54823-00-6; {Pt[CSN(CH3)2][P(C6H5)3]2}2{SnCl5}2, 54823-02-8; Pt[P(C6H5)3]4, 14221-02-4; Pt[PCH3(C6H5)2]4, 27121-53-5; ClC(S)OCH3, 2812-72-8; CH3SO3F, 558-25-8; [(C2H5)3O][BF4], 368-39-8; (CH3O)2SO2, 77-78-1; benzyl bromide, 100-39-0; allyl bromide, 106-95-6; CH3HgCl, 115-09-3; SnCl4, 7646-78-8.

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(21) This value for the concentration is based on mol wt 2206 for the formula given.

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada

Ligand-Induced Fluxionality in Some η^3-Allylplatinum(II) Complexes Containing Chelating Ligands. Isolation of Dynamic 1:1 Adducts

H. C. CLARK* and C. R. JABLONSKI

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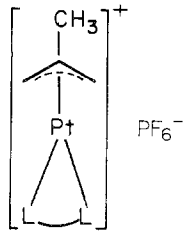
Several static, symmetrically bonded η^3-allyl complexes of the form $(\widehat{LL})Pt(2\text{-}Me(all))^+$ have been prepared (all = allyl). Reaction with neutral bases leads to syn–anti interchange but the effectiveness of conversion to a dynamic system is a function of nucleophilicity toward Pt(II). Good nucleophiles such as PPh_2Me give stable 1:1 adducts which are dynamic in solution at room temperature and appear to have a η^1-allyl (σ-allyl) structure at low temperature. A mechanism is proposed to account for the base-induced fluxionality.

Platinum(II) lacks the overwhelming preference of palladium(II) to form η^3-allyl complexes.[1] Although several η^3-allyl complexes of Pt(II) have been prepared,[2-7] little is known concerning their reactivity[8-10] or the nature and occurrence of the fluxional processes which are characteristic of η^3-allyl complexes in general and of Pd(II) in particular.

It is well-known that many static η^3-allyl complexes of Pd(II) become dynamic in the presence of added base.[11] The suggestion has been made[11,12a] that the major intermediates involved in these dynamic systems are four-coordinate η^1-allyl rather than five-coordinate η^3-allyl complexes implying a concerted reaction with base. Preliminary evidence relating to the observation of such four-coordinate η^1-allyl compounds of Pd(II) has recently been reported.[12b] η^1-Allyl complexes of Ir(I) have also been isolated.[12c]

Both the increasing number of five-coordinate complexes of Pt(II) reported in the recent literature[13] and the compelling nature of the evidence[12a] proposed to eliminate five-coordinate η^3-allylic species as important intermediates for Pd(II) make extrapolation of this concerted mechanism to Pt(II) systems somewhat tenuous. Hence we have prepared several chelated allyl complexes of Pt(II) with the expectation that they should be less labile than their Pd(II) analogs in the presence of a greater variety of nucleophilic bases.[12a] The direct observation of four-coordinate η^1-allyl complexes of Pt(II) might then be a real possibility. In addition, the presence of a chelating ligand, LL, should preclude the rapid ligand exchange which has complicated many of the previous studies of Pd(II) systems.

We therefore report the preparation and properties of several cationic 2-methylallyl complexes, I, where LL is a chelating



I

diphosphine or diarsine ligand.[14,15]

Results and Discussion

Preparation of the Allylic Complexes. (a) $\widehat{LL}$ = 1,2-Bis(diphenylphosphino)ethane (diphos). (diphos)$PtMe_2$,[16] II, was readily prepared by reaction of dimethyl(π-1,5-cyclooctadiene)platinum(II),[17] III, with diphos

$$(1,5\text{-}C_8H_{10})PtMe_2 \underset{\text{III}}{} + \text{diphos} \xrightarrow{CH_2Cl_2} \underset{\text{II}}{(\text{diphos})PtMe_2} \xrightarrow[HCl]{1\text{ equiv}} \underset{\text{IV}}{(\text{diphos})PtMeCl}$$

Reaction of II with 1 equiv of hydrogen chloride prepared in situ from 1 equiv of acetyl chloride and excess methanol gave the methylchloro derivative IV via an oxidative addition–

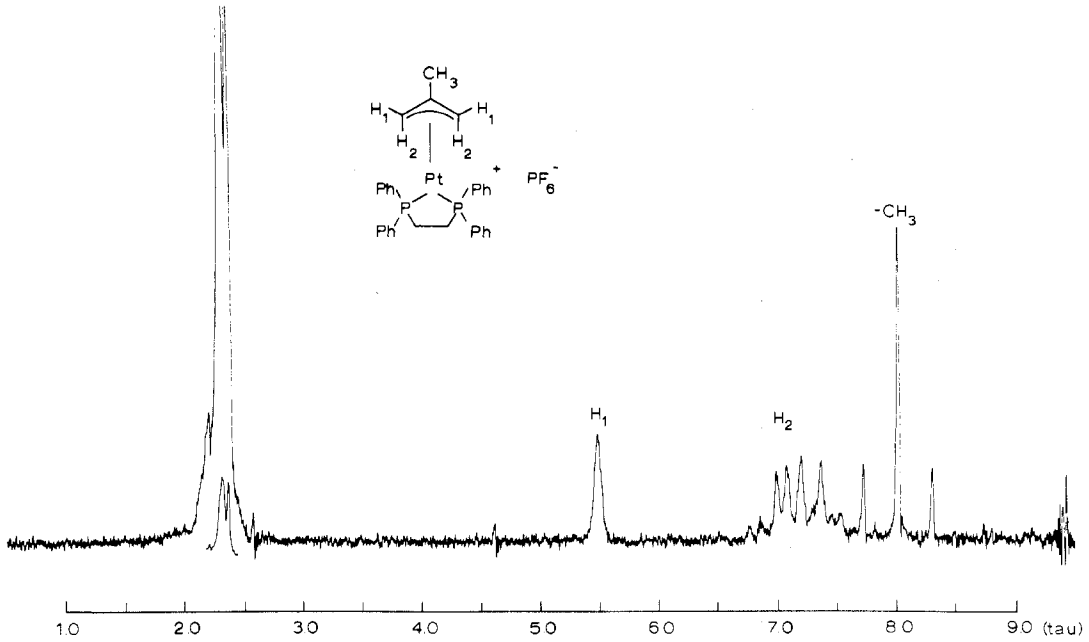
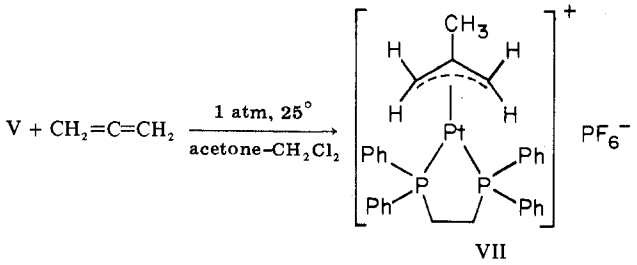


Figure 1. ^{1}H NMR spectrum of diphosPt(2-Me(all))$^+PF_6^-$.

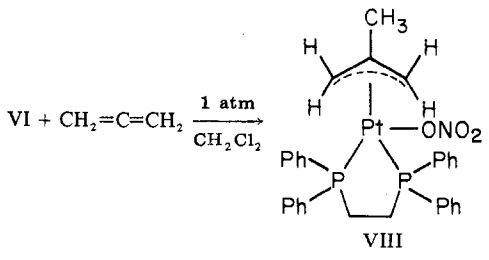
reductive elimination reaction sequence. The chloride of IV is labile due to the strong trans influence of diphos and is easily abstracted with $AgPF_6$ or $AgNO_3$ to give the corresponding cationic and neutral derivatives V and VI

$$\underset{\text{V}}{\text{(diphos)PtMe(acetone)}^+PF_6^-} \xleftarrow[\text{acetone}]{AgPF_6} \text{IV} \xrightarrow[\text{acetone}]{AgNO_3} \underset{\text{VI}}{\text{(diphos)PtMe(ONO}_2\text{)}}$$

Reaction of either V or VI with allene gave rapid insertion into the Pt–C bond[6,7] to give the corresponding 2-methylallyl complexes VII and VIII. The methylchloro derivative IV was



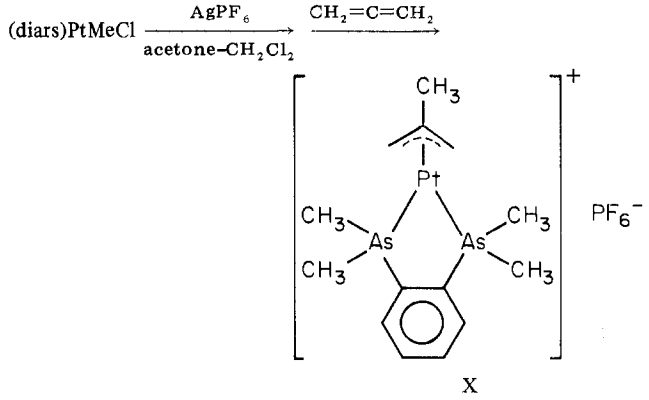
VII



VIII

unreactive and only unchanged starting material was recovered after reaction with excess allene for 48 hr in a sealed tube at 100°. This contrast in reactivity toward insertion of the cationic vs. the neutral species is consistent with other studies[18] which indicate the greater reactivity of carbon–carbon multiple bonds when complexed to electron-deficient metals.

(b) $\widehat{LL}$ = *o*-Phenylenebis(dimethylarsine) (diars). Addition of allene to acetone–CH_2Cl_2 solutions of (diars)PtMeCl[19] which had been treated with $AgPF_6$ gave, in an analogous fashion, the allyl complex X



X

^{1}H NMR Spectra of the Allyl Complexes. The ^{1}H NMR spectra of symmetrically bonded static η^3-allylpalladium(II) complexes have been interpreted in terms of AM_2X_2 (AB_2C_2) or more properly AMM'XX' (ABB'CC') spin systems.[20] The second-order spectra apparent when geminal coupling is not negligible account[12a] for the proposed "slight asymmetry"[4] in bonding thought to be responsible for the PMR spectra for compounds of the type PdL_2(2-Me(all))$^+BF_4^-$.

The so-called "dynamic" allyl complexes,[21] on the other hand, show AX_4 patterns and several proposals have been made regarding the nature of the fluxional processes responsible for exchange.[2-5,8,9]

Examination of ^{1}H NMR spectra of the 2-methylallyl complexes VII, VIII, and X prepared in this study indicate a static, symmetrical η^3 (trihapto) bond to platinum[6,7] (cf. Table I and Figures 1 and 2) rather than a dynamic allyl.[8,10] The PMR spectra of VIII and X in *o*-dichlorobenzene were temperature independent in the range 35–150°, showing no tendency toward syn–anti exchange.

The overall geometry about platinum is expected[1,8] to be roughly square planar with "side on" bonded allyl having the two terminal carbons approximately in the plane. This is very easily verified by the observation of two sets of diastereotopic arsine methyl groups for X (cf. Figure 2) due to differing axial environments about platinum. This situation persists at elevated temperatures (to ca. +130°) so that rapid rotation of

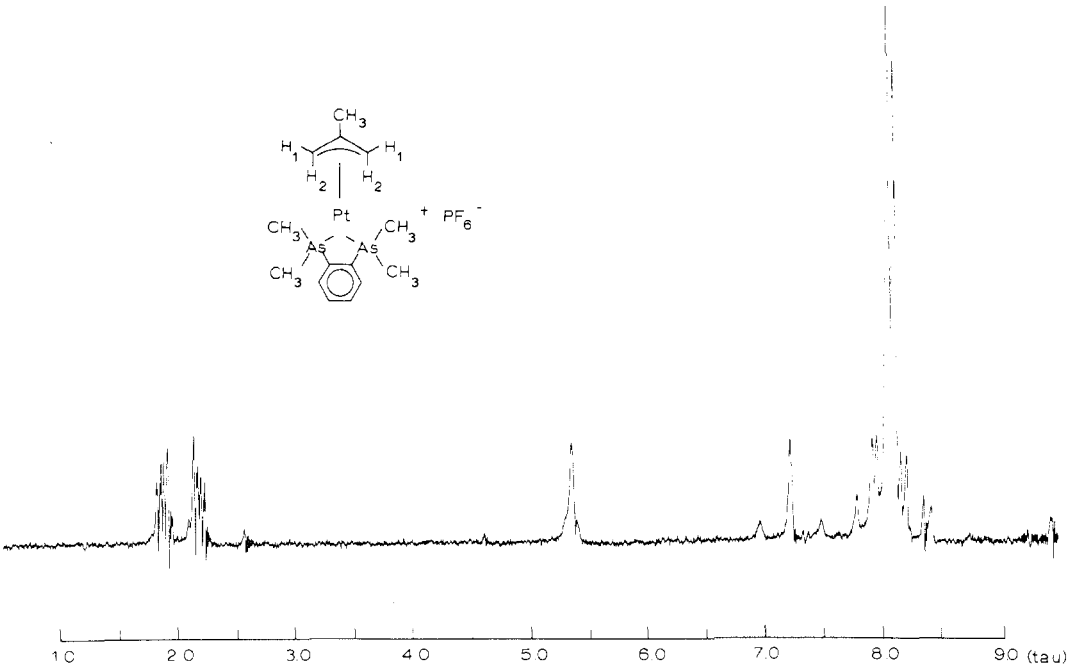
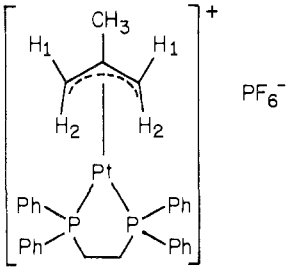
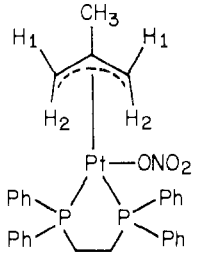
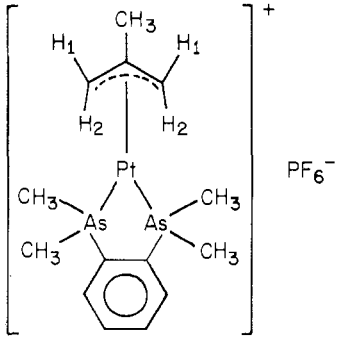


Figure 2. ^{1}H NMR spectrum of diarsPt(2-Me(all))$^+$PF$_6^-$.

Table I. ^{1}H NMR Spectra of the Static η^3-Allyl Complexes[a]

	τ_{H_2}	τ_{H_1}	τ_{CH_3}	Other
 VII	7.07 (d) (J_{PH} = 9.0 Hz, J_{PtH} = 44.5 Hz)	5.5 (s, br; $w_{1/2}$ = 7 Hz)	8.03 (s) (J_{PtH} = 57.0 Hz)	2.57 (Ph, m); 7.28 (-CH_2CH_2, d)
 VIII	7.04 (d) (J_{PH} = 9.0 Hz, J_{PtH} = 44.0 Hz)	5.48 (s, br; $w_{1/2}$ = 7.5 Hz)	8.00 (J_{PtH} = 56.8 Hz)	2.57 (Ph, m); 7.27 (-CH_2CH_2, apparent d)
 X	7.21 (J_{PtH} = 52.3 Hz, J_{12}, J_{12}' = 1.0, 1.7 Hz)	5.33 (m) (J_{PtH} = 9.4 Hz)	8.10 (J_{PtH} = 63.2 Hz)	1.62 (Ph, sym AA', BB'); 8.07 (*As*-CH_3, s, J_{PtH} = 25.6 Hz) 8.03 (*As*-CH_3, s, J_{PtH} = 24.0 Hz)

[a] In $CDCl_3$, 32°.

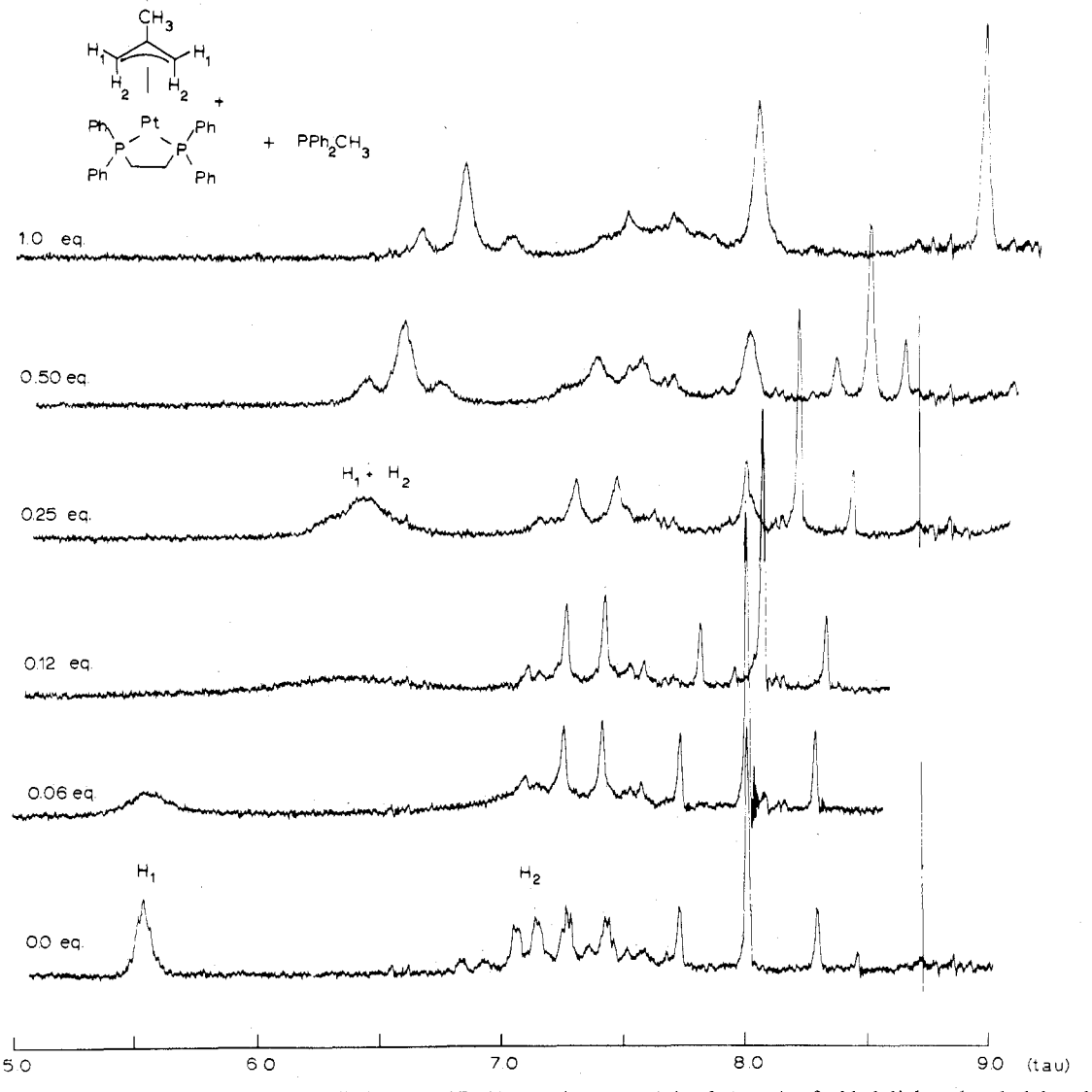


Figure 3. ^{1}H NMR spectrum of diphosPt(2-Me(all))$^+PF_6^-$ in CD_2Cl_2 solutions containing 0–1 equiv of added diphenylmethylphosphine.

the allyl moiety in its own plane, tending to average axial environments, does not occur in these four-coordinate complexes, at least under the presently described conditions.

Assignment of the allylic portion of the PMR spectra assumes[1] a higher chemical shift for the anti protons, H_2, due to their proximity to Pt.[22] As found for related static η^3-allyl complexes of Pt(II),[6,7] only the anti protons (H_2) show strong coupling to ^{195}Pt or ^{31}P (see Table I). Coupling of the syn protons (H_1) to ^{195}Pt is usually too small to be observed due to the broadness of the signal. In the case of compound X, however, double-resonance experiments revealed a small coupling with ^{195}Pt of 9.4 Hz (compare J_{PtH_2} = 52.3 Hz).

Reactions with Donor Ligands. Addition of neutral bases to solutions of the static η^3-allyl compounds VII and X caused varying degrees of collapse of the PMR signals due to the distinct anti and syn protons, H_2 and H_1. The ability of added bases to induce fluxionality is a function of their nucleophilicity[23] toward Pt(II). Thus as little as 0.1–0.2 equiv of PPh_2Me (n^0_{Pt} = ~9) or PPh_3 (n^0_{Pt} = 8.93) effectively averaged PMR signals for H_1 and H_2 at 32° for VII while pyridine (n^0_{Pt} = 3.2) required much higher temperatures (see Table II).[24]

Addition of incremental quantities of PPh_2Me to CD_2Cl_2 solutions of VII changed the chemical shift of the averaged signal for the allylic protons. In addition monotonic changes in both chemical shift and J_{PtMe} were observed for the allylic

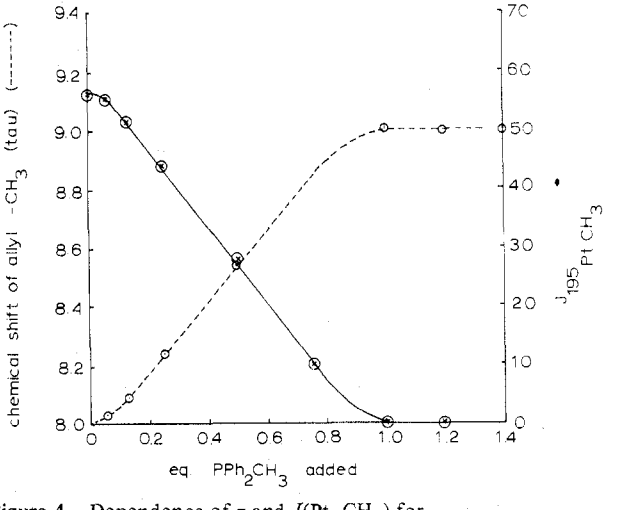


Figure 4. Dependence of τ and $J(Pt-CH_3)$ for diphosPt(2-Me(all))$^+PF_6^-$ on concentration of added diphenylmethylphosphine.

methyl group (see Figures 3 and 4). A limiting spectrum was obtained upon the addition of 1 equiv of phosphine although a yellow color developed when excess phosphine was added. These results are consistent with the formation of a 1:1 adduct

Table II. PMR Spectra of the π-Allyl Complexes in the Presence of Neutral Bases, L

L	Solvent	Temp, °C	Static η^3-allyl $\tau(H_{syn})$	Static η^3-allyl $\tau(H_{anti})$	Dynamic allyl $\tau(H_{syn})$, $\tau(H_{anti})$	$-CH_3$
			diphosPt(2-Me(all))$^+PF_6^-$			
	CD_2Cl_2	+32	5.54	7.16 (J_{PH} = 8.5, J_{PtH} = 45)[b]		8.02 (J_{PtH} = 56.5)
	o-Dichlorobenzene	+150	5.68	7.11 (J_{PH} = 9)		8.20 (J_{PtH} = 57)
PPh_2Me[a] (0.12 equiv)	CD_2Cl	+32[a]			6.41 (vb)	8.09 (J_{PtH} = 52)
PPh_2Me[a] (1.0 equiv)	CD_2Cl	+32[a]			6.88 (J_{PtH} = 37)	9.02 (J_{PtH} = 0)
py[a] (10.0 equiv)	*o*-Dichlorobenzene	+90[a]			6.36 (b)	8.18 (J_{PtH} = 56)
DMSO (neat)	DMSO	+32	5.41	6.93		8.05 (J_{PtH} = 56.5)
DMSO (neat)	DMSO	+140	5.52 (b)	7.01 (b)		8.09 (J_{PtH} = 56)
PPh_3[a] (0.10 equiv)	CD_2Cl_2	+32[a]			6.35 (b)	8.04 (J_{PtH} = 56.6)
PPh_3[a] (1.0 equiv)	CD_2Cl_2	+32[a]			6.44 (J_{PH} = 6.0, J_{PtH} = 27.2)	8.20 (J_{PtH} = 50.2)
			diarsPt(2-Me(all))$^+PF_6^-$			
	CD_2Cl_2	+32	5.46 (J_{PH} = 10)	7.26 (J_{PtH} = 50)		8.10 (J_{PtH} = 61)
	o-Dichlorobenzene	+130	5.45	7.32 (J_{PH} = 52)		8.20 (J_{PtH} = 63)
PPh_2Me[a] (0.7 equiv)	CD_2Cl_2	+32[a]			6.50 (vb)	8.30
PPh_2Me (1.0 equiv)	CD_2Cl_2	+32			6.52 (J_{PtH} = 48)	8.24 (J_{PtH} = 0)
py[a] (10.0 equiv)	*o*-Dichlorobenzene	+130[a]			Ca. 6.30 (vb)	8.28 (J_{PtH} = 62)
PPh_3[a] (0.2 equiv)	CD_2Cl_2	+32[a]			6.5 (vb)	8.13 (J_{PtH} = 56)
PPh_3 (1.0 equiv)	CD_2Cl_2	+32			6.55 (J_{PtH} = 47)	8.57 (J_{PtH} ≅ 70)

[a] Conditions required for coalescence to a single resonance for syn and anti protons. [b] All J values in Hz.

(diphos)Pt(2-Me(all))$PPh_2Me^+PF_6^-$, **XI**, which is dynamic in solution.

It is apparent from consideration of Figure 3 that rapid intermolecular exchange of PPh_2Me occurs at +32°. The phosphine methyl resonance at τ 8.02 appears as a slightly broadened singlet and no coupling with ^{195}Pt is evident.[25-27]

On cooling the above solution to −50°, phosphine exchange was slowed, resulting in a very broad signal for the *P*-CH_3 group due to coupling with two ^{31}P and one ^{195}Pt nuclei (Figure 5).

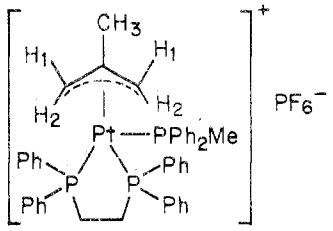
Figure 5 also shows that, at temperatures low enough to stop the averaging processes responsible for the observation of a dynamic allyl system, only a single compound is present. Two structures are possible. The static 1:1 adduct may have either a five-coordinate η^3-allyl or a four-coordinate η^1-allyl structure, XII or XIII.

The broad peak at τ 6.21 observed in the low-temperature limiting spectrum of the 1:1 adduct (Figure 5) appears to be at too high field to be assigned to the vinylic protons (H_3, H_3') of XIII,[28] but is in the correct range for H_4H_4'. Assuming that the position of the averaged allylic resonances in the high-temperature limiting spectrum lies at the weighted mean, a chemical shift of τ 7.6 is calculated[29] for the remaining allylic protons.

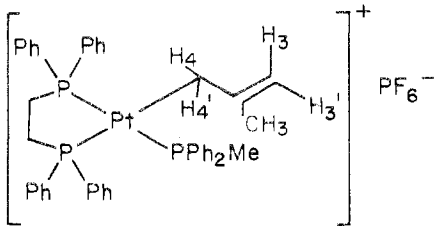
Since this is in the region expected for anti protons (H_2) *or* methylene protons (H_4), the static structure of the 1:1 adduct is not clear.

A crystalline 1:1 adduct having PMR parameters identical with those of solutions containing equimolar concentrations of PPh_2Me and VII was isolated. The infrared spectrum both in solution (CH_2Cl_2) and in the solid state did not conclusively indicate the presence of a $\nu C{=}C$ mode attributable to XIII due to weak aromatic absorption in the region about 1600 cm^{-1}.[3]

The related diars complex X behaved similarly to VII in the presence of neutral bases. Addition of small amounts of PPh_2Me gradually broadened the syn and anti proton signals of the static η^3-allyl complex. Further aliquots resulted in a broad coalesced signal at τ 6.5 which sharpened and developed distinct ^{195}Pt satellites when a total of 1 equiv had been added, indicating the presence of a dynamic 1:1 adduct (diars)Pt(2-Me(all))$PPh_2Me^+PF_6^-$, XIV.



XII (η^3)



XIII (η^1)

A 1:1 adduct which gave a PMR spectrum identical with those of solutions containing equimolar mixtures of PPh_2Me and X was isolated. This adduct, analogous to XI showed a temperature-dependent PMR spectrum (Figure 6).

The limiting high-temperature spectrum shows an averaged signal for the four allylic protons (Figure 6). Again, as with XI, no coupling of the allylic methyl group (τ 8.33) with ^{195}Pt

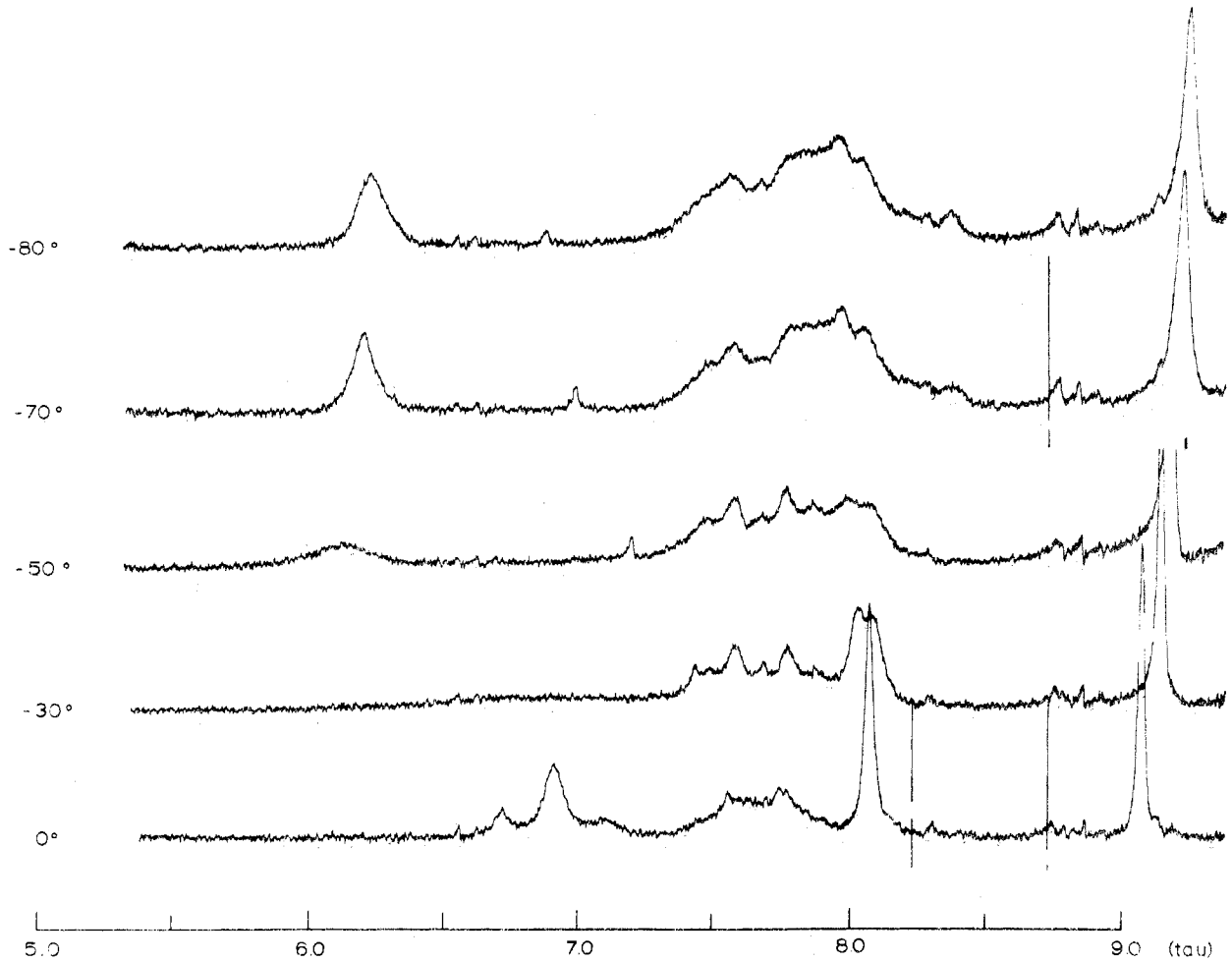


Figure 5. Variable-temperature ^1H NMR spectrum of a CD_2Cl_2 solution containing an equimolar mixture of diphosPt(2-Me(all))$^+PF_6^-$ and PPh_2Me.

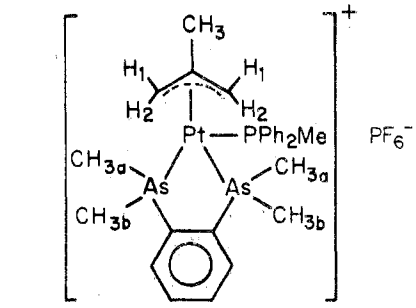
is observed. Rapid intermolecular phosphine exchange is evidenced by the lack of coupling of the *P*-CH_3 signal at τ 7.66 with ^{195}Pt. In contrast to the static η^3-allyl complex X, rapid averaging of the arsine methyl environments occurs at +32° and all four methyl groups are equivalent.

Phosphine exchange ceases at −10° and the phosphine methyl group appears as a doublet with coupling to ^{195}Pt (J_{PH} = 9.5 Hz, J_{PtH} = 37 Hz). Fairly rapid exchange of the allylic protons and of the arsine methyl groups is, however, still evident.

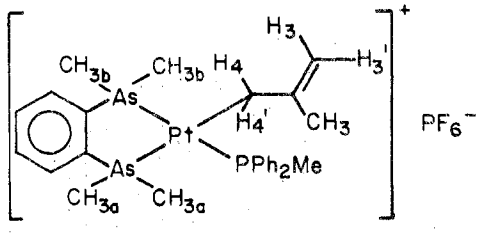
A limiting spectrum is obtained at −70°. The low-field doublet at τ 5.46 (J_{PH} = 20 Hz) can be assigned to H_1 of XV or H_3 and H_3' of XVI. The remaining allylic and phosphine methyl protons are accidentally degenerate at τ 7.6 and are consistent with assignment as H_2 of XV or H_4 and H_4' of XVI.

The low-temperature limiting spectrum indicates *two* sets of magnetically distinct arsine methyl groups. Both XV and XVI have, in principle, two sets of nonequivalent arsine methyl groups, but we believe a distinction can be made between these two structures on the following grounds.

The static symmetrically bound η^3-allyl structure XV, by virtue of its different axial environments, has two sets of arsine methyl groups. Comparison of the spectra at −10 and −70° shows, however, that even when phosphine exchange is stopped (−10°) and the time-average symmetry plane destroyed, the arsine methyl groups still occupy *averaged* environments. It is only when the allyl group is "frozen" that two distinct arsine methyl signals emerge. In addition the coupling of the arsine methyl groups to ^{195}Pt appears to be different (ca. 16 Hz vs.



XV



XVI

<10 Hz) indicating the presence of two groups of different trans influence in the plane.[19] Further, the 1:1 adduct XIV shows a medium-intensity band at 1620 cm^{-1} (Raman) not present in X or PPh_2Me. This is assigned to $\nu_{C=C}$ in the four-coordinate η^1-allyl complex XVI[11] and would not be observed in η^3-allyl systems. These data are thus consistent with XVI rather than XV, although an unambiguous con-

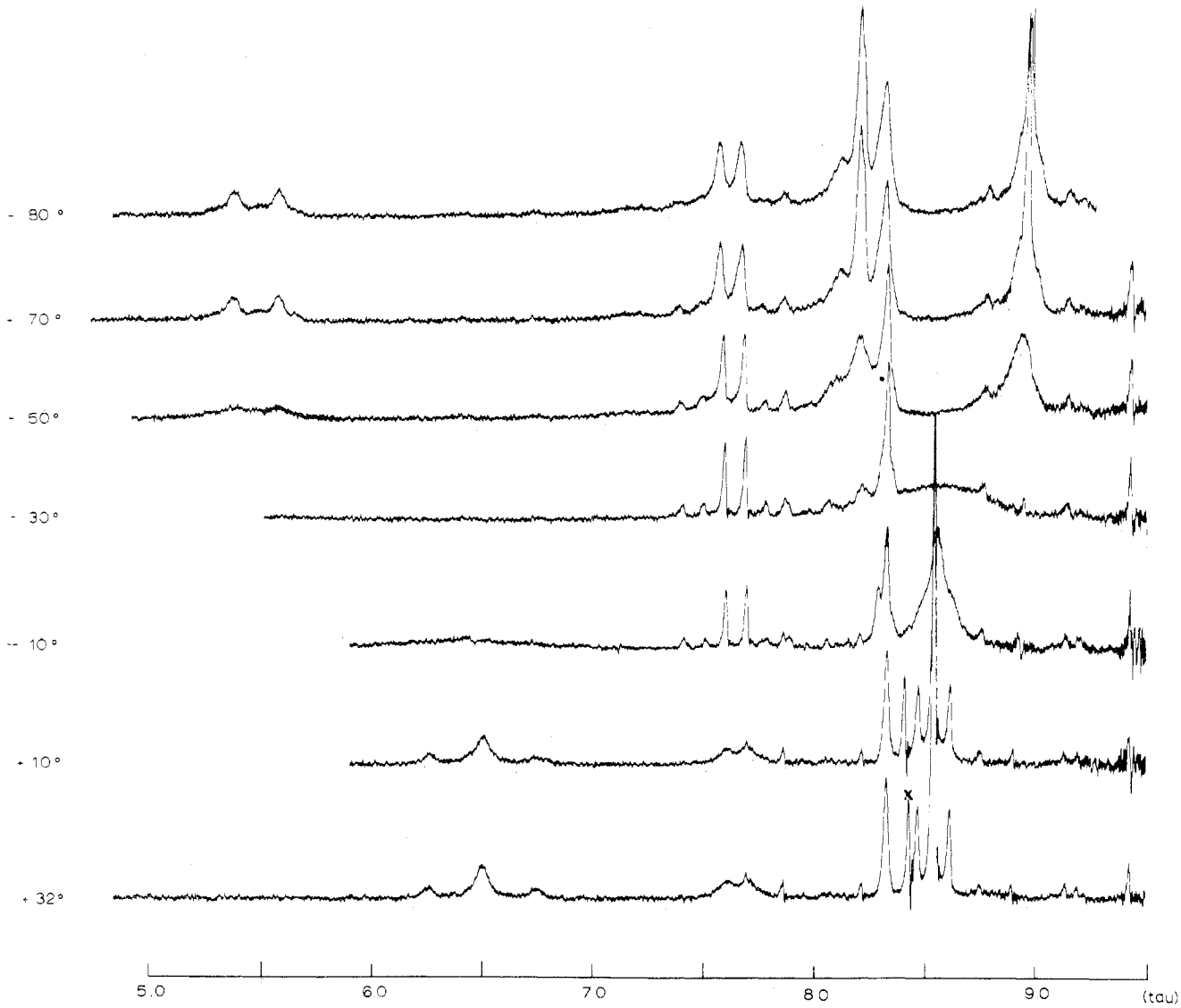


Figure 6. Variable-temperature ^{1}H NMR spectrum of CD_2Cl_2 solution containing an equimolar mixture of diarsPt(2-Me(all))$^+PF_6^-$ and PPh_2Me (X = impurity).

firmation must await the results of an X-ray crystallographic structure determination.

It is generally agreed[12a,30] that mechanisms other than σ–π allyl ($\eta^1 \rightleftharpoons \eta^3$) interconversion are unlikely to account for the base-induced fluxionality of related Pd(II) systems. Since both VII and X retain their static η^3-allyl structures at elevated temperature in the absence of bases, the observed syn–anti exchange can be accounted for in terms of Scheme I.

It is not clear whether XVIII and XX are intermediates[14,28] or transition states.[12a] The low-temperature PMR data obtained for the 1:1 adduct XIV which shows a single species assigned structure XVI indicate that if XVIII and XX are intermediates K_2 (and K_2') is large. In either case, however, stronger nucleophiles will tend to facilitate exchange, and conversion to a η^1-allyl species is unlikely in the absence of a suitable B:.

Experimental Section

diphosPtMe$_2$. To a stirred solution of 1.82 g of (COD)PtMe$_2$[17] in 30 ml of acetone was added dropwise a solution of 3.65 g of diphos in 20 ml of CH_2Cl_2. A white precipitate developed and the reaction mixture was stirred overnight. Removal of solvent left a white solid which was washed with several portions of pentane and dried in vacuo to remove cyclooctadiene. The yield is 2.60 g (76%) of white powder, mp 215–216° dec (lit.[16] 221–223°).

diphosPtMeCl. To a stirred solution of 1.50 g of diphosPtMe$_2$ in 100 ml of CH_2Cl_2 was slowly added a solution of 172 μl of freshly distilled acetyl chloride in 50 ml of CH_2Cl_2 containing 10 ml of methanol. The reaction mixture was stirred for 1.0 hr. Removal of solvent gave a white solid which was recrystallized from CH_2Cl_2–Et_2O to give 1.43 g (94%) of diphosPtMeCl as white needles, mp 265–267°.

Anal. Calcd for $C_{27}H_{27}P_2PtCl$: C, 50.35; H, 4.22. Found: C, 50.03; H, 4.30.

Ir (KBr disk) (cm^{-1}): 3050 (m), 2920 (w), 2870 (m), 1480 (m), 1430 (s), 1405 (m), 1306 (m), 1272 (w), 1182 (m), 1156 (w), 1100 (vs), 1068 (m), 1035 (m), 998 (m), 880 (m), 824 (s), 745 (s), 700 (vs, br), 655 (m), 525 (vs), 490 (s). PMR ($CDCl_3$): τ 2.00, 2.40 (m, Ph); 7.76 (m, $-CH_2CH_2-$); 9.38 (dd, $J_{P_{cis}H}$ = 3.5 Hz, $J_{P_{trans}H}$ = 7.7 Hz, $J_{^{195}PtH}$ = 56.2 Hz, $-CH_3$).

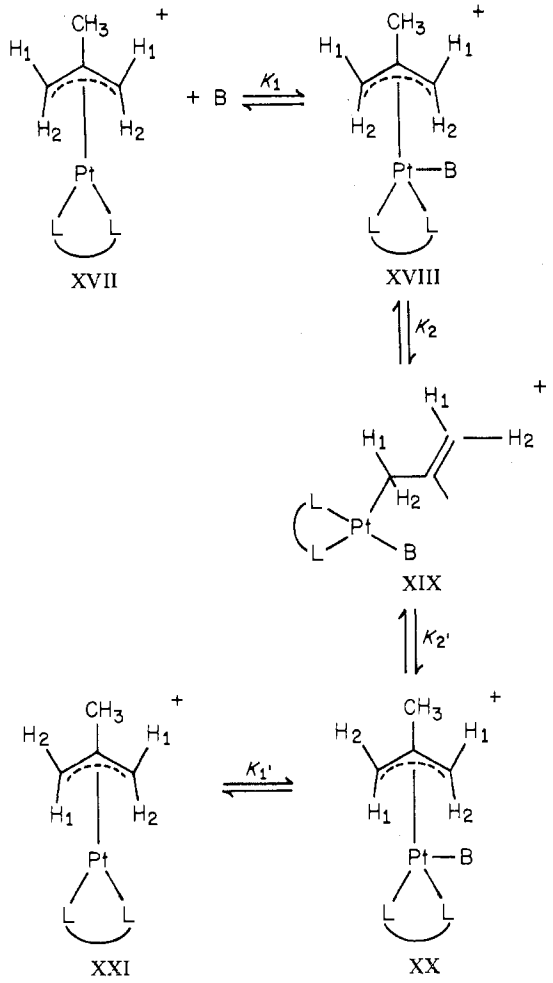
diphosPtMe(ONO$_2$). To 500 mg of diphosPtMeCl in 50 ml of 1:1 CH_2Cl_2–MeOH was added 132 mg of $AgNO_3$ dissolved in 5 ml of 1:10 H_2O–MeOH. The resulting white precipitate of AgCl was filtered to give a pale yellow solution. Removal of solvent left a pale yellow solid which was purified by chromatography through a small Florisil column eluted with CH_2Cl_2. Recrystallization from CH_2Cl_2–Et_2O gave 402 mg (77%) of white needles, mp 206–207° dec.

Anal. Calcd for $C_{27}H_{27}P_2PtNO_3$: C, 48.36; H, 4.06. Found: C, 47.93; H, 4.08.

PMR ($CDCl_3$): τ 2.55 (m, Ph); 7.90 (m, $-CH_2CH-$); 9.50 (dd, $J_{P_{cis}H}$ = 2.0 Hz, $J_{P_{trans}H}$ = 7.6 Hz, $J_{^{195}PtH}$ = 48.8 Hz, $-CH_3$).

diphosPt(2-Me(all))$^+$PF$_6^-$. To 500 mg of diphosPtMeCl in 30 ml

Scheme I



of CH_2Cl_2 was added a solution of 197 mg of $AgPF_6$ in 20 ml of CH_2Cl_2 containing 150 μl of acetone. The white precipitate of AgCl was filtered off and the clear colorless filtrate transferred to a 100-ml round-bottomed flask fitted with a magnetic stirrer and serum cap. Allene was bubbled through the solution for 10 min and the reaction mixture was allowed to stir for an additional 0.5 hr. Removal of solvent left an off-white residue which was recrystallized from CH_2Cl_2–Et_2O to give 449 mg (73%) of white crystals, mp 208–209°.

Anal. Calcd for $C_{30}H_{31}P_3PtF_6$: C, 45.41; H, 3.94. Found: C, 45.50; H, 3.74.

Ir (KBr disk) (cm^{-1}): 3145 (w), 3060 (m), 2905 (w), 1480 (m), 1435 (s), 1410 (m), 1380 (mw), 1330 (mw), 1305 (mw), 1185 (mw), 1160 (w), 1100 (s), 1070 (w), 1025 (m), 998 (m), 955 (m), 915 (mw), 840 (vs), 750 (s), 700 (vs), 650 (m), 550 (s), 525 (s), 490 (m), 478 (m).

diphosPt(2-Me(all))(ONO_2). A solution of 150 mg of diphosPtMe(ONO_2) in 30 ml of CH_2Cl_2 was stirred under a pressure of 1 atm of allene for 24 hr. The resulting yellow solution was chromatographed through a Florisil column which was then eluted with CH_2Cl_2. Removal of solvent gave 144 mg of a sticky solid. Repeated chromatography and recrystallization from CH_2Cl_2–Et_2O gave white needles, mp 260–261°.

Anal. Calcd for $C_{30}H_{31}P_2PtNO_3$: C, 50.71; H, 4.40. Found: C, 50.57; H, 4.79.

Ir (KBr disk) (cm^{-1}): 3050 (w), 2950 (w), 2875 (w), 1480 (m), 1430 (s), 1405 (m), 1370 (m), 1330 (m), 1305 (mw), 1270 (w), 1185 (mw), 1100 (s), 1070 (w), 1025 (mw), 998 (m), 880 (mw), 825 (m), 750 (m), 710 (s), 690 (s), 660 (w), 525 (s), 485 (m).

diarsPt(2-Me(all))$^+PF_6^-$. The title compound was prepared from 319 mg of diarsPtMeCl, 152 mg of $AgPF_6$, and excess allene as described for diphosPt(2-Me(all))$^+PF_6^-$. Purification by Florisil chromatography and recrystallization from CH_2Cl_2–Et_2O gave 248 mg (61%) of the π-allyl complex as white needles, mp 182–182.5°.

Anal. Calcd for $C_{14}H_{23}As_2PtPF_6$: C, 24.76; H, 3.12. Found: C, 24.56; H, 3.27.

Ir (KBr disk) (cm^{-1}): 3100 (w), 3055 (w), 2925 (mw), 1418 (w), 1400 (m), 1380 (m), 1330 (w), 1280 (w), 1262 (w), 1100 (m), 1030 (mw), 968 (mw), 915 (m), 885 (s), 840 (vs), 760 (s), 620 (mw), 595 (mw), 550 (vs), 340 (m), 270 (mw), 260 (m).

diphosPt(2-Me(all))$PPh_2Me^+PF_6^-$. A solution of 25 mg of Ph_2Me in 10 ml of methylene chloride was added to a solution of 100 mg (0.126 mmol) of diphosPt(2-Me(all))$^+PF_6^-$. A yellow color developed toward the end of the addition. The solution was concentrated and chromatographed through a short Florisil column, eluting with CH_2Cl_2. Two recrystallizations from CH_2Cl_2–pentane gave the product as small white crystals, mp 152° dec.

Anal. Calcd for $C_{43}H_{44}P_4PtF_6$: C, 51.97; H, 4.46. Found: C, 51.78; H, 4.46.

Ir (KBr) (cm^{-1}): 1490 (m), 1440 (vs), 1420 (m), 1315 (m), 1300 (w), 1270 (w), 1200 (w), 1160 (w), 1100 (vs), 1080 (w), 1030 (m), 1000 (s), 885 (m), 840 (vs), 750 (s), 700 (s), 550 (m).

diarsPt(2-Me(all))$PPh_2Me^+PF_6^-$. To a solution of 100 mg of diarsPt(2-Me(all))$^+PF_6^-$ in methylene chloride was added via syringe 29.5 μl of PPh_2Me. A yellow color appeared which dissipated after 48 hr at room temperature. Removal of solvent left a gummy solid which was chromatographed through a short Florisil column and recrystallized several times from CH_2Cl_2–pentane to give 66 mg (48%) of the title complex as well-formed colorless needles, mp 210° dec.

Anal. Calcd for $C_{27}H_{36}As_2PtP_2F_6$: C, 36.79; H, 4.12. Found: C, 37.04; H, 3.93.

Raman spectrum (cm^{-1}): 1620 (m), 1585 (m), 1570 (mw), 1435 (w), 1920 (w), 1410 (w), 1390 (m), 1365 (mw), 1275 (m), 1165 (vs), 1130 (m), 1100 (m), 1030 (s), 1000 (vs), 970 (w), 820 (w), 795 (w), 740 (m), 720 (w), 705 (w), 690 (w), 620 (vs), 600 (vs), 590 (vs), 465 (m), 370 (s), 350 (m).

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Registry No. HCl, 7647-01-0; $diphosPtMe_2$, 15630-18-9; diphosPtMeCl, 27711-50-8; diphosPtMe(ONO_2), 39584-15-1; diphosPt(2-Me(all))$^+PF_6^-$, 54788-65-7; allene, 463-49-0; diphosPt(2-Me(all))(ONO_2), 54788-66-8; diarsPtMeCl, 52594-56-6; diarsPt(2-Me(all))$^+PF_6^-$, 54788-68-0; diphosPt(2-Me(all))$PPh_2Me^+PF_6^-$, 54814-55-0; diarsPt(2-Me(all))$PPh_2Me^+PF_6^-$, 54814-57-2; pyridine, 110-86-1; DMSO, 67-68-5; PPh_3, 603-35-0.

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Contribution from the Laboratorio CNR and Istituto di Chimica Generale ed Inorganica dell'Università di Firenze, Florence, Italy

Proton Magnetic Resonance Spectra of Bis(*N*-alkylsalicylaldiminato)copper(II) Complexes

I. BERTINI,* A. DEI, and A. SCOZZAFAVA

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Proton magnetic resonance spectra of a series of bis(*N*-alkylsalicylaldiminato)copper(II) complexes have been recorded and the isotropic shifts have been factorized into their dipolar and contact contributions. The contact shift pattern has been compared with that of other bis(*N*-alkylsalicylaldiminato)metal(II) complexes. The PMR line width as well as the contact shift values are found to increase along the series from *N*-methyl to *N*-*tert*-butyl.

Introduction

It is generally believed that PMR spectra of copper(II) complexes are not useful owing to unfavorable electronic relaxation times which broaden up the signals.[1-7] However, the observation of proton signals for some bis(*N*-alkylsalicylaldiminato)copper(II) complexes[5,8] ($Cu(sal\text{-}N\text{-}R)_2$) induced us to investigate a series of these complexes by means of PMR spectroscopy in order to determine the nature of the isotropic shifts and to investigate the factors which determine the PMR line width.

Experimental Section

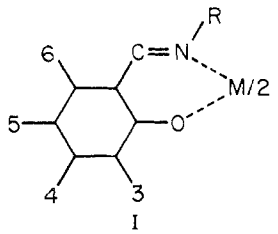
Materials. The complexes were prepared according to literature methods[9,10] and analyzed satisfactorily for C, H, and N.

PMR Measurements. Proton magnetic resonance spectra were recorded with a Varian DA-60-IL spectrometer at 60 MHz. Shifts were calibrated from internal tetramethylsilane (TMS). The spectra were recorded both in HR mode (side-band technique used for calibration) and in HA mode in internal lock. Deuteriochloroform (Merck, 99.8%) was used as solvent.

ESR Measurements. ESR spectra of ca. 10^{-3} *M* "glassy" solutions of bis(*N*-alkylsalicylaldiminato)copper(II) complexes in chloroform were obtained with a Varian E-9 spectrometer, using diphenylpicrylhydrazone (DPPH) as external standard.

Results

All the investigated complexes give reasonably sharp PMR signals for the 4 and 5 protons of the salicylaldiminate ligand (I). In the cases of bis(*N*-methylsalicylaldiminato)- and



I

bis(*N*-ethylsalicylaldiminato)copper(II) complexes, broad signals, attributable to the 3 and 6 proton resonances, respectively, have been detected; however in the other cases investigated (R = *n*-propyl, isopropyl, *tert*-butyl) the resonance peaks of these protons were not detected, presumably because they were very broad or were covered by intense *N*-alkyl resonances.

Assignments of the proton absorptions have been performed through substitution of the protons by methyl or halide groups. The broad and strong signals which appear near TMS in the spectra of all the complexes (with the exception of bis(*N*-methylsalicylaldiminato)copper(II)) are attributable to the β and γ protons of the aliphatic chains. The observed isotropic shifts of the aromatic protons are shown in Table I. The room-temperature PMR spectra of bis(*N*-methylsalicylaldiminato)- and bis(*N*-ethylsalicylaldiminato)copper(II) complexes are reported in Figure 1.

The signal half-widths strongly depend on the nature of the

Table I. Isotropic Shifts (ppm) of Bis(*N*-alkylsalicylaldiminato)copper(II) Complexes in $CDCl_3$ at 26°[a]

Alkyl group	3-H	4-H	5-H	6-H
Methyl[b]	16	−2.3	1.2	−23
Ethyl		−2.6	1.6	−29
n-Propyl		−2.7	1.8	
Isopropyl		−3.2	3.0	
tert-Butyl		−3.3	3.2	

[a] The isotropic shifts are determined relative to the reported shifts for the bis(*N*-alkylsalicylaldiminato)zinc(II) complexes: J. D. Thwaites, I. Bertini, and L. Sacconi, *Inorg. Chem.*, **5**, 1036 (1966). [b] Methyl isotropic shifts (ppm) of *n*-CH_3 derivatives: 3-CH_3, −0.2; 4-CH_3, 6.5; 5-CH_3, −2.7.

Table II. 4-H Signal Half-Widths (Hz) of Bis(*N*-alkylsalicylaldiminato)copper(II) Complexes in $CDCl_3$ at 26°

Derivative				
Methyl	Ethyl	*n*-Propyl	Isopropyl	*tert*-Butyl
90	100	110	150	250

Table III. Temperature Dependence of 4-H Signal Half-Width (Hz) for Bis(*N*-ethylsalicylaldiminato)copper(II) and Bis(*N*-*n*-propylsalicylaldiminato)copper(II) Complexes in $CDCl_3$

	Temp, °C			
Derivative	57	26	−11	−31
Ethyl	70	100	210	250
n-Propyl	75	110	220	270