Rearrangements of Neophylplatinum(II) and Related Derivatives via Intramolecular Aromatic and Aliphatic δ-Carbon–Hydrogen Bond Activation: The Crystal and Molecular Structure of *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)$

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Summary: Asymmetric complex *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)$ (**2**) in toluene solution favors aromatic over aliphatic δ-C–H transfer during metallacyclization to platinaindan $(Et_3P)_2Pt(2\text{-}C_6H_4CMe_2CH_2)$ (**3**) but is not intermediary in the more rapid formation of **3** from isomeric dineophyl complex $(Et_3P)_2Pt(CH_2CMe_2Ph)_2$ (**1**) under the same conditions. Single-crystal X-ray diffraction and solution NMR studies both suggest conformation restrictions in **2**.

The mechanistics of activation of C–H bonds by metals are currently topical.[1] Recently we reported that dineophyl (2-methyl-2-phenylpropyl) derivatives of platinum(II) in toluene solution readily undergo an intramolecular δ-hydrogen transfer from an aromatic carbon, forming 1-platinaindan with elimination of *tert*-butylbenzene.[2] In mechanistic studies of this apparently simple rearrangement it is important to prove that other conceivable pathways do not contribute significantly. From THF/methanol solutions of *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)_2$ (**1**) which had been maintained at low temperatures, we have recovered, in low yield, the isomeric *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)$ (**2**). The molecular structure was suggested by ^1H and ^{31}P NMR characteristics[3] and confirmed by an X-ray diffraction study. Such isomerization of neophylmetals has been proposed,[4] but the 2-*tert*-butylphenyl derivative could not be isolated. Complex **2** is also accessible by reaction of $(COD)Pt(CH_2CMe_2Ph)I$ with $Mg(2\text{-}C_6H_4CMe_3)Br$,[5] and subsequent replacement of 1,5-cyclooctadiene (COD) by 2 equiv of PEt_3.

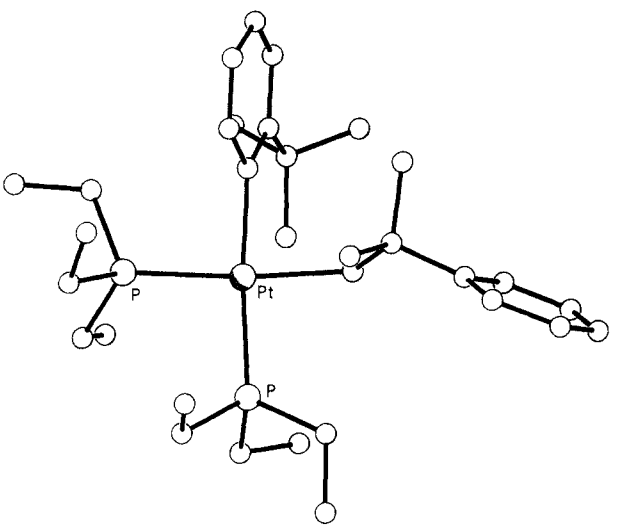
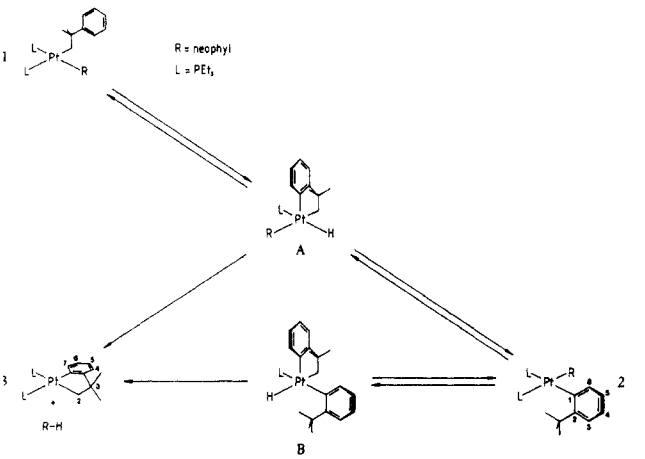


Figure 1. Molecular structure of *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CMe_3)$ (**2**).

Scheme I



Crystal data: $PtC_{32}H_{56}P_2$, monoclinic, a = 10.052 (2) Å, b = 16.222 (3) Å, c = 20.593 (3) Å, β = 98.87 (1)°, U = 3317.8 Å^3 (at 20 °C), space group $P2_1/n$, Z = 4. X-ray data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω-scan technique with Cu Kα radiation. A total of 3385 independent reflections were measured (to θ = 50°), of which 625 were "unobserved". Least-squares refinement of the structure has now reached R = 0.039.

Figure 1 shows the molecular structure of **2**. Within the square-planar coordination of platinum, the two cis Pt–P bonds are 2.322 (3) and 2.331 (2) Å, typical for the type of compound.[6] Of the two Pt–C bonds, the one to phenyl carbon, 2.080 (9) Å, is slightly shorter than that to the neophyl moiety, 2.133 (7) Å. There is a slight tetrahedral distortion of the platinum coordination, such that the trans P–Pt–C angles are ca. 174°. Other significant features are the direction of the neophyl phenyl substituent away from the metal, and the relatively close encroachment (Pt···H = 2.77 Å) by the *tert*-butyl group which occupies axial space and holds the aryl ligand perpendicular to the coordination plane.

In toluene, **2** (like **1**) undergoes thermal rearrangement

(1) See, for example: (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *Ibid.* **1984**, *106*, 1121. (c) Stoutland, P. O.; Bergman, R. G. *Ibid.* **1985**, *107*, 4581. (d) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (f) *Ibid.* **1985**, *107*, 620. (g) Hoyano, J. K.; Graham, W. A. G.*Ibid.* **1982**, *104*, 3723. Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *Ibid.* **1983**, *105*, 7190. (h) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *Ibid.* **1982**, *104*, 107. (i) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *Ibid.* **1982**, *104*, 6994. (j) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (k) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425. (l) Baudry, D.; Ephritikhine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235. (m) Kitajima, N.; Schwartz, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 2220. (n) Foley, P.; DiCosimo, R.; Whitesides, G. M. *Ibid.* **1980**, *102*, 6713. (o) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *Ibid.* **1982**, *104*, 124. (p) Tulip, T. H.; Thorn, D. L. *Ibid.* **1981**, *103*, 2448. (q) Saillard, J.-Y.; Hoffman, R. *Ibid.* **1984**, *106*, 2006. (r) Rothwell, I. P. *Polyhedron* **1985**, *4*, 2.

(2) Griffiths, D. C.; Young, G. B. *Polyhedron* **1983**, *2*, 1095.

(3) NMR data for **2**: $\delta(^{31}P_A)$ 0.7; $\delta(^{31}P_B)$ −4.5; $^1J(P_A\text{–}Pt)$ = 1771 Hz; $^1J(P_B\text{–}Pt)$ = 1718 Hz; $^2J(P_A\text{–}P_B)$ = 11 Hz. ^1H NMR (C_6D_6, 250 MHz): δ 8.06 m (^3J(Pt–H) = 59 Hz, ^3J(H–H) = 7 Hz) [*tert*-butylphenyl H_6], 7.71 dd (^3J(H–H) = 8 Hz, ^4J(H–H) = 1.2 Hz) [neophyl H_2], 7.40 ddd (^4J(Pt–H) = 18 Hz, ^3J(H–H) = 8 Hz, ^4J(H–H) = 3 Hz, ^5J(H–H) = 1.5 Hz) [*tert*-butylphenyl H_3], 7.26 t (^3J(H–H) = 7.7 Hz [neophyl H_3], 7.13–7.00 m [neophyl H_4 and *tert*-butylphenyl H_4, H_5], 2.10 m (^2J(Pt–H) = 85 Hz) [$PtCH_2$–], 1.85 [$-C_4H_9$], 1.61 [$PtCH_2CC^aH_3$], 1.42–1.23 m [PCH_2], 1.18 [$PtCH_2CC^bH_3$], 0.85–0.71 [PCH_2CH_3].

(4) Åkermark, B.; Ljungqvist, A. *J. Organomet. Chem.* **1978**, *149*, 97. Heck, R. F. *Ibid.* **1972**, *37*, 389.

(5) Crawford, M.; Stewart, F. H. *J. Chem. Soc.* **1952**, 4443 and references therein.

(6) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13.

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to $(Et_3P)_2Pt(2\text{-}C_6H_4CMe_2CH_2)$ (**3**) *tert*-butylbenzene. Although it is undetectable (by NMR) during cyclization of **1** in the range +60 to −20 °C, there is a suspicion that **2** may lie on the mechanistic pathway between **1** and **3** either by a second aromatic C–H scission via B or by reversion to A (Scheme I)[7] by aliphatic C–H activation. The rate of conversion of **2** to **3** ($k_{35°C}$ = 1.5 × 10^{-5} s^{-1}) is, however, considerably slower than that of **1** to **3** ($k_{35°C}$ = 1.8 × 10^{-4} s^{-1}). This effectively excludes **2** as a thermal intermediate between **1** and **3**, in toluene solution at least. Corresponding isomerization of the dineopentylplatinum analogue was also shown to be unimportant during its metallacyclization.[1n]

It remained of interest to discover if metallacyclization of **2** occurs by aromatic or aliphatic H migration. To this end we examined the reactions of deuterated analogues *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6HD_3CMe_3)$ (**2a**)[8] and *cis*-$(Et_3P)_2Pt(CH_2CMe_2C_6D_5)(2\text{-}C_6H_4CMe_3)$ (**2b**). In thermolyses of **2a** in benzene[9] at 65 °C, an average of 28% of transferred hydrogen originates from the *tert*-butyl group.[10] Thence we estimate[11] that the difference in activation energy, $\Delta\Delta G^{\ddagger}_{338K}$ is 7.0 ± 1.0 kJ mol^{-1} in favor of aromatic site activation via B (Scheme I), in spite of the crystallographic indications that the aromatic C–H bonds are conformationally the less accessible (vide infra). On the other hand, rearrangement of **2b** at 54 °C yields both **3**-d_0 and **3**-d_4 in 73:27 ratio. The kinetic isotope effect on metallacyclization of **1** has now been established: k_H/k_D = 3.4. Adopting a similar value as reasonable for **2b** compared with **2**, with statistical allowance for differing aromatic and aliphatic site availabilities, leads to an estimate of $\Delta\Delta G^{\ddagger}_{327K}$ = 4.5 ± 1.0 kJ mol^{-1}, again in favor of aromatic C–H activation. Qualitatively similar conclusions have emerged from recent studies on intermolecular attack on C–H bonds,[1a,e,g] but the relatively small energy difference indicated here is not necessarily a truly quantitative measure of discrimination between aromatic and aliphatic sites; the two pathways followed in this case do not have strictly comparable intermediates, and the intimate nature of the mechanisms and their rate limiting steps are not yet known. Experiments aimed at more precise understanding are in progress. Similar controls clearly operate for the related isopropylphenyl derivative *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CHMe_2)$ (**4**) which also cyclizes predominantly to **3** and isopropylbenzene.

The slower cyclization, via aromatic activation, of **2** (and **4**) compared with **1** may have a primarily steric origin. The molecular structure shows that the phenyl ring of the neophyl ligand is oriented away from the metal. Any approach by this group toward the metal will be hindered (relative to **1**) by the bulky *tert*-butyl substituent obstructing one axial entry to the coordination sphere. Some such conformational restriction is maintained in solution; the two methyl elements of the neophyl ligand give rise to different chemical shifts at 1.61 and 1.18 ppm in the ^1H NMR spectrum of **2** at ambient temperature. Restricted rotation about either or both of the Pt–C bonds accounts for this; the consequent absence of a molecular plane of symmetry places the methyl groups in diastereotopic environments. These signals show no significant change at temperatures up to the onset of metallacyclization. We are thus unable to distinguish which ligand is conformationally locked, nor can we estimate the rotational barrier(s). It is conceivable, of course, that surmounting this restriction is part of the energetic requirement for metallacyclization. The related species *cis*-$(Et_3P)_2Pt(2\text{-}C_6H_4CHMe_2)Me$ displays similar nonequivalence of the methyl substituents of the isopropyl group, clearly due to restricted platinum–aryl rotation. These signals do coalesce below cyclization temperatures, and we are evaluating the energetics of this system.[12]

In methanol/tetrahydrofuran (1:1) solution at 0 °C, we find by ^{31}P NMR that **2** is indeed formed as an accompaniment to **3** to a relative extent of 1–2%. The reasons for such an apparent increase in steric congestion[13] are not entirely clear, but a polar, coordinating solvent may favor the isomeric configurations of A from which the reductive C–H elimination which yields **2** becomes more likely (Scheme I).

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Supplementary Material Available: Listings of structure factors, atom coordinates and temperature factors, bond angles, and bond lengths (22 pages). Ordering information is given on any masthead page.

(7) Both isomers A and B have only one coordinated Et_3P. Cyclizations of **1** and **2** are both inhibited by the presence of Et_3P in solution, consistent with phosphine dissociation as a prerequisite step (cf. ref 1n,o). While the behavior of **1** is straightforward, rearrangement of **4** to **3** in presence of Et_3P is more complex and occurs partly via competitive pathways and new *trans*-diorganoplatinum species which are still being evaluated: Griffiths, D. C.; Young, G. B., unpublished observations.

(8) Preparation of 2-bromo-*tert*-butylbenzene-3,5,6-d_3 (see ref 5) leads to appreciable H/D scrambling on C_3 and C_5 (which become C_6 and C_4, respectively, in **2**) at the reduction step. This does not affect the integrity of labeling experiments since the extent of site deuteration can be precisely measured by ^1H NMR.

(9) Reactions were carried out in benzene-d_6 since the peaks due to residual methyl protons in toluene-d_8 overlap with C_2 hydrogens in **3** (see ref 10).

(10) Relative extents of aromatic and aliphatic C–H migration are determined from the amount of H substitution on C_7 in **3** (see Scheme I for numbering), measured from the 250-MHz ^1H NMR spectrum by comparing the integral for that signal with that for the hydrogens on C_2 as internal standard.

(11) From $\Delta\Delta G^{\ddagger} = RT \ln (k_1/k_2)$, where k_1 and k_2 are the rate constants for aliphatic and aromatic C–H activation respectively. Since formation of **3** is irreversible the ratio k_1/k_2 is that of the products, after statistical adjustment.

(12) Rzepa, H. R.; Wilkes, D. J.; Young, G. B., unpublished observations.

(13) We have not yet been able to obtain crystallographic data on **1** (or **3**), for a critical comparison.

A General Route to $C_6H_6(CO)_2Mn$–R Complexes via $C_6H_6(CO)_2Mn^-Na^+$. Alkyl Group Migrations from Manganese to the Coordinated Arene Ring

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Summary: A convenient and general entry into $C_6H_6(CO)_2Mn$–R complexes has been achieved via preparation of $C_6H_6(CO)_2MnI$ and reduction in $Na/NH_3(l)$ to yield $C_6H_6(CO)_2Mn^-$ followed by alkylation with R–X (R = $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$, $-CH_2C_6H_5$, $-Si(CH_3)_3$, –H). A study of the migration of alkyl groups from manganese to the arene ring to give 6-endo-substituted cyclohexadienyl complexes is reported.

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