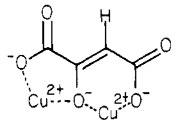
by Raghavan and Leussing[10] favor the formation of the inactive binuclear Cu(II)–enolate complex, Cu_2L^+ (**14**), as the pH is increased.



14

In the work of Munakata et al.[14] the much lower stability constant reported for OAA with Cu(II) ($\log K_{ML} = 4.1^{31}$) relative to OPA–Cu(II) interaction reported here ($\log K_{ML} = 5.82^{27}$) shows that hydroxide ion competition for the metal ion is much stronger for the OAA system. Thus hydrolysis of the catalytic metal ion would be expected to decrease the concentration of the catalytic OAA complex, ML, as the pH is increased near the neutral pH range.

Conclusions

Decarboxylation of OPA and other α-keto β-carboxy carboxylic acids is catalyzed by metal ions through the formation of the bidentate metal chelate, ML, involving the α-keto acid functions. A high formation constant of the metal chelate does not necessarily indicate that the rate of decarboxylation will be increased. Although an increase in the magnitude of the stability constant results in greater conversion of the substrate to the chelated form in solution, the tendency for the substrate to be in the inactive enolic form also increases. Competition by hydrogen ion for the substrate and hydroxide ion for the metal ion as well as the tendency to form additional metal chelate species beyond the simple 1:1 metal chelate are important considerations. The 1:2 complex, ML_2, and the binuclear chelate, M_2L, have characteristic catalytic activities that differ from that of the 1:1 chelate and may also exist partially in the form of the corresponding inactive enolate complexes. Polynuclear complexes such as the dimer M_2L_2 may exist in several forms, all of which are relatively inactive.

Acknowledgment. This research was supported by a Grant AM-11694 from the National Institute of Arthritis, Metabolic and Digestive Diseases, U.S. Public Health Department.

Registry No. OPA, 642-93-3; Zn^{2+}, 23713-49-7; Al^{3+}, 22537-23-1; Cu^{2+}, 15158-11-9; $CuCl_2$, 7447-39-4; $ZnCl_2$, 7646-85-7; $AlCl_3$, 7446-70-0; D_2O, 7789-20-0.

Trans 2,6-Bis[(dimethylamino)methyl]phenyl-*N*,*N'*,*C* Complexes of Pd(II) and Pt(II). Crystal Structure of $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]BF_4$: A Cyclohexadienyl Carbonium Ion with a σ-Bonded Metal Substituent

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Abstract: The complexes $[MBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (M = Pd, Pt) prepared from the reaction of *cis*-$[PtCl_2(SEt_2)_2]$ or $[PdBr_2(c\text{-}1,5\text{-}C_8H_{12})]$ with the anion derived from lithium and o,o'-$(Me_2NCH_2)_2C_6H_3Br$ contain a divalent metal center with the N donor atoms positioned mutually trans as a result of the geometric restraints of the terdentate monoanionic ligand. Treatment of these complexes with $AgBF_4$ can be used to generate the species $[M(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]BF_4$ (M = Pd, Pt), which are suitable not only as precursors for neutral $[MX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (M = Pd, Pt; X = Cl, Br, I) but also for the study of the coordination chemistry induced by the terdentate ligand. The reaction of the cationic platinum analogue with MeI proceeds smoothly to $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]BF_4$ in which the incoming methyl group has ended up transferred to the aryl ring system. A single-crystal X-ray study has revealed the structure of this complex $C_{13}H_{22}IN_2PtBF_4$: monoclinic space group $P2_1/c$ with unit cell dimensions $a = 11.033$ (2) Å, $b = 11.553$ (1) Å, $c = 13.915$ (3) Å, $\beta = 98.34$ (11)°, and $Z = 4$. The crystal structure was solved by standard Patterson and Fourier techniques. Anisotropic full-matrix least-squares refinement with 3499 observed reflections converged at $R = 0.056$. The most interesting molecular feature is a "boat" type puckering of the aryl ring which is coordinated in a novel way to the Pt(II) center exhibiting a slightly distorted square-planar coordination. Together with ^1H NMR and CNDO/S calculations on model systems these data suggest that the positive charge of the cation is to a large degree accommodated within the C_6 ring system; i.e., the complex is an example of a stable σ-metal-substituted arenonium ion (cyclohexadienyl cation) analogous to the Wheland intermediates formed during substitution reactions on free aromatic sytems.

Introduction

The $[C_6H_3(CH_2NMe_2)_2\text{-}o,o']^-$ anion is one of the few multidentate ligand systems capable of placing two hard N donor atoms mutually trans across a metal center. By virtue of the rigid coordination of this chelate ligand there remain available a restricted number of specific coordination sites exclusively in a plane perpendicular to that of the ligand. Such a system that can also give enhanced nucleophilic character to a metal offers interesting potential for the study of basic reactions, e.g., electron transfer and oxidative addition (where trans products usually result).

We have in fact used this ligand to isolate many noteworthy complexes, examples being $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(\mu\text{-}(p\text{-}tolNYNR))HgBrCl]$ (Y = CH, N)[2] and [Pt(C_6H_3-

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$(CH_2NMe_2)_2$-*o,o′*)(μ-(*p*-tolNC(H)NR))AgBr],[3] in which there are heteronuclear metal–metal interactions, as well as [SnMe(Ph)($C_6H_3(CH_2NMe_2)_2$-*o,o′*)]$^+$,[4] the first example of a cationic triorganotin species wherein the positive charge is stabilized by the trans N–Sn–N coordination of this terdentate ligand. In this paper we now describe the syntheses of several Pd(II) and Pt(II) derivatives of this ligand and present the X-ray crystal structure data of the unusual arenonium ion [PtI($MeC_6H_3(CH_2NMe_2)_2$-*o,o′*)]$^+$ derived from the reaction of MeI with [Pt($C_6H_3(CH_2NMe_2)_2$-*o,o′*)(H_2O)]BF_4.

Experimental Section

The general techniques and apparatus used were the same as in other recent papers from this laboratory.[2,3] [$PdBr_2$(c-1,5-C_8H_{12})][5] and *cis*-[$PtCl_2(SEt_2)_2$][6] were synthesized by literature procedures.

[MBr($C_6H_3(CH_2NMe_2)_2$-*o,o′*), M = Pd (1c), Pt (2c). A solution of [Li($C_6H_3(CH_2NMe_2)_2$-*o,o′*)] (15.0 mmol) was prepared by adding dropwise the aryl halide *o,o′*-$(Me_2NCH_2)_2C_6H_3Br$ (4.1 g, 15.1 mmol) as a solution in diethyl ether (20 mL) to a stirred suspension of excess lithium shavings (0.42 g, 60 mmol) in diethyl ether (20 mL). The reaction was initiated by warming the solution gently, thereafter the addition of the halide was adjusted to maintain a gentle reflux of the ether, and after complete addition the mixture refluxed for a further $^1/_2$ h. The clear pale yellow solution of the lithium compound was slowly added dropwise to a stirred suspension of the appropriate metal salt ([$PdBr_2$(c-1,5-C_8H_{12})] 5.6 g, 15.0 mmol; *cis*-[$PtCl_2(SEt_2)_2$], 6.7 g, 15.0 mmol) in diethyl ether (20 mL) at room temperature in the platinum case and at 0 °C for the palladium salt. After completion of the addition, the mixture was stirred for a further 1 h at room temperature. The product was collected by filtration, washed with ether (10 mL) and pentane (30 mL), and dried in vacuo. Traces of lithium salts and transition-metal impurities were removed by recrystallization from CH_2Cl_2 or warm benzene, and the product was washed well with pentane before drying in vacuo. The yields are 4.0–4.6 g (70–80%) and 6.0–6.6 g (85–95%) for the pale orange palladium compound and its white platinum analogue, respectively. Anal. Calcd for $C_{12}H_{19}BrN_2Pd$ (1c): C, 38.17; H, 5.07; Br, 21.16; N, 7.42. Found: C, 38.27; H, 5.11; Br, 21.29; N, 7.36. Calcd for $C_{12}H_{19}BrN_2Pt$ (2c): C, 30.91; H, 4.11; Br, 17.14; N, 6.02. Found: C, 30.59; H, 4.05; Br, 17.72; N, 6.01.

[M($C_6H_3(CH_2NMe_2)_2$-*o,o′*)(H_2O)]BF_4, M = Pd (1a), Pt(2a). A stirred suspension of [MBr($C_3H_6(CH_2NMe_2)_2$-*o,o′*)] (M = Pd (1c) 378 mg, 1.0 mmol; M = Pt (2c) 422 mg, 1.0 mmol) in an acetone/H_2O medium (19.8/0.2 mL) was reacted with 1 equiv of $AgBF_4$ (195 mg, 2.0 mmol) at room temperature. After 5 min the AgBr was filtered off and washed with acetone (10 mL), and the combined filtrate and washings were evaporated to dryness in vacuo. The resultant oily solid was washed with diethyl ether (10 mL) and the off-white product recrystallized from acetone by the addition of diethyl ether to yield white analytically pure **1a** (370 mg, 92%) or **2a** (470 mg, 96%). Anal. Calcd for $C_{12}H_{21}N_2OPdBF_4$ (**1a**): C, 35.80; H, 5.26; N, 6.96; F, 18.88. Found: C, 35.63; H, 5.18; N, 6.77; F, 18.94. Calcd for $C_{12}H_{21}N_2OPtBF_4$ (**2a**): C, 29.34; H, 4.31; N, 5.70; F, 15.47. Found: C, 28.80; H, 4.23, N, 5.68; F, 15.75.

[MX($C_6H_3(CH_2NMe_2)_2$-*o,o′*)]: M = Pd, X = Cl (1b), Br (1c), I (1d); M = Pt, X = Cl (2b), Br (2c), I (2d). The following synthesis is suitable for all complexes: To a stirred suspension of [M($C_6H_3(CH_2NMe_2)_2$-*o,o′*)(H_2O)]BF_4 (M = Pd (**1a**) or Pt (**2a**), 1 mmol) in H_2O (10 mL) was added a solution of NaX (2 mmol) in H_2O (5 mL). After 5 min the solid was filtered off, washed with H_2O (10 mL), and dried in vacuo. The products were crystallized from CH_2Cl_2 or warm benzene to afford the analytically pure product **1b** (cream), **1c** (pale orange), **1d** (light brown), and **2b–d** (white) in greater than 99% yield. Anal. Calcd. for $C_{12}H_{19}ClN_2Pd$ (**1c**): C, 43.26; H, 5.75; Cl, 10.64; N, 8.41. Found: C, 42.54; H, 5.71; Cl, 10.82; N, 8.16. Calcd for $C_{12}H_{19}IN_2Pd$ (**1d**): C, 33.94; H, 4.51; I, 29.89; N, 6.60. Found: C, 33.88; H, 4.53; I, 30.02; N, 6.50. Calcd for $C_{12}H_{19}ClN_2Pt$ (**2c**): C, 34.17; H, 4.54; Cl, 8.40; N, 6.64. Found: C, 34.18; H, 4.54; Cl, 8.36; N, 6.70. Calcd for $C_{12}H_{19}IN_2Pt$ (**2d**): C, 28.08; H, 3.73; I, 24.72; N, 5.46. Found: C, 28.12; H, 3.71; I, 24.80; N, 5.43.

Pt($C_6H_3(CH_2NMe_2)_2$-*o,o′*)CO]BF_4 (2e). Through a stirred solution of the aquo complex **2a** (491 mg, 1.0 mmol) in acetone (5 mL) was bubbled a steady stream of CO gas at room temperature for 5 min. To this clear solution was then slowly added an excess of diethyl ether (ca. 25 mL). The white microcrystalline product separated out and was filtered off, washed with diethyl ether (5 mL), and dried in vacuo; yield 430 mg, 86%. Anal. Calcd for $C_{13}H_{19}N_2OPtBF_4$ (**1e**): C, 31.15; H, 3.82; N, 5.59; F, 15.16. Found: C, 30.72; H, 4.07; N, 5.04; F, 13.14. (In view of this not totally satisfactory analysis we have obtained a field desorption mass spectrum of **2e**. The only ions observed were *m/e* 414 (31.5%), 415 (100%), and 416 (24.0%), in agreement with the postulated stoichiometry.)

[Pt($C_6H_3(CH_2NMe_2)_2$-*o,o′*)PPh_3]BF_4 (2f). To a stirred solution of the aquo complex **2a** (491 mg, 1.0 mmol) in acetone (5 mL) was added solid PPh_3 (395 mg, 1.5 mmol). After 5 min to the then clear solution was slowly added an excess of diethyl ether (ca. 25 mL). Workup was as for **1e** and yielded 610 mg, 83%, of **1f**. Concentration of the filtrate to 2 mL and addition of diethyl ether at 0 °C gave a further crop of crystals (80 mg, 11%). Anal. Calcd for $C_{30}H_{34}N_2PPtBF_4$: C, 48.99; H, 4.66; N, 3.81. Found: C, 48.89; H, 4.68; N, 3.73.

[PtI($MeC_6H_3(CH_2NMe_2)_2$-*o,o′*)]BF_4 (3). To a solution of [Pt($C_6H_3(CH_2NMe_2)_2$-*o,o′*)(H_2O)]BF_4 (**2a**) (980 mg, 2 mmol) in acetone (10 mL) was added an excess of freshly distilled MeI (5 mL). (Traces of insoluble impurities that may have formed at this point, if, for example, free iodine was present, were always filtered off.) The clear solution was then allowed to stand undisturbed for 24 h, during which time the solution became dark red and large ruby red crystals formed. The crystals so produced were collected by filtration, washed with a little acetone and diethyl ether, and then dried in vacuo to give 950 mg, 77%, of **3**. Evaporation of the filtrate and washings in vacuo followed by washing of the solid with a little water and then acetone and diethyl ether produces a second crop of **3** (125 mg, 10%) as a dark orange red powder. Both crops of complex are analytically pure. It is not necessary or advisable to recrystallize the product since it has a low solubility in acetone and H_2O in which it slowly reacts to give [Pt($C_6H_3(CH_2NMe_2)_2$-*o,o′*)(H_2O)]BF_4 (**2a**). (The reversibility of this reaction is discussed in detail in a forthcoming paper from this laboratory.) Anal. Calcd for $C_{13}H_{22}IN_2PtBF_4$ (**3**): C, 25.38; H, 3.61; N, 4.56; F, 12.36. Found: C, 25.47; H, 3.60; N, 4.55; F, 12.36.

Theoretical Calculations. Calculations on the model aromatic systems were done by using a CNDO/S program[12] as developed by Jaffé and

Table I. Crystal Data and Details of the Structure Determination

a. Crystal Data	
formula	$C_{13}H_{22}N_2IPtBF_4$
mol wt	615.13
space group	$P2_1/c$, No. 14
cyrst syst	monoclinic
a, Å	11.033 (2)
b, Å	11.553 (1)
c, Å	13.915 (3)
β, deg	98.34 (1)
V, Å^3	1755.0 (5)
Z	4
D(calcd), g cm^{-3}	2.328
F(000), electrons	1144
μ(Mo Kα), cm^{-1}	102.25
cryst faces and dist to origin, mm	(100), $(\bar{1}00)$, 0.125; (011), $(0\bar{1}\bar{1})$, 0.225; $(01\bar{1})$, $(0\bar{1}1)$, 0.225; $(\bar{1}02)$, $(\bar{1}10)$, 0.210
cryst vol, mm^3	0.048
no. of grid points	1008
max transmission	0.132
min transmission	0.042
b. Data Collection	
θ min, max	0.1, 27.5
radiation, Å	Mo Kα (Zr filtered), 0.710 69
ω, 2θ scan, deg	0.70 + 0.35 tan θ
horiz and vert aperture, mm	6.0, 2.0
max time/reflectn, s	180
ref reflectn	142
total reflectn data	5548
total unique reflectns	4021
obsd data ($I > 2.5\sigma(I)$)	3499
c. Refinement	
no. of refined parameters	254
weighting scheme	$w^{-1} = (\sigma^2(F) + 0.0076F^2)$
final R_F and R_{wF}	0.056, 0.062
variance (rms dev of a reflectn of unit wt)	2.43

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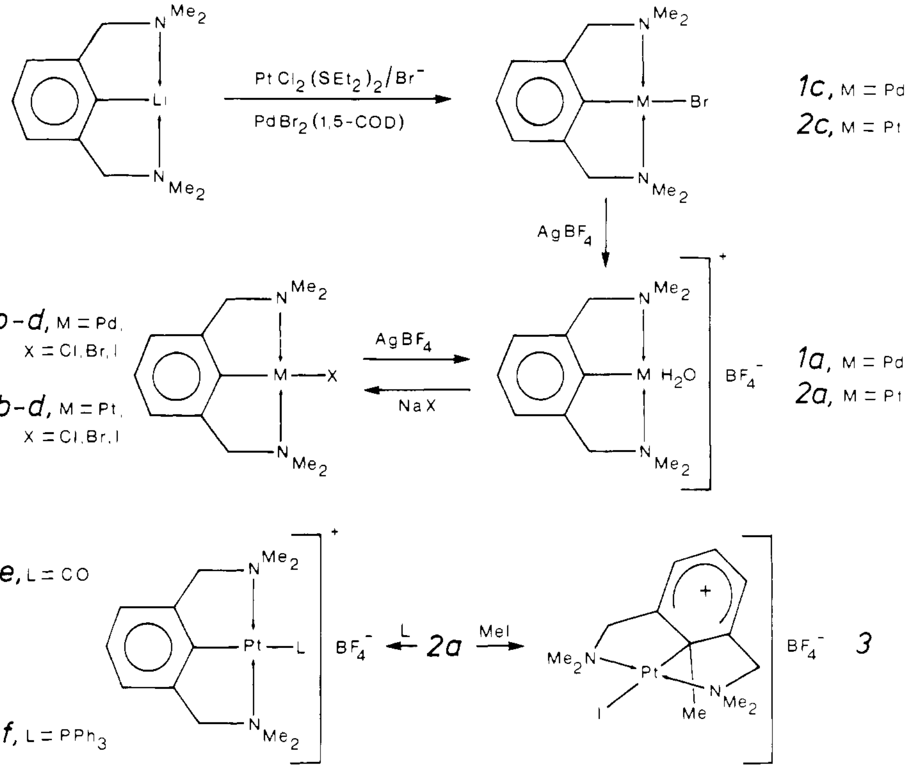
Scheme I. Synthetic Chemistry of $[C_6H_3(CH_2NMe_2)_2\text{-}o,o']^-$ with Pd(II) and Pt(II)



co-workers. Parameterization used was that described in ref 12c.

Collection and Treatment of X-ray Diffraction Data. A red-brown crystal of $C_{13}H_{22}IN_2PtBF_4$ (3), preliminarily examined with a Weissenberg photograph, was glued on top of a glass fiber and transferred to an Enraf-Nonius CAD4 diffractometer for data collection. Unit cell dimensions, their corresponding standard deviations, and a complete data set were obtained via previously described standard procedure using zirconium-filtered Mo Kα radiation.[7] The crystal data and details of the data collection and structure refinement are summarized in Table I. The intensity of one reflection was monitored every hour of X-ray exposure time. There was no indication for decay during data collection. The data were subsequently corrected for absorption, Lorentz, and polarization effects and averaged into a unique set of data in the previously described way.[7]

Structure Determination and Refinement of $C_{13}H_{22}IN_2PtBF_4$. The structure was solved by standard Patterson and Fourier techniques and subsequently refined by full-matrix least-squares techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced on calculated positions and refined in the riding mode with one overall temperature factor on corresponding non-hydrogen atom positions. Weights based on counting statistics were introduced in the final stages of the refinement. Convergence was reached at $R = 0.056$ for 3499 observed reflections. A final difference Fourier showed no significant features. The final values of the refined parameters are given in Table II (deposited as supplementary material), except for the $U(\text{iso}) = 0.128$ (4) Å^2 overall temperature factor of the hydrogen atoms. Neutral scattering factors were taken from ref 8 and corrected for anomalous dispersion effects.[9] All calculations were carried out on either the in-house Eclipse S/230 minicomputer with the program ILIAS[10] (structure determination and refinement) or on the Cyber-175 of the University of Utrecht computer center with the programs of the EUCLID package[11] (molecular geometry and illustrations).

Results

Syntheses and Solution Structures. A summary of the synthetic chemistry, some of which has appeared in a preliminary communication,[13a] is shown in Scheme I. The terdentate anionic ligand $[C_6H_3(CH_2NMe_2)\text{-}o,o']$ can be readily coordinated to platinum and palladium centers, and the complexes $[MX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (M = Pd, Pt; X = Cl, Br, I) have been characterized. The most easily obtained species are the bromo derivatives, synthesized with use of the reaction of a suitable divalent metal precursor (i.e., *cis*-$[PtCl_2(SEt_2)_2]$ and $[PdBr_2(c\text{-}1,5\text{-}C_8H_{12})]$) with the anion[13b] derived from the reaction of lithium foil with $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Br$ in diethyl ether. With use of $AgBF_4$ these bromo derivatives suspended in an acetone/H_2O medium yield isolable complexes $[M(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]BF_4$ (M = Pd, Pt), which on treatment with NaX readily generate the neutral complexes mentioned above.

All available evidence, in particular ^1H NMR data (Table III), points to the metal complexes (both neutral and ionic) as being square-planar M(II) species with the $o,o'\text{-}(Me_2NCH_2)_2C_6H_3-$ fragment acting as a monoanionic ligand σ coordinated to the metal. As a result of geometric restraints, the two hard N donor atoms of the "built-in" $-CH_2NMe_2$ ligands then coordinate mutually trans across the metal center, leaving a further coordination site trans to the σ-bound aryl system and cis to these N atoms. The favorable arrangement that this offers to the metal center is reflected by various physical properties. The main one among these is the fact that the neutral species $[MX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ are all air stable (in solution and the solid state) at ambient temperature and can be sublimed fairly easily (~150 °C, 10^{-3} torr).

Evidence for rigid donor atom coordination for all the platinum complexes, both neutral and cationic, comes from ^1H NMR (60 MHz) signals of the NCH_2- and NMe_2 groups, which show sharp ^{195}Pt ($I = {}^1/_2$, 34% abundance) satellites of significant magnitude (38–50 Hz). These values are characteristic for trans-positioned N atoms.[14a] For the palladium analogues this type of evidence

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(10) ILIAS is a DG-Eclipse S/230 adaptation and extension (by A. L. Spek) of the SHELX-76 package (by G. Sheldrick).

(11) EUCLID is a program package for the calculation and tabulation of geometrical data and structure illustrations including an extended version of the program PLUTO (S. Motherwell, B. Clegg) by A. L. Spek.

(12) (a) CNDO/S is a modification of CNDO successful in describing energy levels in free aromatics. (b) Bene, J. D.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807. (c) Kuehnlenz, G.; Jaffé, H. H. *Ibid.* **1973**, *58*, 2238.

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Table III. 60-MHz ^{1}H NMR Data for Complexes **1a–d** and **2a–f**[e]

complex	$\delta_{C_6H_3}$	δ_{CH_2} (J_{PtH})	δ_{CH_3} (J_{PtH})
$[Pd(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]^+$ (1a)[a]	6.95 m	4.17	2.87
$[PdCl(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (1b)[b]	6.8 m	3.98	2.93
$[PdBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (1c)[b]	6.85 m	4.00	2.97
$[PdI(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (1d)[b]	6.9 m	4.00	3.03
$[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]^+$ (2a)[a]	6.9 m	4.15 (50)	2.97 (38)
$[PtCl(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (2b)[b]	6.8 m	4.00 (46)	3.07 (38)
$[PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (2c)[b]	6.85	4.02 (46)	3.13 (38)
(2c)[c]	6.75 d, 7.2 t	3.43 (46)	2.90 (38)
$[PtI(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (2d)[b]	6.9	4.00 (46)	3.17 (40)
$[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(CO)]^+$ (2e)[a]	7.1 m	4.55 (51)	3.43 (45)
$[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(PPh_3)]^+$ (2f)[a]	7.1 m[d]	4.28 (53)	2.55 (45)

[a] In acetone-d_6. [b] In $CDCl_3$. [c] In benzene-d_6. [d] $\delta_{C_6H_5}$ = 7.5–8.1 m (15 H). [e] Chemical shifts are relative to Me_4Si (δ 0.0), and coupling constants are in Hz; m = multiplet, d = doublet, t = triplet.

is not available but, from the observed ^{1}H chemical shifts of the CH_2NMe_2 protons (see Table III), there is no doubt that the bonding situation is comparable. These ^{1}H NMR data show no unexpected features though (as illustrated for $[PtBr(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$) benzene-$d_6$, compared to $CDCl_3$, produces some characteristic shift changes that are particularly useful for assignment of the aryl protons; this particular solvent/solute interaction seems to be common for complexes containing the $[C_6H_3(CH_2NMe_2)_2\text{-}o,o']^-$ ligand.[14c]

It should be mentioned that with the knowledge that there is N donor coordination the multiplicity and number of the ^{1}H NMR signals of the CH_2 and NMe_2 groups become a powerful probe into the symmetry of the metal center and the surrounding groupings (see ref 14a and below).

Cationic $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]BF_4$ (**2a**), which was originally formulated as $[Pt(BF_4)(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$,[13a] has now been correctly identified as the aquo complex by a combination of IR, analytical, and NMR techniques. The water molecule can be readily displaced from this complex by coordinating donor molecules such as PPh_3 and CO (see Scheme I). The resulting cationic species $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')L]^+$ (L = CO (**2e**), PPh_3 (**2f**)) are not air sensitive, and experimental data (e.g., ν_{CO} = 2086 cm^{-1} for **2e** and J_{PtP} = 2100 Hz for **2f**) are in agreement with the incoming ligand being trans to the σ-bonded aryl ring (cf. ν_{CO} = 2079 cm^{-1} for $[Pt(Et)CO(PEt_3)_2]^+$ [15] and the ^{31}P NMR data in ref 16).

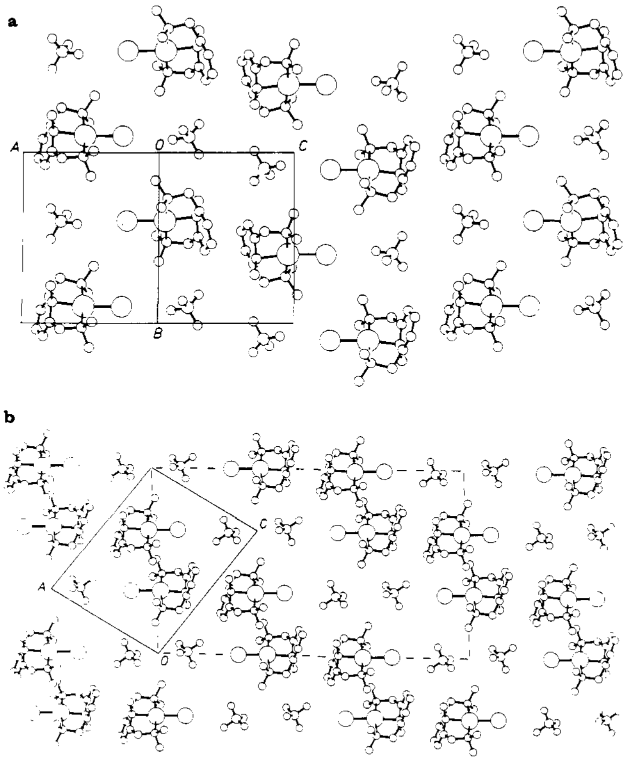

Figure 1. Packing plot of the ions: (a) on the *ac* plane as viewed down the *b* axis; (b) on (102) down [101] showing the layer structure of the crystal structure and the outline of a pseudoorthorhombic supercell.

On reaction with MeI the complex $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]BF_4$ (**2a**) affords, instead of the expected five-coordinate oxidative-addition product $[Pt(Me)I(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]^+$, the dark red complex $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]BF_4$ (**3**) in which the methyl group of the alkyl halide has become bonded to the carbon atom of the aryl ring originally σ bonded to the platinum center. The ^{1}H NMR data of **3** (acetone-d_6, 250 MHz), as regards the three aryl ring protons, show unexpected features (δ_A = 8.70 (1 H), δ_B = 7.60 (2H); J_{AB} = 7 Hz). In addition both multiplets possess ^{195}Pt satellites (J_{PtA} = 42 Hz, J_{PtB} = 15 Hz), suggesting the presence of a good σ skeleton for the transmission of coupling information. Furthermore, the molecular symmetry planes of the starting material have been lost, giving rise to diastereotopic CH_2 and NMe_2 groupings whose ^{1}H NMR signals also show ^{195}Pt satellites (δ_{CH_2} = 3.97 and 5.08, J_{HH} = 13 Hz, J_{PtH} = 34 and 19 Hz, respectively; δ_{CH_3} = 2.69 and 3.15, J_{PtH} = 28 and 36 Hz, respectively); i.e., the rigid N donor coordination to the platinum center has been retained. The ^{1}H NMR data of the unique Me group may be used to infer that it too is involved in the bonding situation close to the metal (δ_{CH_3} = 3.27, J_{PtH} = 8 Hz).

However, so that detailed unambiguous information concerning the nature of this complex, in particular with respect to the bonding mode of the aryl system, could be provided an X-ray single-crystal structure determination has been carried out.

Description of the Molecular and Crystal Structure of $C_{13}H_{22}IN_2PtBF_4$ (3). The monoclinic unit cell contains four cation–anion pairs. An analysis of their packing shows that the ions are essentially located in a net plane with Miller indices (102). Figure 1a depicts the packing within this plane. The perpendicular view in Figure 1b shows the way in which these layers are stacked into a pseudoorthorhombic supercell lattice. The iodine atoms are stacked into an infinite and approximately linear array running along the twofold screw axis. The two shortest contacts between the I and F atoms are I···F(2) = 3.596 (14) Å and I···F(3) = 4.179 (10) Å, so a significant nonionic interaction between the ions is not indicated. The BF_4 ion has a regular geometry with no signs of rotational disorder. The Pt–I bond is approximately collinear with the I–B vector to the nearest BF_4 ion.

The geometry of the Pt complex along with the adopted numbering scheme is shown in the PLUTO drawing in Figure 2a. Two additional and mutually perpendicular views of the molecule are

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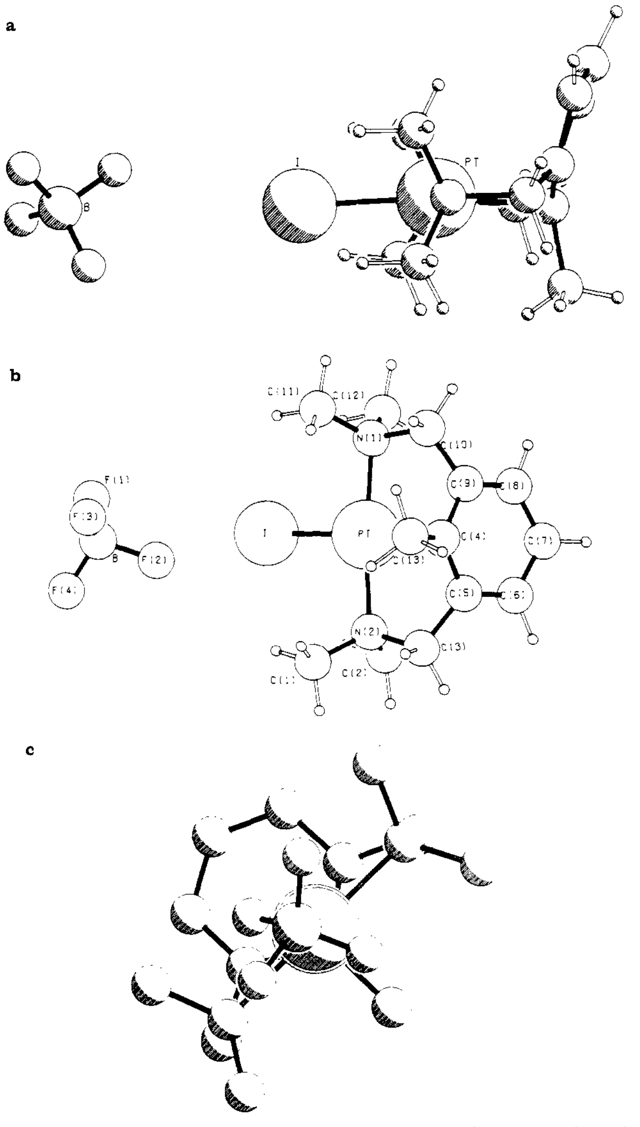

Figure 2. PLUTO drawings of the ions as viewed from three approximately perpendicular directions along with the adopted numbering scheme for **3**.

given in Figure 2b,c. An ORTEP drawing (Figure 3, deposited as supplementary material) gives a stereoview of the thermal vibrational ellipsoids. Bond distances and angles and some relevant torsion angles are presented in Table IV. The cation $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]^+$ exhibits a noncrystallographic mirror plane that contains the atoms I, Pt, C(4), C(7), and C(13).

The Pt(II) center, to which are bonded two mutually trans NMe_2 moieties, an iodine atom, and the aryl nucleus (via C(4)), exhibits a slightly distorted square-planar coordination, the N–Pt–N and I–Pt–C(4) angles being 172.1 (2) and 171.8 (2)°, respectively. A projection of the heavy-atom skeleton as viewed from along the Pt–I vector (Figure 2c) shows clearly the disposition of the carbon and nitrogen atoms relative to the platinum center. Evidently C(4), only 2.183 (7) Å distant from the metal, is the atom most heavily involved in the bonding of the aryl nucleus to the metal center. The significance of this is discussed later in detail; at this point it is worth mentioning that this Pt–C(4) separation falls within the range for η^2-bonded olefinic species; a Pt–C σ bond trans to a halo atom is in general much shorter, a typical value being the 2.079 (14) Å found in *trans*-$[PtCl(CH_2SiMe_3)(PPhMe_2)_2]$.[17]

In the cation of **3** the C–C bond lengths of the phenyl moiety are normal for arylmetal systems despite the fact that there is a small but noticeable "boat" type puckering of the ring (see Figure 2b). This is illustrated by the distances of the six C atoms from a least-squares plane through them, the values being as follows: C(4), –0.08 (4); C(5), +0.06 (4); C(6), +0.02 (4); C(7), –0.08 (4); C(8), +0.06 (4); C(9), + 0.02 (4) Å.

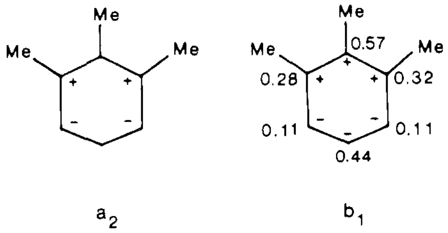

Figure 4. HOMO's of 1,2,3-trimethylbenzene.

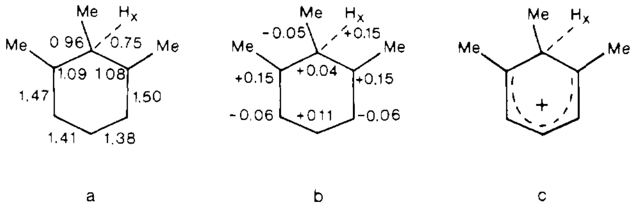

Figure 5. Calculated protonated 1,2,3-trimethylbenzene (a) bond order, (b) charge distribution, and (c) combined result.

Such bending obviously points to a significant rehybridization of some of the sp^2 centers. In fact C(5) and C(9) also no longer possess pure trigonal sp^2 hybridization, owing to the restraints of the metal-bonded–CH_2NMe_2 groups, which are attached to the ring at these "ortho" positions. The C(4)–C(13) separation of 1.549 (12) Å is suggestive of an aliphatic C–C bond (1.537 ± 0.005 Å) rather than a Me–aryl bond, which is much shorter (1.505 ± 0.005 Å).[18] There is no apparent interaction of this C(13) Me group with the platinum coordination sphere; the closest calculated atom approach being with H(22) 2.89 (1) Å distant.

Calculations on Wheland Type Model Structures. To aid our interpretation of the crystallographic data we have done some CNDO/S calculations[8] on the model organic compound 1,2,3-trimethylbenzene using C–C distances and bond angles as found in the related puckered aryl system of platinum complex **3** (with C(4) at the top, the numbering is counterclockwise as in Figure 2a). As expected the two HOMO's of such a C_{2v} substituted benzene are b_1 and a_2 (deriving from e_{1u} in benzene), with the former being the higher. The calculated orbital coefficients of b_1 (see Figure 4) clearly indicate that a bonding interaction at C(4) with an unoccupied MO would be favorable on the basis of frontier orbital theory. As a test of this a proton $H(x)^+$ was placed in a situation of 1.08 Å from C(4), with retention of the approximate trigonal symmetry of this atom, in order to simulate the presence of a Pt^+ center within bonding distance. The results of the ensuing calculation on interatomic bond orders and charge distribution within this system are shown for the most important atomic centers in Figure 5a,b. There is clearly indicated a significant bond order (0.75) between C(4) and H(*x*) with a resultant charge distribution that makes the ortho and para carbon atoms particularly electron deficient. These combined data give a simplistic view of this molecule as a Wheland intermediate[19] in which C(4) approaches a tetrahedral tertiary carbon geometry (Figure 5c). When the above calculations were repeated with use of a planar 1,2,3-trimethylbenzene molecule, the results although qualitatively similar indicated a less favorable interaction with the incoming H(*x*) proton than that found for the puckered system. In particular there was an energy difference of 217.8 eV in favor of the latter nonplanar aryl arrangement. These computational data are discussed below as regards their relevance to the inter-

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Table IV

Bond Distances (Å) for $C_{13}H_{22}IN_2PtBF_4$

Pt-I	2.5811 (7)	N(1)-C(10)	1.50 (1)	C(4)-C(9)	1.40 (1)
Pt-N(1)	2.106 (6)	N(1)-C(11)	1.50 (1)	C(4)-C(13)	1.55 (1)
Pt-N(2)	2.123 (6)	N(1)-C(12)	1.50 (1)	C(5)-C(6)	1.39 (1)
Pt-C(4)	2.183 (7)	N(2)-C(1)	1.49 (1)	C(6)-C(7)	1.39 (1)
F(1)-B	1.37 (1)	N(2)-C(2)	1.49 (1)	C(7)-C(8)	1.38 (1)
F(2)-B	1.35 (2)	N(2)-C(3)	1.50 (1)	C(8)-C(9)	1.39 (1)
F(3)-B	1.31 (2)	C(3)-C(5)	1.51 (1)	C(9)-C(10)	1.48 (1)
F(4)-B	1.32 (1)	C(4)-C(5)	1.40 (1)		

Bond Angles (Deg) for $C_{13}H_{22}IN_2PtBF_4$

I-Pt-N(1)	94.2 (2)	Pt-N(1)-C(10)	103.2 (4)	Pt-C(4)-C(9)	88.9 (5)
I-Pt-N(2)	93.6 (2)	Pt-N(2)-C(1)	115.0 (6)	Pt-C(4)-C(13)	104.2 (5)
I-Pt-C(4)	171.8 (2)	C(1)-N(2)-C(2)	108.1 (7)	C(5)-C(4)-C(9)	116.7 (7)
I-Pt-C(9)	151.9 (2)	C(1)-N(2)-C(3)	109.8 (6)	C(5)-C(4)-C(13)	119.7 (7)
N(1)-Pt-N(2)	172.1 (2)	C(2)-N(2)-C(3)	109.2 (6)	C(9)-C(4)-C(13)	120.9 (7)
N(1)-Pt-C(4)	87.1 (3)	Pt-N(2)-C(2)	107.9 (5)	C(3)-C(5)-C(4)	116.3 (7)
N(1)-Pt-C(9)	60.2 (2)	Pt-N(2)-C(3)	106.8 (5)	C(3)-C(5)-C(6)	120.4 (7)
N(2)-Pt-C(4)	85.0 (3)	F(3)-B-F(4)	113.6 (9)	C(4)-C(5)-C(6)	121.4 (7)
N(2)-Pt-C(9)	112.5 (2)	F(2)-B-F(3)	106 (1)	C(5)-C(6)-C(7)	119.3 (8)
C(4)-Pt-C(9)	33.1 (3)	F(2)-B-F(4)	104 (1)	C(6)-C(7)-C(8)	119.3 (8)
Pt-N(1)-C(11)	113.4 (5)	F(1)-B-F(2)	108.7 (9)	C(7)-C(8)-C(9)	120.4 (8)
Pt-N(1)-C(12)	108.9 (5)	F(1)-B-F(3)	114 (1)	C(4)-C(9)-C(8)	120.8 (7)
C(10)-N(1)-C(11)	109.4 (6)	F(1)-B-F(4)	110 (1)	C(4)-C(9)-C(10)	116.6 (7)
C(10)-N(1)-C(12)	109.8 (6)	N(2)-C(3)-C(5)	104.3 (6)	C(8)-C(9)-C(10)	121.2 (7)
C(11)-N(1)-C(12)	111.8 (7)	Pt-C(4)-C(5)	93.4 (5)	N(1)-C(10)-C(9)	106.3 (6)

Some Relevant Torsion Angles (Deg) for $C_{13}H_{22}IN_2PtBF_4$

C(6)-C(7)-C(8)-C(9)	14.2 (13)	C(8)-C(7)-C(6)-C(5)	−10.2 (13)
C(7)-C(8)-C(9)-C(10)	−170.5 (9)	C(7)-C(6)-C(5)-C(3)	160.1 (8)
C(8)-C(9)-C(10)-N(1)	97.6 (9)	C(6)-C(5)-C(3)-N(2)	−98.6 (8)
Pt-N(1)-C(10)-C(9)	23.6 (6)	Pt-N(2)-C(3)-C(5)	−26.4 (7)
Pt-C(4)-C(9)-C(10)	64.5 (6)	Pt-C(4)-C(5)-C(3)	−61.0 (7)

pretation of both the crystallographic and ^1H NMR data of cationic platinum complex **3**.

Discussion

While there are many divalent complexes of the nickel triad containing trans monodentate tertiary phosphines, the number of analogous species containing hard amines is limited. This in general may be attributed to a lack of p-back-bonding ability of the coordinated nitrogen atom.

However, the ready isolation of $[MX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ (M = Pd, Pt; X = Cl, Br, I) as well as the cationic derivatives thereof described in this work shows that the combination of the metal–C σ bond and the chelate effect can apparently overcome any adverse influence that trans amines may have on complex stability. It has been realized for some time that this latter effect is an important factor in enabling hard bases (e.g., amines) to coordinate to soft metal ions (e.g., Ni^{II}, Pd^{II}, and Pt^{II}), and there are several Ni triad derivatives of ethylenediamine and its close relatives.[20-22] With use of diethylenetriamine (dien, $NH_2(CH_2)_2NH(CH_2)_2NH_2$), for example, the palladium and platinum species $[M(dien)S]^{2+}$ (S = H_2O; M = Pd,[23] Pt[24]) are isolable. The latter palladium species where S is acetone could not be prepared since traces of water coordinate far more readily, and although there is a difference in the electronic charge on the ions, the $[M(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]^+$ system behaves similarly, yielding aquo species **1a** and **2a**. In both cases it seems likely that electron donation from the coordinated amine ligands reduces the electrophilicity of the cationic metal center so that only water, a much better Lewis base than acetone, can coordinate effectively. This concept is consistent with the available evidence on the aquo species $[M(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]BF_4$ that indicates that the protons of the coordinated water are not acidic. For example, in their IR spectra there are no B–F absorptions indicative of an interaction of the tetrafluoroborate anion with the water molecule, a phenomenon seen for some other cationic platinum complexes, e.g., cis-$[PtCl(PR_3)_2(H_2O)]BF_4$.[25]

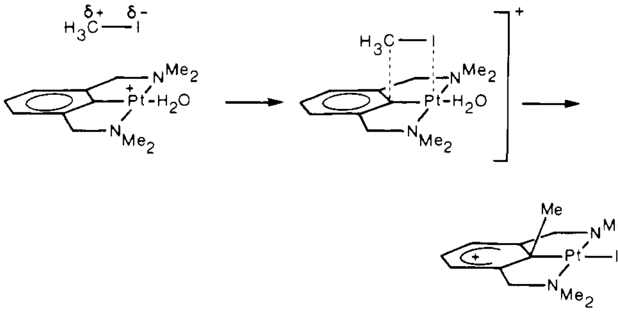

Figure 6. Direct addition of MeI to **2** affording **3**.

With this in mind the water substitution reactions of the platinum aquo complex with neutral donor ligands are to be anticipated, while the observation that the "built-in" CH_2NMe_2 groups are not displaced from the metal coordination sphere by CO and PPh_3 emphasizes the stability of the trans N-donor arrangement.

Bonding Description of $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]BF_4$ (3). Attack of methyl iodide on the aquo complex $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(H_2O)]BF_4$ (**2a**) results in **3**, a complex possessing a methyl group on the aryl nucleus and an iodide atom on the metal center. Normally such a configuration would be expected to result in elimination of the organic fragment (in this instance $o,o'\text{-}(Me_2NCH_2)_2C_6H_3Me$), but owing to the restraints of the trans-chelated CH_2NMe_2 groups, this organic molecule remains close to the platinum center. It is not possible to say whether this final configuration is a result of an intramolecular rearrangement of an initially formed five-coordinate addition product $[Pt(Me)I(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]BF_4$ or arises directly from a direct interaction of the alkyl halide with the platinum substrate (the latter possibility is shown schematically in Figure

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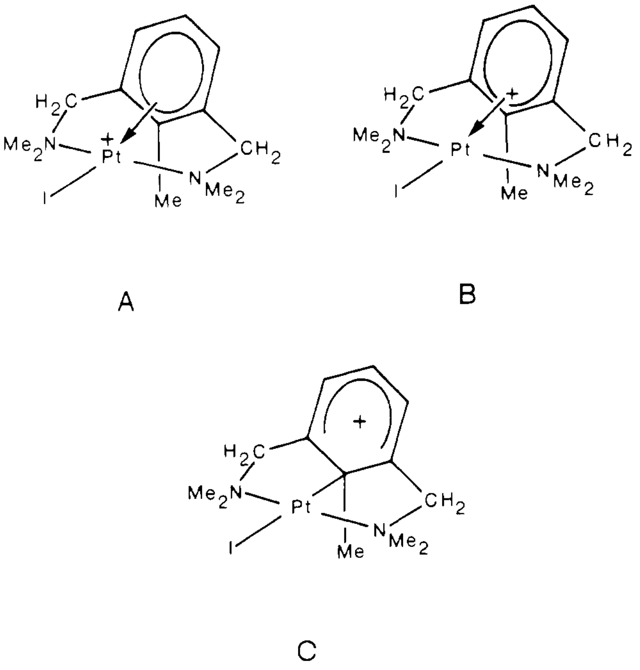

Figure 7. Possible bonding modes of the aryl fragment in **3**.

6). However, in either case the resultant complex **3** may be considered as a "frozen intermediate" in a reductive-elimination process, a situation that can be formally described in terms of the three extreme canonical forms A, B, and C in Figure 7. Form A represents the case where a neutral aryl ring interacts via its π system with the metallic center which has the localized positive charge of the cation. This bonding situation requires that orbitals on C(5) and C(9) have a significant participation in the metal organic fragment bonding because the organic HOMO involves C(5), C(9), and C(4) (see Figure 4). In comparison to the Pt–C(4) distance of 2.183 (7) Å the Pt–C(5) and Pt–C(9) separations are much greater (2.665 (7) and 2.572 (7) Å, respectively) and so weigh heavily against such a description. Furthermore, the CNDO/S calculations inferred that the metal is likely to distribute positive charge into the organic fragment, and this option favors the two remaining canonical forms B and C. In the first of these there is an interaction of an organic carbonium ion with the metal using the π system of a unipositive allylic type moiety. A clear example of this is deep red $[Pt(C_7H_7)(c\text{-}1,5\text{-}C_8H_{12})]BF_4$,[26] where both spectroscopic and synthetic information justify a formulation with a zerovalent platinum center bonded to a planar $C_7H_7^+$ aromatic system. Theory predicts that in molecules of this type metal overlap is primarily with orbitals localized on the "outer" carbons of the allylic grouping. This has been substantiated by X-ray single-crystal structure determinations, which show the metal lying closer to these carbon atoms than the unique central carbon.[27] For complex **3** this allylic type bonding mode (Figure 7B) therefore has as a prerequisite that C(5) and C(9) should lie within closer bonding distance of the platinum center than C(4) and this (as seen above) they do not.

The last bonding mode to be considered is shown in Figure 7C, in which the metal forms a two-electron two-center σ bond to the organic carbonium system via C(4). Accordingly, positive charge is distributed primarily over the other five carbon centers as is the case with arenonium ions. Our CNDO/S calculations on this system (see Results) not only point to this being the most likely situation but, furthermore, they also show that a puckered C_6 skeleton (as actually observed in the crystal structure of **3**) has a lower energy than a planar one. It is therefore likely that this description of complex **3** is feasible, and careful examination of the crystallographic data should reveal other evidence that might support such a conclusion.

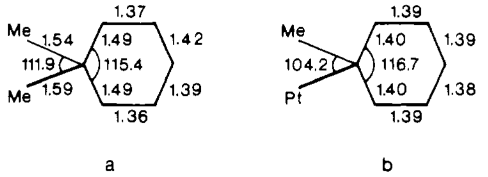

Figure 8. Bond distances (Å) and angles (deg) of the related carbon skeletons of (a) $[C_6(CH_3)_7]^+$ and (b) **3**. For esd's see ref 28 and this work.

The obvious place to begin is with atom C(4), which, if form C is dominant, should be approaching sp^3 hybridization. With the severe geometrical restraints imposed by the cyclic C_6 system taken into account, as well as the two five-membered rings containing the platinum center (Pt–C(4)–C(5)–C(3)–N(2) and Pt–C(4)–C(9)–C(10)–N(1)), this appears to be the case. The fact that C(4) lies 0.152 (2) Å above the plane of C(5), C(9), and C(13) in the direction of the platinum center taken together with the bond angles C(13)–C(4)–Pt and C(5)–C(4)–C(9) (104.2 (5) and 116.7 (7)°, respectively) is good evidence for an attempted tetrahedral coordination. Indeed, in several respects the results of the X-ray crystallographic study of the purely organic heptamethylbenzonium ion $[C_6(CH_3)_7]^{+}$[28] are comparable with those from the platinum complex $[PtI(MeC_6H_3(CH_2NMe_2)_2\text{-}o,o')]^+$. The relevant skeletons are shown diagrammatically in Figure 8. The C–C separations within the C_6 ring of the platinum complex do not vary as dramatically as those of the organic carbonium ion though the bonds involving the four-coordinate carbon center are in both cases the longest. Probably the most significant similarity is the length of the C–Me bonds at this center, in both structures far exceeding a normal C_{aryl}–Me distance of 1.505 ± 0.005 Å and falling into the range of C_{tert}–Me distances, 1.537 ± 0.005 Å. (One of the geminal C–CH_3 bonds in the organic ion is exceptionally long, 1.586 (9) Å.) It is therefore to be expected that if the analogy of the platinum complex to this carbonium ion is reasonable then the Pt–C(4) separation should be somewhat longer than a comparable Pt–C single σ bond. This is indeed the case, and the observed distance (2.183 (7) Å, which would normally be a Pt–C π interaction) is consistent with the lenghtening of a Pt–C σ bond due to the presence of positive charge within the aryl ring.

The hypothesis that complex **3** can be best considered as a σ-substituted arene carbonium ion (Figure 7C) has also full support from the spectroscopic data. First, a cyclohexadienyl cation is anticipated to exhibit an absorption band at ~400 nm in its UV/vis spectrum[19] (423 nm observed for **3**). Second, the ^1H NMR spectrum of **3** shows the para proton resonance at δ 8.70 shifted to lower field of the normal region for aryl protons, where it is found that the meta protons resonate (δ 7.60); this compares favorably with the data from arene carbonium ions generated in highly acidic media.[19] Interestingly, the ^1H NMR shift of the C(13) methyl group (δ 3.27) is to low field of that of toluene (δ 2.32) though in general methyl groups close to platinum centers in both σ-bonded ethyl[29] and π-bonded 2-methylallyl[30] groups exhibit shielding and are moved to higher field.

Finally, both the meta and the para as well as the unique C(13) methyl group protons all exhibit spin–spin coupling with ^{195}Pt (the $^5J_{PtH}$ value of 42 Hz for the para proton being exceptionally large), and this is only likely if the metal center is σ bound to the aryl nucleus.

On the basis of all this evidence there is little doubt that complex **3** represents an unusual type of organometallic complex bearing remarkable similarities to pure organic arenonium ions of the type postulated in arene substitution reactions and known as Wheland intermediates. In a further paper the reactions of nucleophilic

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reagents with **3** are shown to provide further evidence in support of this comparison.[31]

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Registry No. 1a, 82112-95-6; **1b**, 82112-98-9; **1c**, 67507-30-6; **1d**, 83311-96-0; **2a**, 82112-93-4; **2b**, 82112-96-7; **2c**, 67507-09-9; **2d**, 82112-97-8; **2e**, 67507-15-7; **2f**, 67507-13-5; **3**, 83311-98-2; Li(C_6H_3-($CH_2NMe_2)_2$-*o,o′*), 66479-07-0; *o,o′*-($(Me_2NCH_2)_2C_6H_3Br$), 66479-06-9; $PdBr_2(c\text{-}1,5\text{-}C_8H_{12})$, 12145-47-0; *cis*-$[PtCl_2(SEt_2)_2]$, 15442-57-6.

Supplementary Material Available: Listings of observed and calculated structure factors for $C_{13}H_{22}IN_2PtBF_4$ (**3**) and positional and thermal parameters, bond distances, and bond angles for **3** (Table II) and an ORTEP drawing giving a stereoview of **3** (Figure 3) (29 pages). Ordering information is given on any current masthead page.

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NMR Spectroscopic Studies on Chalcogen Compounds. 4.[1] Carbon-13 Isotope Effect on Selenium-77 and Tellurium-125 Nuclear Shielding and Its Correlation with C–Se Bond Distances. Tellurium-123 Isotope Effect on Tellurium-125 Nuclear Shielding

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Contribution from the Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, D-4630 Bochum, Germany. *Received February 10, 1982*

Abstract: A one-bond isotope effect of ^{13}C on the nuclear shielding of ^{77}Se and ^{125}Te was observed for the first time. Thirty values for Se(II) and Se(IV) compounds containing sp^3-, sp^2-, and sp-hybridized carbon were measured, and a wide range of low frequency shifts was found between −0.012 and −1.099 ppm. A correlation was established between the isotope shift and the C–Se bond distance for CF_3- and CH_3-substituted selenium compounds. The isotope shift of the linear molecules SeCO, SeCS, and SeCSe is inversely dependent on the force constant of the C═Se bond. This is attributed to different vibrational amplitudes. The CSe bond order plays an important role for the isotope shift and appreciable substituent effects were observed. Five Te(II) and Te(IV) compounds were studied. The isotope shifts are larger than for the corresponding Se compounds, and the results can be qualitatively interpreted in analogy to those found for the selenium compounds. The isotope shift can be temperature dependent; this was shown, for example, on liquid samples of CF_3SeCN and SeCO. This behavior is explained by a substantial contribution of vibrationally excited states. Furthermore, an isotope effect of ^{123}Te on the screening of ^{125}Te (and vice versa) in $CF_3TeTeCF_3$ was detected, and the coupling constant $^1J(^{125}Te{-}^{123}Te)$ was determined.

Introduction

Numerous isotope shift effects in nuclear magnetic resonance spectroscopy have been observed,[2–5] and theoretical aspects of this effect have been considered.[6,7] Recently, several interesting papers on ^{18}O-induced isotope shifts in ^{13}C[3,8–10] and ^{31}P[11,12] NMR spectra have been published (see also review article ref 4). The data provide evidence for the dependence of the isotope shift on substituents and bond order. However, the effect of ^{13}C on the chemical shift of an adjacent nucleus has been found only in ^{19}F, ^{59}Co, ^{13}C,[13,14] and ^{111}Cd[15] NMR spectroscopy. This paper reports for the first time the observation of ^{13}C isotope effects on the nuclear screening of ^{77}Se and ^{125}Te and the correlation of one-bond isotope shifts with bond distances. Furthermore, the isotope effect of ^{123}Te on ^{125}Te (and vice versa) nuclear screening in $CF_3TeTeCF_3$ was detected.

In a current investigation of CF_3-substituted selenium and tellurium compounds[16] and compounds containing a C═Se double

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