolysis (up to 30 h), A disappeared progressively and platinacycle 2 was formed as well as further B (≤9 mol %, total). Deviation from the initially first-order decay of 1 was evident in the latter stages of the reaction. After complete reaction, 2 and B were the only platinum-containing species present. The precipitate B dissolved in chloroform and also in acetone. In chloroform-d, the ^{31}P NMR spectrum displayed a characteristic 1:4:1 pattern at δ_P 41.2, with $^1J_{Pt-P}$ = 3617 Hz, establishing the identity of the solute as $PtCl_2(dppe)$.[24] When B was dissolved in acetone-d_6, the ^{31}P NMR spectrum also comprised a signal at δ_P 36.3 with ^{195}Pt satellites ($^1J_{Pt-P}$ = 3468 Hz).

Photolysis of $Pt(CH_2CMe_2Ph)_2(dppe)$ for 12 h in toluene-d_8, however, yielded only $\overline{Pt(2\text{-}C_6H_4CMe_2C}H_2(dppe)$ and a minor amount (ca. 6 mol %) of B. Complete photolysis (30 h) again gave the metallacycle and B (ca. 9 mol %) as the sole products. At no time throughout the course of these photolyses was A detected. Exactly parallel results emerged from photolysis in benzene (d_0 and d_6).

Linkage isomerization of $Pt(CH_2CMe_2Ph)_2(dppe)$ was investigated initially as a route to A. Successive H-transfers, under certain conditions, may generate a (2-*tert*-butylphenyl)-platinum derivative from *cis*-$Pt(CH_2CMe_2Ph)_2(PEt_3)_2$.[25] Synthesis of an authentic sample of $Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)(dppe)$ and measurement of its ^{31}P NMR characteristics (δ_P 40.02, $^1J_{Pt-P}$ = 1699 Hz; $\delta_{P'}$ 35.15, $^1J_{Pt-P'}$ = 1666 Hz) confirmed a different identity for A. Reaction of $PtCl(CH_2CMe_2Ph)(cod)$ with $Mg(CH_2Ph)Cl$, however, followed by displacement of the diene with dppe, afforded $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$, whose ^{31}P, ^1H, and ^{13}C NMR characteristics (Tables III and IV) were indistinguishable from those of A.

The absence of $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$ among the photolytic products in benzene is now self-explanatory. Its absence in toluene-d_8 implies a substantial isotopic inhibition on the process of solvent metalation. The lack of solvent metalation at aromatic sites mitigates against direct intermolecular oxidative addition to (neophyl)-

Scheme III



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[23] (a) Ferraudi, G. J. *Elements of Inorganic Photochemistry*; Wiley: New York, 1988; Chapter 1. (b) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970; Chapter 1. (c) Wayne, R. P. *Principles and Applications of Photochemistry*; Oxford Univ. Press: Oxford, England, 1988.

[24] Anderson, G. K.; Clark, H. C. *Inorg. Chem.* 1981, 20, 3607.

[25] Griffiths, D. C.; Joy, L. G.; Wilkes, D. J.; Skapski, A. C.; Young, G. B. *Organometallics* 1986, 5, 1744.

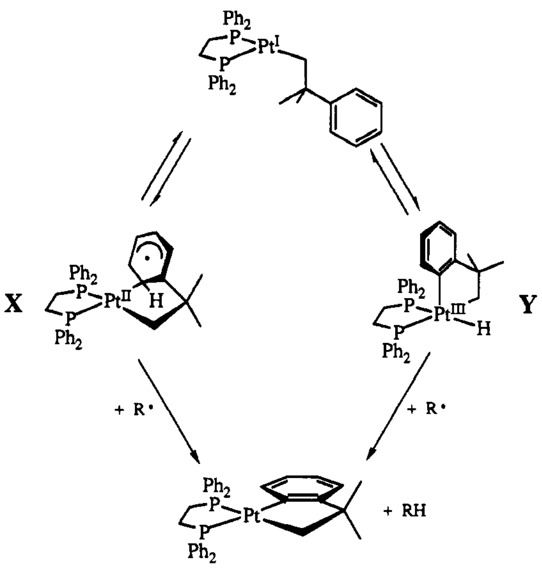
platinum(II); our previous observations suggest that aromatic carbon is the preferred site for attack by Pt.[23] A more plausible route to photoproduction of the (benzyl)platinum(II) derivative is outlined in Scheme III. After generation of 1*—a photoexcited state of 1—initial Pt–C homolysis generates a solvent-caged pair, comprising a neophyl radical and the univalent, paramagnetic (neophyl)platinum(I) species $Pt^I(CH_2CMe_2Ph)(dppe)$. The neophyl radical may then capture a hydrogen from one of the molecules comprising the solvent cage; the aliphatic site on toluene is a ready source of abstractable H.[26] The resultant benzyl radical now can recombine with the univalent metal complex, generating the observed product $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$ (A). This explanation not only is consistent with the photolysis results from benzene solutions but also corresponds with the effect of toluene deuteration; a substantial kinetic isotope effect on radical abstraction of aliphatic hydrogen from toluene is expected. Estimates of 4.5 at 125° C, where the abstracting radical was methyl,[24] and 7.0 at 60 °C, with phenyl radical as the scavenger,[27] have been reported.

The organic products of (overall) photolysis were monitored by HPLC. Invariably, the major component was *tert*-butylbenzene (90–95 mol %), in addition to smaller quantities of 2,5-dimethyl-2,5-diphenylhexane (bineophyl; 4–6 mol %) and 2-methyl-1-phenylprop-1-ene (1–4 mol %). Clearly, the first two may derive, in part at least, from reactions of neophyl radicals. Notably, no benzyldimethylmethane was detected but configurational rearrangement of the neophyl radical is generally slower than its diffusion from the solvent cage where it is formed.[28]

In an effort to support further the proposition of Pt–C homolysis, photolysis of 1 was carried out in the presence of the spin-trapping reagent 2-methyl-2-nitrosopropane, Bu^tNO. The radical $Bu^t(PhCMe_2CH_2)NO$ (as well as some Bu^t_2NO) was, indeed, detected by ESR measurement immediately subsequent to irradiation of 1 in toluene-d_8. An independent experiment in the absence of 1 established that the spin trap is itself a photolytic (*tert*-butyl) radical source. The production of neophyl radicals under these conditions by an S_H2 process[29] cannot, therefore, be excluded entirely, but it would seem an unlikely coincidence that this was universally the case, particularly in view of the already strong indications of radical participation.

Formation of the metallacycle $\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}$(dppe) also stems, most plausibly, from the transient Pt(I) product of initial Pt–C homolysis. There was no significant difference in cyclization efficiency between $Pt(CH_2CMe_2Ph)_2(dppe)$ and $Pt(CH_2CMe_2C_6D_5)_2(dppe)$ when they were photolyzed in benzene (Table II), indicating little or no kinetic isotope effect—in contrast with thermolytic metallacyclization. A scheme in which photoinduced Pt–P dissociation provides a facile entry to the thermolytic C–H activation pathway at the (nominally) tricoordinate Pt(II) intermediate (cf. Scheme II) can be effectively excluded on energetic grounds. At >110 °C in the thermolytic rearrangement, Pt–P scission is *not* rate-limiting (vide supra) and H-transfer is a major energetic demand. It is not reasonable that this same sequence would be less energetic if prefaced by a photochemically induced Pt–P dissociation. Its rate at −5 °C will be negligible. On the other hand, there is good evidence that Pt–C homolysis *is* occurring under the prevailing conditions (vide supra). The absence of isotopic rate suppression indicates that the most energetic process precedes hydrogen transfer. The organic product of photocyclization of $Pt(CH_2CMe_2C_6D_5)_2(dppe)$ (in benzene-d_0) was identified (by ^1H NMR and GCMS methods) as $C_6D_5CMe_2CH_2D$; in this case, the migrating aromatic hydrogen is transferred quantitatively to the departing carbon, as in the thermolytic reaction. This and the lack of rearranged, benzyldimethylcarbinyl-derived products reinforce the impression that this hydrogen transfer also takes place rapidly within the solvent cage, subsequent to Pt–C homolysis. A "crossover" experiment—irradiation of a 1:1 mixture of 1-d_0 and 1-d_{10} and examination of the deuterium distribution, to exclude absolutely the incidence of H-abstraction by a neophyl radical which had migrated from a *different* platinum parent—was, therefore, deemed superfluous. In toluene-d_0, a significant fraction (ca. 45 mol %) of the organic photoproduct was $D_5C_6C(CH_3)_3$ and some $H_5C_6CH_2D$ was also evident. These figures cannot, however, be used as a reliable measure of the relative importance of the two paths under normal circumstances, since they will certainly reflect contributions by kinetic isotope effects of indeterminate magnitude.

Scheme IV



R = CH_2CMe_2Ph or CH_2Ph

Two plausible H-transfer pathways can be envisaged, which differ only in the extent to which the metal interacts with the migrating hydrogen (Scheme IV). Present data do not allow discrimination between them. At one extreme, the rearrangement can be visualized essentially as an intramolecular S_H2 attack by Pt(I) at aromatic carbon, generating the (η^1-cyclohexadienyl)platinum species X, from which hydrogen is rapidly—perhaps synchronously—scavenged by the caged neophyl radical. This is a common outcome in conventional bimolecular nucleophilic subsitution reactions at aromatic carbon sites, which are frequently characterized by the notable absence of primary hydrogen isotope effects on rate.[30] In this instance, either Pt–C homolysis might be truly rate-limiting or else formation of the hexadienyl intermediate may

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(26) Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754.

(27) Wilen, S. H.; Eliel, E. L. *J. Am. Chem. Soc.* **1958**, *80*, 3309.

(28) Whitesides, G. M.; Panek, E. J.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 232.

(29) (a) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345. (b) Davies, A. G.; Roberts, B. P. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 547.

(30) (a) Connery, R. J.; Price, C. C. *J. Am. Chem. Soc.* **1958**, *80*, 4101. (b) Eliel, E. L.; Meyerson, S.; Welvart, Z. *J. Am. Chem. Soc.* **1960**, *82*, 2936. (c) Saltiel, J. S.; Curtis, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 2056.

have the most energetic transition state.

Alternatively, while thermolytic oxidative addition to Pt(II) is not feasible in the prevalent temperature regime, the same is likely not to be true for addition to a 15-electron Pt(I) center. A parallel may be drawn with 17-electron species, which have been shown in general to be highly reactive compared to their 18-electron counterparts, particularly in sequences which result in 19-electron derivatives.[31] Expulsion of (atomic) hydrogen from the resultant hydridoplatinum(III) complex Y may then be spontaneous or be assisted by a neighboring neophyl (or benzyl) radical. In any event, Pt–C homolysis would necessarily be rate-controlling in this instance.

The platinaindan itself was recovered unchanged after photolysis in toluene for 20 h (Table II). Thus, neither $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$ nor B is produced from $Pt(2\text{-}C_6H_4CMe_2CH_2)(dppe)$ once it has formed. Photolysis of $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$ alone in toluene-d_0, on the other hand, afforded $Pt(2\text{-}C_6H_4CMe_2CH_2)(dppe)$ and B in amounts closely similar to those in the reaction of $Pt(CH_2CMe_2Ph)_2(dppe)$. No other organoplatinum products were detectable. Clearly, on the reasonable assumption of mechanistic parallels (Scheme III), generation of the benzyl radical is more favorable than homolytic ejection of the neophyl fragment from A. This is also apparent in the small but significant increase in decay rate of A relative to that of 1. The low apparent photoefficiency for these rearrangements[32] may be attributed in large part to the readiness of radical recapture within the solvent cage. In relation to this, the substantial rate advantage for photolytic disappearance of 1 in toluene-d_0, relative to that in toluene-d_8, is in accord with the parasitic role of the neophyl/benzyl radical exchange reaction (which ultimately generates A) in depleting the availability of solvent-caged neophyl radicals for regeneration of 1.

Photolytic rearrangement of $PtR_2(dppe)$ in chlorocarbon media also involved facile Pt–C homolysis and release of alkyl radicals (R = Me, Et, CH_2Ph).[8] This was not the primary photochemical process, however, but occurred subsequent to a photoinduced reaction with a solvent molecule to generate a Pt(III) (or Pt(IV)) intermediate. Little or no reactivity was observed in hydrocarbon solvent (benzene), although there was some indication that ethyl radicals *are* primary photoproducts from $PtEt_2(dppe)$ under these conditions. The reaction times, though, were extremely short compared to those in the present work.

The identity of the minor product B (≤9 mol % of the total) and, therefore, the nature of the minor photochemical process for both $Pt(CH_2CMe_2Ph)_2(dppe)$ and $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$ remain unclear. Comparably small amounts of insoluble residues—recovered from (thermolytic) reactions involving zerovalent platinum–phosphine species—also eluded characterization.[4a] The small quantities in which B is formed, its limited solubility (even in acetone-d_6), and its correspondingly poor crystallinity precluded ^{13}C NMR, molecular weight, or diffractometeric studies. Infrared spectroscopy was inconclusive, as were ^1H NMR measurements, although no indications of hydridometal derivatives were detectable. Several possibilities for B can, however, be excluded. The ^{31}P NMR characteristics (in toluene-d_8) of an independently synthesized sample of the (yellow) zerovalent metal derivative $Pt(dppe)_2$(δ 29.8, $^1J_{Pt-P} = 3730$ Hz, in acetone-d_6) differ from those of B (δ 36.3, $^1J_{Pt-P} = 3468$ Hz). The η^2-alkene complex $Pt(\eta^2\text{-}C_2H_4)(dppe)$ does display broadly similar coupling ($^1J_{Pt-P} = 3640$ Hz) but did not react (below its decomposition temperature) to form a corresponding complex with 2-methyl-1-phenylprop-1-ene, which is itself a minor reaction product (vide supra). In any event, for the two phosphorus nuclei to appear equivalent (as observed for B), the coordinated alkene must be undergoing rapid stereochemical exchange (mere rotation about the $Pt–C_2$ axis would not be sufficient); cooling an acetone-d_6 solution of B to −20 °C produced no change in the observed ^{31}P NMR spectrum other than intensity loss and slight broadening, due to precipitation. The ready reactivity of B with chloroform-*d* prompted an investigation of whether the NMR characteristics observed in acetone-d_6 might also be the result of solvent reaction. Formation of a (pinacolato)platinum(II) species, $Pt(OCMe_2CMe_2O)(dppe)$, by oxidative cycloaddition seemed one likely possibility; the corresponding dimethoxoplatinum(II) derivative displays $^1J_{Pt-P} = 3287$ Hz.[33] $Pt(OCMe_2CMe_2O)(dppe)$ was found, however, to have $^1J_{Pt-P} = 3199$ Hz (in acetone-d_6).[34] The incidence of a dimeric (or higher nuclearity) Pt(I) species is also inconsistent with the NMR data; longer range Pt–P coupling should be observable, in the presence of Pt–Pt bonding. A dimeric structure where dppe acts as a monodentate ligand to two distal Pt centers—$[(OCMe_2CMe_2O)Pt(\mu\text{-}dppe)_2Pt(OCMe_2CMe_2O)]$, for example—cannot be excluded. In view, however, of the evident stability of the mononuclear isomer $Pt(OCMe_2CMe_2O)(dppe)$, this must be considered unlikely, although the insolubility does seem to indicate an oligomeric or polymeric composition.

Summary

$Pt(CH_2CMe_2Ph)_2(dppe)$ (1) undergoes thermolytic rearrangement via intramolecular aromatic C–H activation and H-transfer to give the platinacycle $Pt(2\text{-}C_6H_4CMe_2CH_2)(dppe)$ (2) and *tert*-butylbenzene. The indications are that scission of one Pt–P bond is an important mechanistic prerequisite but that oxidative C–H addition to the 14-electron metal center involves the most energetic transition state (Scheme II). Photolytically induced rearrangement of 1 yields predominantly the same organoplatinum product. In this case, primary Pt–C homolysis is most probably rate-limiting and the resultant 15-electron intermediate is highly labile. In a solvent with sufficiently reactive C–H bonds—namely, toluene-d_0—a rapid radical-exchange and -recapture sequence may occur to generate the benzylplatinum derivative $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$ (A). This species is similarly photoreactive, again affording mainly platinaindan 2, following homolysis of the more labile benzyl–platinum link (Scheme III). We are continuing to explore the en-

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[31] Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

[32] For example, the overall quantum yields for (initial) photoproduction of $Pt(2\text{-}C_6H_4CMe_2CH_2)(dppe)$ from $Pt(CH_2CMe_2Ph)_2(dppe)$ and $Pt(CH_2CMe_2Ph)(CH_2Ph)(dppe)$ in toluene-d_8 are estimated to have upper limits of $\phi = 1.13 \times 10^{-4}$ and 1.26×10^{-4}, respectively. Although they correspond interestingly, these figures have little absolute, quantitative significance, due to the uncertainties in such factors as the nature of the photoexcitation, the wavelength responsible, inner filter effects, the lifetime(s) of the excited state(s), and the variety of quenching processes (other than product formation) which may be envisioned. See, for example, ref 23.

[33] Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.

[34] $Pt(OCMe_2CMe_2O)(dppe)$ was synthesized by treatment of $PtCl_2(dppe)$ with dilithium pinacolate in pinacol. We shall report independently on the behavior of this new cyclic dialkoxoplatinum(II) derivative: Hardy, D. T.; Young, G. B. Unpublished work.

hanced reactivities of odd-electron organometallic fragments.

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Registry No. 1, 88864-12-4; 1-d_{10}, 141439-21-6; 2, 141439-19-2; A, 141439-24-9; Pt(Ch_2CMe_2Ph)$_2$(cod), 88864-93-1; $ClCH_2CMe_2Ph$, 515-40-2; $PtCl_2$(cod), 12080-32-9; Pt($CH_2CMe_2C_6D_5$)$_2$(cod), 118334-63-7; PtCl(CH_2CMe_2Ph)(cod), 141439-20-5; PtCl(CH_2CMe_2Ph)(dppe), 141439-22-7; Pt(CH_2Ph)(CH_2CMe_2Ph)(cod), 141439-23-8; $ClCMe_2CH_2Ph$, 1754-74-1; Mg(CH_2CMe_2Ph)Cl, 35293-35-7; Pt(CH_2CMe_2Ph)(CMe_2CH_2Ph)(cod), 141439-25-0; Pt(PhCH$=$$CMe_2$)(dppe), 141439-26-1; PhCH$=$$CMe_2$, 768-49-0; Pt($C_2H_4$)(dppe), 83571-74-8; Pt($CH_2CMe_2Ph$)(2-$C_6H_4CMe_3$)(dppe), 141439-27-2; D_2, 7782-39-0.

OM910515M

Preparation, Solution Structures, and Nucleophilic Reactions of Chiral, Bimetallic Complexes: [(μ-η^2,η^3-propargylium)$Co_2(CO)_5P(C_6H_5)_3$]BF_4

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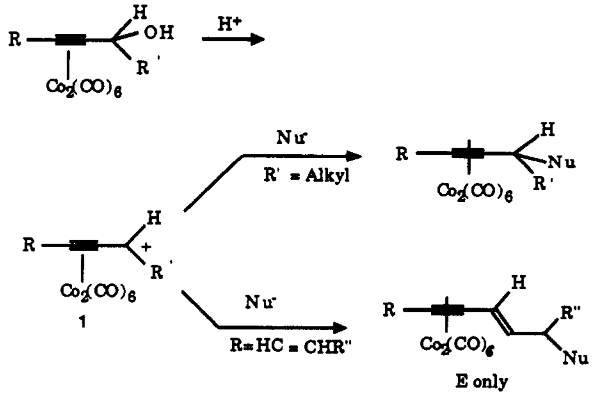
Chiral complexes of the type [(μ-η^2,η^3-$R^1C_2CR^2R^3$)$Co_2(CO)_5PPh_3$]BF_4 (**3**) have been synthesized and characterized. Formation of **3** via protonation of the corresponding alcohol complexes [(μ-η^2,η^2-R^1C_2C(OH)R^2R^3)$Co_2(CO)_5PPh_3$ (**2**) proceeds readily. Where diastereomeric alcohol complexes are available (smaller R^2 substituents), protonation of either isomer gives the same initial mixture of cations with good stereoselectivity; single isomeric cations are obtained where R^2 = ^{i}Pr or ^{t}Bu. The preferred (or exclusive) isomer has an anti geometry on the basis of difference NOE NMR experiments with the –$Co(CO)_2PPh_3^+$ unit η^3-bonded. The isomeric mixtures slowly equilibrate (ΔG^{*} = 17–20 kcal/mol) in acetone solution to ca. a 1:1 anti/syn ratio. Spin saturation transfer experiments failed to detect the intervention of an enantiomerization process. Quenching those complexes having smaller R^2 groups with oxygen-centered nucleophiles yields primarily the less stable (1*S**,2*S**,3*R**) diastereomers, whereas the complexes **3** with R^2 = ^{i}Pr or ^{t}Bu are quenched to re-form the original (1*R**,2*S**,3*R**) isomer. Carbon nucleophiles have not been successfully added. Structural and mechanistic models are proposed to explain these results.

Introduction

Transition metal-directed asymmetric synthesis has been an important goal of organic and organometallic chemists for several years. Some impressive success has been achieved using monometallic complexes in both stoichiometric[1] and catalytic[2] reactions. On the other hand, success with polynuclear systems has been negligible, in part because of the limited access to and stereochemical instability of such complexes[3] and also because of the paucity of synthetically useful organic transformation of metal clusters.[4]

One of the few classes of polynuclear complexes with demonstrated synthetic organic utility is the (μ-η^2,η^2-alkyne)$Co_2(CO)_6$ system. Two aspects of the chemistry of these complexes have received the most attention synthetically. Their thermal cyclization reactions with olefins (Pauson–Khand reaction[5]) have been widely used as a route to substituted cyclopentenone derivatives. Additionally, the propargylium complexes **1** react as electrophiles with a variety of carbon nucleophiles to provide propargylated organics (following demetalation) with complete regioselectivity (eq 1[6]). Recently, we have been



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