

of a complex of type 2 (δ 4.7, 3.5 and 2.9 (s); -18.6 and -23.0 (dt, 8, 16); -29.2 (t, 16)). The complex was observed by method B and was isolated with Et₂O as an unstable colorless solid.

Iodobenzene. Method A gave no isolable products. Method B gave the spectra shown in Table I, which we assign to [IrH₂(C₆H₅I)₂L₂]BF₄. Displacement study (L = PPh₃): EtOH, dis.

Iodomethane. [IrH₂(MeI)₂(PPh₃)₂]BF₄ could be made by method A from the acetone complex (50 mg, 0.054 mmol) and MeI (0.2 mL, 2.2 mmol) in CH₂Cl₂ (20ml) and was isolated with Et₂O; yield 22 mg, 0.2 mmol (40%). Method B gave the same complex which was formed in essentially quantitative yield but could only be isolated in poor yield (~20%) as colorless crystals with Et₂O (ν (IrH) 2210 (w) cm⁻¹). Displacement studies: EtOH, equil in favor of 1; MeCN, dis. EtI and *i*-PrI gave analogous complexes by method B, but these were not isolated. CH₂I₂ did not give identifiable materials by either method. Satisfactory analyses were never obtained, probably due to the thermal instability of the complexes at 20 °C over several days, except for the MeI complex. Anal. Calcd for C₃₈H₃₈I₂F₄Br: C, 41.87; H, 3.49. Found: C, 41.96; H, 3.66.

Catalytic Studies. The method described in ref 7 was used to measure the effect of the halocarbons (1 molar equiv/mol of Ir) on cyclohexene hydrogenation by [Ir(cod)(PMePh₂)₂]PF₆.

Rates observed relative to CH₂Cl₂ (100%) were as follows: C₆H₅I₂, 0%; C₆H₅Br₂, 78%; C₆H₅Cl₂, 105%; C₆H₅I, 60%; C₆H₅Br, 110%; C₆H₅Cl, 60%.

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Registry No. *cis,trans*-[IrH₂(*o*-C₆H₄I₂)(PPh₃)₂]BF₄, 82582-50-1; *cis,trans*-[IrH₂(*o*-C₆H₄I₂)(PPh₂Me)₂]BF₄, 82598-64-9; *cis,trans*-[IrH₂(*o*-C₆H₄I₂)(PPh₃)₂]BF₄, 82582-52-3; *cis,trans*-[IrH₂(*o*-C₆H₄Br₂)(PPh₃)₂]BF₄, 82582-54-5; *cis,trans*-[IrH₂(*o*-C₆H₄Cl₂)(PPh₃)₂]BF₄, 82582-56-7; [IrH₂(IPh)₂(PPh₃)₂]BF₄, 82582-58-9; [IrH₂(IPh)₂(PPh₂Me)₂]BF₄, 82582-60-3; [IrH₂(IPh)₂(C₆H₄Me-*p*)₂]BF₄, 82582-62-5; [IrH₂(IPh)₂(C₆H₄Cl-*p*)₂]BF₄, 82582-64-7; [IrH₂(IMe)₂(PPh₃)₂]BF₄, 82582-66-9; *cis,cis,trans*-[IrH₂(Me₂CO)₂(PPh₃)₂]BF₄, 82582-67-0.

Supplementary Material Available: A listing of observed and calculated structure factors and tables further bond lengths and angles and molecular planes (13 pages). Ordering information is given on any current masthead page.

Regio- and Stereospecific Nucleophilic Additions to a Metal-Substituted Carbonium Ion, [PtI{MeC₆H₃(CH₂NMe₂)₂-*o,o'*}]BF₄. A Unique Reversible Aryl to Cyclohexadiene Conversion at a Platinum(II) Center

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The cationic complex [PtI{MeC₆H₃(CH₂NMe₂)₂-*o,o'*}]BF₄, 1, which can be described as a metal-substituted arenonium ion, is susceptible to attack by anionic nucleophilic reagents. At room temperature or above aqueous reagents give rise to products resulting from cleavage of either the single C-Me or C-Pt σ bond. At lower temperature in appropriate solvents bases such as PhC⁻, CH(CO₂Me)₂⁻, OMe⁻, and OH⁻ produce neutral products arising from nucleophilic addition to the substituted C₆H₃ ring. Two types of product are possible with a metal-substituted cyclohexa-2,4-diene or cyclohexa-2,5-diene ring system, corresponding respectively to either "ortho" or "para" addition to the arenonium ion. Of these neutral species only the phenylacetylide complex does not react with anhydrous HBF₄ to regenerate 1. Together with the formation of 1 from the interaction of [Pt{C₆H₃(CH₂NMe₂)₂-*o,o'*}(H₂O)]BF₄, 2, with MeI the reactions reported form a unique, fully reversible, aryl-to-cyclohexadiene conversion in a metal coordination sphere.

Introduction

One of the most fundamental areas in organometallic chemistry is the study of the activation of organic molecules by metal centers. Surveys of the coordination chemistry of nickel,¹ palladium,^{2,3} and platinum^{3,4} have been made, and there is current interest in complexes of these metals containing delocalized systems such as allyl,⁵ arene,⁶ and cyclopentadienyl.⁷⁻⁹ During studies of a

platinum system containing a σ -bonded aryl ring with "built-in" ligand substituents, i.e., [PtBr{C₆H₃(CH₂NMe₂)₂-*o,o'*}], which has trans-situated N donor atoms, we isolated an unusual complex, [PtI{MeC₆H₃(CH₂NMe₂)₂-*o,o'*}]BF₄, 1,^{10,11} the structure of which (determined by X-ray methods) is shown in Figure 1. This information together with ¹H NMR data and CNDO/S calculations suggests that the C₆ ring is σ bonded to the square-planar platinum(II) center and as a consequence the positive charge of this cation is to a large degree located within the clearly nonplanar ring. This description infers

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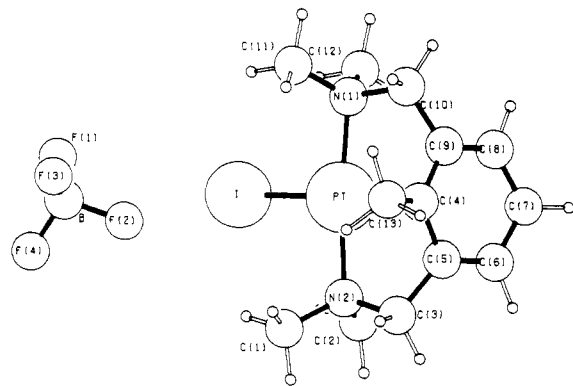


Figure 1. A PLUTO drawing of 1 showing the adopted numbering scheme.

that the cation is in fact an organic arenonium ion of the Wheland intermediate type¹² which has been stabilized by having as substituents a σ -bonded metal atom and two chelate-bonded CH_2NMe_2 ligands.

This unique organometallic analogue of one of the intermediates (transition states) formed in the electrophilic addition reactions on aryl ring systems should possess interesting reactivity toward nucleophilic reagents. In this paper we report the syntheses and characterization of the varied products resulting from such reactions.

Experimental Section

General techniques and apparatus were the same as in other recent papers from this laboratory.¹³ [2,6-Bis(dimethylamino)methyl]toluene-*N,N',C'*iiodoplatinum(II) tetrafluoroborate, $[Pt\{MeC_6H_3(CH_2NMe_2)_{2-o,o'}\}]BF_4$, 1, was prepared as previously described.^{10,11} KOH and NaOMe were commercially available products. The dimethyl malonate anion was used as a suspension of the sodium and potassium salts in Et_2O , prepared from the reaction of $CH_2(CO_2Me)_2$ with $NaK_{2,8}$ alloy based on a method described for $CH_2(CO_2Et)_2$.¹⁴ $PhC\equiv CLi$ and $PhC\equiv CNa$ were used as suspensions in Et_2O , prepared from the reaction of $PhC\equiv CH$ with *n*-BuLi¹⁵ and sodium foil,¹⁶ respectively.

"Ortho" Addition Products 4 from 1. (a) $PhC\equiv C^-$. To a suspension of dark red 1 (200 mg, 0.325 mmol) in THF (10 mL) at $-50^\circ C$ was added dropwise an approximate twofold excess of $PhC\equiv C^-$ (Na^+ or Li^+ salt) suspended in Et_2O . After being stirred at -50 to $-30^\circ C$ for 0.5 h, the yellow cloudy solution was evaporated to dryness at $0^\circ C$ in vacuo. The residue was extracted with benzene, the solution, after filtration, evaporated to dryness, and the precipitate recrystallized from benzene/pentane to afford 4a (180 mg, 88%). Anal. Calcd for $C_{21}H_{27}IN_2Pt$: C, 40.07; H, 4.32; N, 4.45. Found: C, 40.48; H, 4.32; N, 4.26.

(b) OH^- . To a suspension of 1 (200 mg, 0.325 mmol) in THF/ H_2O (10:1 mL) at $15^\circ C$ was added excess KOH (56 mg, 1.0 mmol), and the mixture was stirred for ca. 2 h until no red starting material could be seen to be present. The mixture was evaporated to dryness in vacuo at this temperature and the residue extracted as above to yield 4c (155 mg, 87%). Like complex 3b, 4c was never satisfactorily freed of traces of the benzene solvent trapped in the crystal lattice. Anal. Calcd for $C_{13}H_{23}IN_2OPt \cdot \frac{1}{12}C_6H_6$: C, 29.38; H, 4.29; I, 22.99; N, 5.07; O, 2.89. Found: C, 29.16; H, 4.33; I, 23.05; N, 5.03; O, 3.09.

(c) OMe^- . In a manner similar to that used in b above, 1 was reacted in a THF/ H_2O (10:0.5 mL) mixture with excess NaOMe

(50 mg, 0.93 mmol) at $-20^\circ C$, and the solvents afterward were removed at $0^\circ C$. Extraction with benzene then afforded pure 4b (165 mg, 91%). Anal. Calcd for $C_{14}H_{25}IN_2OPt$: C, 30.06; H, 4.50; I, 22.69; N, 5.09. Found: C, 30.05; H, 4.53; I, 22.64; N, 4.94.

"Para" Addition Products 3 from 1. (i) $CH(CO_2Me)_2^-$. In a manner identical with that described above for $PhC\equiv C^-$ (a), 1 was treated with an excess of $CH(CO_2Me)_2^-$ (Na^+ and K^+ salt mixture) at -50 to $-30^\circ C$. Extraction of the dry residue with CH_2Cl_2 and evaporation in vacuo afforded 3a (94%). Anal. Calcd for $C_{18}H_{29}IN_2O_4Pt$: C, 32.78; H, 4.44; I, 19.24; N, 4.25; O, 9.71. Found: C, 33.15; H, 4.51; I, 19.24; N, 4.15; O, 9.61.

(ii) OMe^- . Reaction of 1 (200 mg, 0.325 mmol) suspended in MeOH (10 mL) at room temperature with excess NaOMe (60 mg, 1.11 mmol) gave within 30 min a pale yellow solution and suspension. After evaporation to dryness in vacuo at room temperature, extraction with CH_2Cl_2 or C_6H_6 and recrystallization from the latter yielded 3b (155 mg, 89%). Anal. Calcd for $C_{14}H_{24}IN_2OPt \cdot \frac{1}{12}C_6H_6$: C, 30.77; H, 4.54; I, 22.43; N, 4.95. Found: C, 31.01; H, 4.58; I, 22.39; N, 4.95.

Reaction of 1 with NaX. A suspension of 1 (100 mg, 0.163 mmol) in H_2O (20 mL) was reacted with a tenfold excess of NaX at $80 \pm 10^\circ C$ until the original red solid was totally converted into a white precipitate (ca. 1 h). The solid was collected by filtration, washed with water (3 mL), and dried in vacuo. Extraction with CH_2Cl_2 (5 mL), filtration, and evaporation gave a white residue identified as a mixture of $[PtX\{C_6H_3(CH_2NMe_2)_{2-o,o'}\}]$ and $[Pt\{C_6H_3(CH_2NMe_2)_{2-o,o'}\}]$ by 1H NMR spectroscopy (see text). For $X = I$ the product yield was found to be $>95\%$.

Reaction of 1 with NaCN. A suspension of 1 in D_2O was treated with a tenfold excess of KCN; 1H NMR spectra of the resulting cloudy colorless solution showed only one free organic compound identified as *o,o'*-(Me_2NCH_2) $_2$ C_6H_3Me .

Reaction of 3a,b and 4b,c with H^+ . The following procedure is applicable to all complexes. To a finely ground sample of the yellow platinum complex (25 mg) at room temperature was slowly added an excess of 54% HBF_4 in Et_2O (0.5 mL) and the suspension stirred for 5 min. The solution was decanted from the solid (sometimes oil) which was then washed thoroughly several times with Et_2O and pentane. The red solid was dried in vacuo and identified as 1 by IR spectroscopy. Yields are typically $>90\%$.

Results

The ionic complex $[Pt\{MeC_6H_3(CH_2NMe_2)_{2-o,o'}\}]BF_4$, 1, reacts with anionic nucleophiles of several types to give a variety of organometallic products including species in which addition to the cyclic six-membered carbon skeleton has occurred (see Scheme I). Although this benzenonium moiety of 1 is not aromatic, in this paper use of the denotation ortho, meta, and para will be used (for ease of description) with the atom σ bonded to platinum (i.e., C(4) in Figure 1) being considered as the 1-position (C_1) for both 1 and the products shown in Scheme I.

The intensely red complex 1 is soluble in H_2O , in which it has limited stability (vide infra), and upon addition of excess NaCN a colorless solution is formed almost immediately. The 1H NMR spectrum of this reaction mixture only showed the presence of the free organic ligand *o,o'*-(Me_2NCH_2) $_2$ C_6H_3Me ,^{17a} and this shows the cleavage of the Pt-C bond. No attempt was made to identify the inorganic platinum species presumably $[Pt(CN)_3]^{2-}$ and/or $[Pt(CN)_4]^{2-}$.

By comparison, with aqueous solutions of NaX ($X = Cl, Br, \text{ and } I$) complex 1 reacts slowly, even at $70^\circ C$, and

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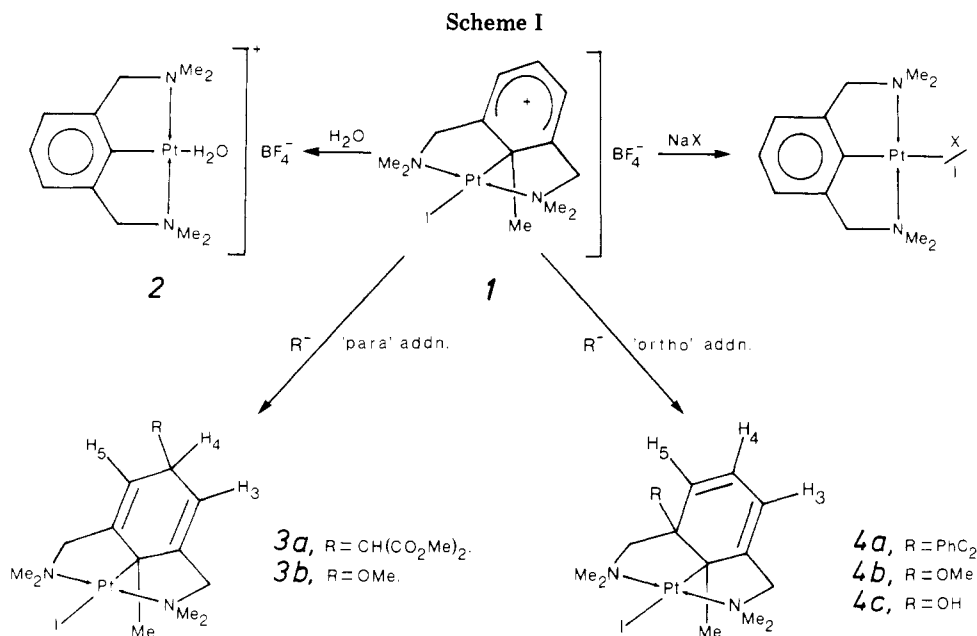
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(17) (a) This reaction with related $[Pt\{C_6H_3(CH_2NMe_2)_{2-o,o'}\}(H_2O)]BF_4$, 2, affords a product whose 1H NMR data is consistent with it being $[Pt(CN)_3\{C_6H_3(CH_2NMe_2)_{2-o,o'}\}]^{2-}$ in which the "built-in" ligands are no longer coordinated to the metal, though the aryl system remains σ Pt bonded. (b) Support for this assumption comes from the observation that 4c in warm H_2O generates neutral $[Pt\{C_6H_3(CH_2NMe_2)_{2-o,o'}\}]$ as the major organometallic species. The absence of stable noncoordinating anion (e.g., BF_4^-) is likely to be the reason that full reversal 4c-2 does not occur.

**Table I^a**

compd {R}, solv	$\delta(\text{H}(4))$	$\delta(\text{H}(3))$ [$J_{4,3}$]	$\delta(\text{H}(5))$ [$J_{4,5}$]	$\delta(\text{NCH}_2)$ [$J_{\text{Pt,H}}$]	$\delta(\text{NCH}_3)$ [$J_{\text{Pt,H}}$]	$\delta(\text{Pt}-\text{C}-\text{CH}_3)$ [$J_{\text{Pt,H}}$]	$\delta(\text{R})$
3a {CH(CO ₂ Me) ₂ }, CD ₂ Cl ₂	3.42	5.29 [4]		2.62, 3.73 [12]	2.93 ^b [40]	1.28 [53]	3.68 ^c 3.16 ^d
3b {OMe}, C ₆ D ₆	4.57	5.19 [5]		1.89, 3.25 [13]	2.57 [42], 2.65 [41]	1.22 [53]	3.19
4b {OMe}, C ₆ D ₆	6.37	5.26 [9]	5.02 [6]	1.78, 3.23 [12], 2.47, 3.44 [13]	2.48 [39], 2.54 [38], 2.63 [38], 2.88 [40]	1.41 [51]	2.99
4a {PhC≡C}, CD ₂ Cl ₂	6.04	5.73 [11]	5.40 [6]	2.53, 3.81 [12], 3.32, 3.51 [13]	2.91 ^b [40], 3.05 [36], 3.30 [41]	1.62 [48]	7.2-7.4
4c {OH}, C ₆ D ₆	6.05	5.46 [9]	5.04 [6]	1.76, 3.21 [12], 2.26, 3.32 [13]	2.48 [40], 2.56 [40], 2.63 [38], 2.83 [40]	1.39 [51]	not obsd

^a J values in hertz. ^b Accidental chemical shift coincidence. ^c CO₂CH₃. ^d C-H ($J_{\text{H},4} = 9$ Hz).

neutral [PtX{C₆H₃(CH₂NMe₂)_{2-*o,o'*}}] species¹¹ eventually precipitate. The rate of the reaction, which involves cleavage of the C_{aryl}-C_{Me} bond (C(13)-C(4) in Figure 1), decreases in the order Cl > Br > I. For X = Cl and Br the isolated material was a mixture of the iodo complex with the corresponding halo complex, the relative ratios being 1:1 and 1:20, respectively, whereas for X = I the iodo complex was isolated virtually quantitatively. The organic products from the reactions are expected to be MeX and/or MeOH though confirmation of this is lacking.

Thus, the reactive nucleophile present when **1** is refluxed in water or aqueous acetone may be OH^{-17b} since under these conditions the final product in >95% yield is cationic [Pt{C₆H₃(CH₂NMe₂)_{2-*o,o'*}}(H₂O)]BF₄, **2**. This is interesting for two particular reasons: first **1** has again formally eliminated MeI (with cleavage of the C_{aryl}-C_{Me} bond), and second, since **2** is the precursor of **1**, through reaction with MeI, one has effectively reversed the original synthetic procedure.

The strong bases CH(CO₂Me)₂⁻, PhC≡C⁻, OMe⁻, and OH⁻, in suitable solvents, react with suspensions of **1** to form neutral platinum complexes in which the nucleophile has added to the benzenonium ring at either the ortho or the para position (see Scheme I). Consequent electron redistribution within the molecule leads to localized bonds in the ring and formation of either a 2,5- or 2,4-cyclohexadiene system with the retention of the Pt-C σ bond at the 1-position of the six-membered carbon ring. The platinum center thus retains its formal oxidation state of +2 with a square-planar geometry in which the built-in ligands remain trans coordinated.

With malonate ion, for example, attack occurs solely at the para position of **1** (C(7) in Figure 1) to afford neutral **3a** containing a nonconjugated 2,5-cyclohexadiene system. The ¹H NMR spectrum (250 MHz) of **3a** shows a distinctive AX₂ pattern, arising from H(3), H(4), and H(5), to high field of the normal aromatic region (see Table I). The proposed structure, with its σ -bonded Pt-C-Me fragment, receives support from the observation of ¹⁹⁵Pt satellites not only on the unique highfield methyl signal but also on the resonances of magnetically and chemically equivalent H(3) and H(5). Attack of dimethyl malonate could theoretically occur at the C(7) atom from either of the two different sides of the benzenonium ring in **1**, thereby giving rise to two possible stereoisomers. Significantly there was no indication in the ¹H NMR spectrum of any resonances attributable to a second organometallic species, and therefore nucleophilic addition is apparently taking place highly stereospecifically.

The phenylacetylide anion, PhC≡C⁻ (as either its sodium or its lithium salt), reacts readily with **1** to afford an uncharged Pt(II) complex **4a** in which, as with the dimethyl malonate ion, attack has occurred stereospecifically on the benzenonium ring system and the Pt-C σ bond is retained. However, in this instance the nucleophiles point of attachment is at an ortho carbon atom (C(5) or C(9) in Figure 1) that bears a -CH₂NMe₂ moiety.

The resultant molecule, which now contains a conjugated 2,4-cyclohexadiene system, is decidedly asymmetric (see Scheme I). This is reflected in the complex ¹H NMR spectrum of **4a**, where the lack of a molecular symmetry plane gives rise to inequivalent CH₂ and NMe₂ groupings,

containing diastereotopic H atoms and Me groups, respectively. The ring protons (H(3), H(4), and H(5)) accordingly produce an allylic resonance pattern for which data and assignments are to be found in Table I.

From the reaction of 1 with OMe^- it is possible to isolate either the ortho or para addition product according to the specific reaction conditions employed (see Experimental Section). Initial studies showed that reaction of this nucleophile (as well as OH^-) could react with 1 to product isomer mixtures and the critical experimental conditions have been optimized to yield single pure compounds. In particular, solvents such as benzene are more suitable for workup than CH_2Cl_2 which on occasion gave rise to mixtures of as yet unidentified species. The pure complexes are readily identifiable by their NMR data, and the isomers show the distinctive features described for 3a and 4a.

The complexes 3a,b and 4a-c are pale yellow to orange solids with fair air stability, though in benzene solution slow decomposition does take place. Furthermore, except for 4a ($R = PhC\equiv C$), they possess one common chemical characteristic: they are susceptible to cleavage of the nucleophilic substituent when treated with strong, non-coordinating acid (HBF_4). The resultant product in high yield is the original cationic complex 1, which is stable to H^+ , and therefore regeneration of the carbonium fragment has occurred.

Discussion

Both 1H NMR and crystallographic data for 1¹¹ give credence to the belief that the organic ligand system can be described as a metal-substituted carbonium ion of the Wheland type and the present results concerning the complexes reactivity towards nucleophiles help confirm this.

The fundamental difference between 1 and the related cationic complex $[Pt\{C_6H_3(CH_2NMe_2)_{2-o,o}\}(H_2O)]BF_4$, 2, is reflected in the varying stabilities of the unique Pt-C σ bonds. With the aqueous cyanide ion complex 1 gives rise to a free organic ligand, o,o' -(Me_2NCH_2)₂ C_6H_3Me , whereas with 2 this σ bond is not disrupted.^{17a} This result may have been anticipated since in 1 the solid-state structure shows an extremely long, and presumably weak, Pt-C(4) bond of 2.183 (7) Å. In general the trans N-donor arrangement of the two NMe₂ units, as found in both 1 and 2, is a stable conformation,² and these reactions with CN^- are examples of the few instances where rupture of the two M-N bonds in complexes containing the o,o' -(Me_2NCH_2)₂ C_6H_3 ligand have been observed. For example, PPh_3 reacts readily with 2 to afford $[Pt\{C_6H_3(CH_2NMe_2)_{2-o,o}\}(PPh_3)]BF_4$ ¹¹ with conserved Pt-N interactions, and it is only with neutral compounds such as $[PtBr\{C_6H_3(CH_2NMe_2)_{2-o,o}\}]$ that tertiary phosphines can compete successfully with the nitrogen groups to give either cis- and trans-bis(phosphine) products.¹⁰

It is therefore not surprising that complexes 3a,b and 4a-c, generated from 1 by reaction with charged nucleophiles under mild conditions, should retain the stable trans N-Pt-N configuration.

The σ -Pt-C₁-CH₃ arrangement can be readily deduced from the valence requirements of C₁, and in all complexes this unique methyl group shows a significant $J(^{195}Pt, ^1H)$ of approximately 50 Hz. The magnitude of this coupling is typical not only for $^2J(Pt-CH_3)$,^{18a} as might first be expected, but also for $^3J(Pt-C-CH_3)$ ^{18b} as found here. The

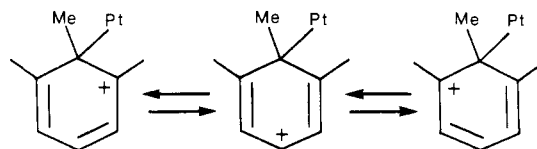


Figure 2. Mesomeric structures for complex 1.

presence of ^{195}Pt satellites for the protons of the $-CH_2NMe_2$ groups readily establishes their N-donor metal coordination¹⁹ while the chemical shifts and coupling pattern of the C_6H_3 ring protons indicate the site of nucleophilic attack.

Explaining why nucleophilic attack occurs on the ring system only at the ortho and para positions is not difficult. CNDO/S calculations on model systems¹¹ pointed to positive charge density at the ortho and para positions, a situation that can be seen as a natural consequence of the mesomeric structures shown in Figure 2. This description of the charge distribution is also fully consistent with 1H NMR shifts of the meta and para protons (δ 7.60 and 8.70, respectively). It is apparent therefore that the ortho and para positions are those activated for nucleophilic attack and with use of two different anionic carbon ligands, namely, $PhC\equiv C^-$ and $(MeO_2C)_2CH^-$, it has been shown that initial attack at the ring is possible at both positions. On the basis of the results from OMe^- and OH^- it is the ortho site, which is also preferentially attacked by the thin flat phenyl acetylide ion, that is the kinetically favorable one.

The preferred site on thermodynamic grounds is the para one, which is attacked by sterically demanding dimethyl malonate and is the ultimate position of methoxide under the slightly more forcing conditions (see Experimental Section). The methoxide complex 4b converts quantitatively into the "para" isomer 3b when suspended in methanol and the use of methanol- d_4 produced almost solely the OCD_3 analogue of 3b. When taken together with the fact that solutions of 4b in benzene do not generate 3b, this indicates an intermolecular mechanism for the isomerization 4b to 3b.

The regioselectivity of nucleophilic attack on 1 is also accompanied by stereospecificity. For the products 3a,b, where the nucleophilic moiety is attached to an ortho carbon atom, a steric explanation only is required. The structure of 1 shows that the hybridization of the ortho carbon centers is clearly distorted from planar sp^2 . Formation of a new σ bond at one of these atoms generates an sp^3 center. This is only possible with retention of the Pt-C σ bond as well as both Pt-N interactions when attack occurs from the more sterically open side of the ring, i.e., exo with respect to the metal. Thus the stereochemical configuration of the products 3a,b is predetermined by the initial geometry of the starting complex 1. Why there should be stereospecific nucleophilic attack at the para position is not immediately apparent since neither the exo nor endo position is particularly hindered. The X-ray structure of 1 does show that these two positions are not equivalent, and for the bulky dimethyl malonate ion a steric factor is likely to be dominant. For the methoxide ion, however, with the assumption that 1H NMR spectroscopy (250 MHz) is sufficiently sensitive to identify the two possible isomers (should they be present), then an electronic factor must be responsible for the observed discrimination. Further study to clarify points such as this is in progress.

Numerous nucleophilic substitution and addition reac-

(18) (a) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* 1972, 11, 1275-1280. (b) Clark, H. C.; Ruddick, J. D. *Ibid.* 1970, 9, 1226-1229.

(19) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* 1982, 21, 2014-2026.

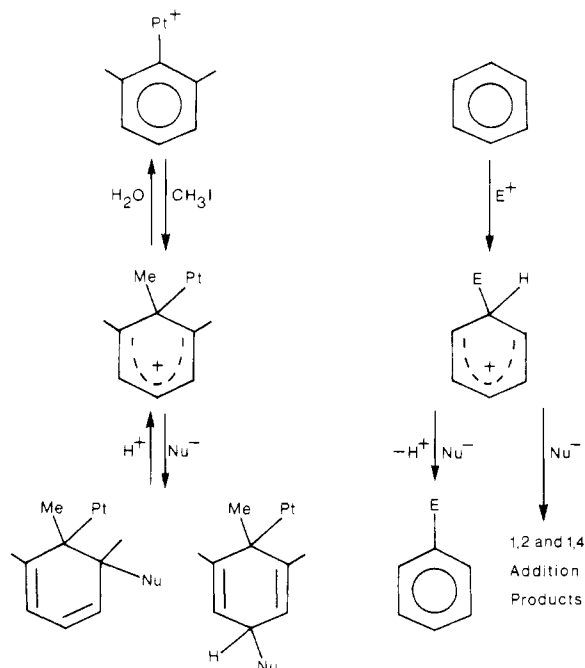


Figure 3. The metal-based aryl-to-cyclohexadiene conversion in relation to aromatic electrophilic substitution.

tions involving organometallic species with η^5 or η^6 ring systems have been reported and in several instances have been shown to have synthetic utility.²⁰ Consequently, to help elucidate the operative mechanism(s), there is currently much interest in those cases where regio- or stereoselectivity is observed.²¹

In our system the nucleophilic additions to arenonium complex 1 (and its synthesis from cationic 2 and MeI) are unique examples of such reactions occurring on a C_6 ring

(20) Birch, A. J.; Jenkins, I. D. "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. I, Chapter I, pp 1-82. Jaouen, G. "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. II, Chapter II, pp 65-120.

(21) See, for example: Birch, A. J.; Stephenson, G. R. *J. Organomet. Chem.* 1981, 218, 91-104 and references therein.

system which has a σ -bonded metal substituent. In many respects the behavior shown has a direct counterpart in electrophilic substitution reactions of benzene rings, with each step stabilized by the Pt-I group (see Figure 3). Some stabilization of the nucleophilic addition products 3 and 4 may be additionally derived from release of ring strain inherent in the two five-membered chelate rings of 1 which contain the CH_2NMe_2 groups. However, much of the chemistry and particularly the stability of 1 can be understood in terms of the nature of the available leaving groups in the various products.

From the organic carbonium ion (Wheland intermediate) the proton, H^+ , is a good leaving group in the presence of a nucleophile. For complex 1 a subsequent step with a nucleophile cannot follow a "normal" electrophilic substitution sequence because both the introduced Me and the Pt-I units are bad leaving groups (due to the presence of a C-C σ bond and strong N-Pt-N coordination, respectively). Under special circumstances however, normal substitution takes place for example with CN^- (which possibly disrupts the Pt-N donor bonds) and those reactions with H_2O and aqueous NaX (that possibly rely on the intervention of hydroxide ion). Unfortunately in the latter instances we know nothing of the intermediates which provide the route to the C-C bond cleavage. Despite this gap in our knowledge the reaction of 1 with H_2O to afford 2 completes a metal center promoted reversible aryl to cyclohexadiene conversion illustrated in Figure 3). The key complex in the various high yield reaction steps is carbonium species 1, and further research is being concentrated on the potential of this complex, not only as a model but also as a route to substituted aryl compounds.

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Registry No. 1, 82581-77-9; 2, 82112-93-4; 3a, 82581-78-0; 3b, 82581-79-1; 4a, 82581-80-4; 4b, 82581-81-5; 4c, 82581-82-6; $PC\equiv C^- Na^+$, 1004-22-4; $PC\equiv C^- Li^+$, 1122-79-8; OH^- , 14280-30-9; NaOMe, 124-41-4; $CH(CO_2Me)_2^- Na^+$, 18424-76-5; $CH(CO_2Me)_2^- K^+$, 61111-62-4; NaI, 7681-82-5; NaCN, 143-33-9; NaCl, 7647-14-5; NaBr, 7647-15-6; $[Pt\{C_6H_3(CH_2NMe_2)_{2-o,o}\}]$, 82112-97-8; $[PtCl\{C_6H_3-(CHNMe_2)_{2-o,o}\}]$, 82112-96-7; $[PtBr\{C_6H_3-(CHNMe_2)_{2-o,o}\}]$, 67507-09-9; HBF₄, 16872-11-0.

Characterization of the Initially Precipitated Complexes from the Reaction of Zeise's Dimer and Hydrocarbons Containing a Cyclopropane Ring

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The initially precipitated complexes resulting from the reaction of Zeise's dimer with four compounds containing a cyclopropane ring have been characterized by MAS/CP NMR spectroscopy. For hydrocarbons 1, 3, and 9, the precipitate has the same *exo*-platinacyclobutane stereochemistry as the pyridine-solubilized complex. The ¹³C NMR resonances for the carbons which are σ bonded to the platinum show an upfield shift of 13-20 ppm on going from the initial precipitated to the pyridine-solubilized complex. In addition, the solid-state NMR spectra were also acquired for (norbornadiene)platinum dichloride (NBD-PtCl₂) and 2-phenylplatinacyclobutane.

Introduction

In nearly all of the examples reported to date, the reaction of Zeise's dimer with compounds containing a cyclopropane ring results in the formation of a yellow pre-

cipitate. Due to its relative insolubility most investigators have chosen to work with a solubilized form that is generated by reacting the precipitate with a coordinating solvent such as pyridine, THF, etc. Except for the work