N(2)–Co–N(4), 97.2°, 0.8 kcal/mol). Bond stretching at the *N*-methyl center is once again observed (Co–N(5), 1.993 Å, 0.6 kcal/mol).

TABLE I

FINAL ENERGY TERMS FOR β_2-Co(trien)(*N*-Me-ala)$^{2+}$ ISOMERS (KCAL/MOL)

	Δ-β_2-(*RRS*)-Co(trien)-(*N*-Me-(*R*)-ala)$^{2+}$	Δ-β_2-(*RRS*)-Co(trien)-(*N*-Me-(*S*)-ala)$^{2+}$	Δ-β_2-(*RSS*)-Co(trien)-(*N*-Me-(*R*)-ala)$^{2+}$	Δ-β_2-(*RSS*)-Co(trien)-(*N*-Me-(*S*)-ala)$^{2+}$
Bond length deformations, $\Sigma U(r_{ij})_{\mathrm{B}}$	1.4	1.5	1.5	1.7
Nonbonded interactions, $\Sigma U(r_{ij})_{\mathrm{NB}}$	6.0	6.2	6.0	6.7
Valence angle deformations, $\Sigma U(\theta_{ijk})$	5.0	5.6	6.9	7.4
Torsional strain, $\Sigma U(\phi_{ijkl})$	5.5	5.1	6.1	5.8
Total conformational energy, *U*	17.9	18.4	20.5	21.6
Energy differences (relative to Δ-β_2-(*RRS*)-Co(trien)(*N*-Me-(*R*)-ala)$^{2+}$ isomer)	0	0.5	2.6	3.7

Final energy terms for the four isomers are listed in Table I. The calculated energy difference between the Δ-*RRS*(*R*) and Δ-*RRS*(*S*) isomers (which differ only in the configuration at the asymmetric α-carbon atom) is 0.5 kcal/mol in favor of the Δ-*RRS*(*R*) isomer. This result is in good agreement with the equilibration studies, where $\Delta G_{25°}$ was found to be 0.7 kcal/mol in favor of the Δ-*RRS*(*R*) isomer. The result was unexpected in view of the considerable steric interaction evident from Dreiding models between the cis *N*-methyl and *C*-methyl groups for the Δ-*RRS*(*S*) isomer. However, it appears that angular deformations can relieve these interactions with the expenditure of only a relatively small amount of bond angle strain energy. The Δ-*RSS*(*R*) isomer was calculated to be 2.6 kcal/mol less stable than the Δ-*RRS*(*R*) isomer, these two complexes being related by inversion at the trien "planar" secondary N atom, N(2). This result is in accord with experiment which showed that the Δ-*RSS*(*R*) isomer is not formed in solution in detectable amounts ($<2\%$) under equilibrium conditions. This places a lower limit of 2.3 kcal/mol on the free energy difference between these isomers.

In the case of the Δ-*RSS*(*S*) isomer, with the unstable *S* configuration at atom N(2) and unfavorable cis methyl groups for the amino acid moiety, the minimization calculations predict this isomer to be less stable than the *RRS*(*S*) isomer by 3.2 kcal/mol; a similar qualitative result is obtained from an examination of Dreiding models. However the equilibration studies show that the Δ-*RSS*(*S*) and Δ-*RRS*(*S*) isomers have approximately equal stabilities. If the calculations correctly predict the relative enthalpy differences between the isomers, it would seem that an entropy term is an important factor in determining the free energy difference. Experiments designed to check this possibility are now in progress.

It can be seen that the strain energy minimization calculations on the β_2-Co(trien)(*N*-Me-ala)$^{2+}$ isomers predict some interesting geometrical distortions. A structural analysis is in progress on one of the isomers with cis methyl groups to establish the validity or otherwise of these predictions and also to determine the configuration about the "planar" N atom of trien.

Acknowledgment.—The authors thank Mr. C. Arandjelovic for the nmr spectra and Drs. R. H. Boyd and M. R. Snow for the computer programs. Minimization calculations were carried out on an IBM 360/50 computer at the Computing Center, Australian National University. Molecular diagrams were produced using Dr. C. Johnson's program ORTEP on a CDC 3600 computer of the CSIRO Division of Computing Research, Canberra.

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Insertion Reactions into the Methylplatinum Bond.
I. Thermal Reactions

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Insertion reactions of tetrafluoroethylene, hexafluorobut-2-yne, and carbon monoxide into the Pt–C bond of methylplatinum complexes of types *trans*-PtXCH$_3$L$_2$ and *cis*-Pt(CH$_3$)$_2$L$_2$ (X = halogen, L = tertiary phosphine or arsine) are described. Insertion into either one or both Pt–C bonds of *cis*-Pt(CH$_3$)$_2$L$_2$ can occur. The reactions are believed to proceed by rearrangement of intermediate π complexes, the stability of which governs the rate of insertion.

Introduction

Insertion reactions of unsaturated compounds into the metal–hydrogen or metal–carbon bond represent an important stage in the catalytic process of hydrogenation or polymerization, respectively.[1] Insertion reactions of fluoroolefins and -acetylenes, which give stable fluoroalkyl- or fluorovinylmetal compounds, have proved particularly useful since the product of a single

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* To whom correspondence should be addressed.

[1] M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 312.

TABLE I

ANALYTICAL DATA AND PHYSICAL CONSTANTS OF THE INSERTION PRODUCTS

Compound		Analysis, %						Mol wt[a]		Yield, %	Mp, °C	ν(C=C), cm^{-1}
		C		H		F						
X	L	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found			
				(A) $PtX(CF_2CF_2CH_3)L_2$								
Cl	$P(CH_3)_2C_6H_5$	36.7	36.7	4.05	4.0	12.2	12.0	622	631	82	129–131	
Br	$P(CH_3)_2C_6H_5$	34.25	34.4	3.8	3.8	11.4	11.1	666		87	130–131	
I	$P(CH_3)_2C_6H_5$	32.0	31.9	3.5	3.55	10.7	10.0	713	702	52	158–160	
Cl	$As(CH_3)_2C_6H_5$	32.15	31.8	3.55	3.6	10.7	10.9	710	710	66	101–102	
Cl	$As(CH_3)_3$	18.5	19.4	3.6	3.9	13.0	12.7	586		39	115	
CH_3	$P(CH_3)_2C_6H_5$[b]	39.9	38.5	4.7	4.55	12.6	15.5	601	634		Oil	
$CH_3CF_2CF_2$	$As(CH_3)_2C_6H_5$	33.5	33.9	3.6	3.4	19.3	19.5	789		58	154–155	
				(B) $PtX[C(CF_3)=C(CF_3)CH_3]L_2$								
Cl	$P(CH_3)_2C_6H_5$	36.9	36.2	3.7	3.5	16.7	16.45	684	676	45	154–156	1610 m
Br	$P(CH_3)_2C_6H_5$	34.6	35.2	3.5	3.1	15.65	15.9	728		60	155–157	1610 m
I	$P(CH_3)_2C_6H_5$	32.5	33.25	3.25	3.3	14.7	14.1	775		50	122–125	1610 m
Cl	$As(CH_3)_2C_6H_5$	32.7	33.05	3.3	3.4	14.8	15.0	772	782	66	149–151	1610 m
Cl	$As(CH_3)_3$	20.4	21.1	3.3	3.4	17.6	19.0	648		58	151–152	1610 m

[a] In benzene solution. [b] Contains impurity of $Pt(CF_2CF_2CH_3)_2L_2$ (see text).

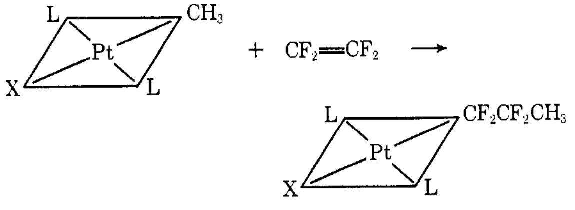
insertion may be easily isolated and characterized.[2–6]

The only known additions of metal–alkyl bonds across fluoroolefins, probably by a free-radical mechanism,[7] occur in the reactions of $CH_3Mn(CO)_5$[2] and $CH_3Au[P(C_6H_5)_3]_2$[3] with tetrafluoroethylene. Reactions of alkylmetal derivatives with acetylenes often give more complex products.[8] Metal hydrides have been studied more thoroughly.[4–6] In particular the reactions of *trans*-$PtHClL_2$ (L = tertiary phosphine) with C_2F_4 may give either a 1:1 insertion product[6] or (in moist methanol) a mixture of a cationic platinum carbonyl and two fluorovinylplatinum compounds.[5,6] We have extended this work to a study of insertions into the platinum–methyl bond, with emphasis on the factors which govern the reactivity of different methylplatinum compounds toward insertion.

Results

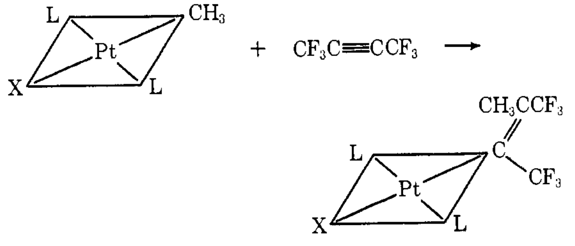
Methylplatinum compounds of types *trans*-$PtXCH_3L_2$ and *cis*-$Pt(CH_3)_2L_2$ where X = halogen and L = tertiary phosphine or arsine were studied. They are among the most stable transition metal alkyls, and a wide variety of such compounds is known.[9–11]

Isolation and Characterization of Insertion Products.—Equations 1 and 2 show the course of the reactions of *trans*-$PtXCH_3L_2$ [X = Cl, Br, or I and L = $P(CH_3)_2C_6H_5$, $As(CH_3)_2C_6H_5$, or $As(CH_3)_3$] with tetrafluoroethylene (C_2F_4) and hexafluorobut-2-yne (C_4F_6), respectively, when the reactants were heated at 60–80° for 24–48 hr in a sealed tube.



I

(1)



II

(2)

Tetrafluoroethylene inserted into both Pt–C bonds of *cis*-$Pt(CH_3)_2L_2$ when L = $As(CH_3)_2C_6H_5$ giving $Pt(CF_2CF_2CH_3)_2L_2$. However insertion took place into only one Pt–C bond of *cis*-$Pt(CH_3)_2L_2$ when L = $P(CH_3)_2C_6H_5$, giving largely $PtCH_3(CF_2CF_2CH_3)L_2$, though this was contaminated with a little of the product of insertion into both Pt–C bonds. The preferred solvent for these reactions was dry benzene though dry acetone or methanol was also satisfactory. The analytical data and physical properties of the crystalline insertion products are shown in Table I.

Other fluoroolefins were less reactive and gave less stable products. Thus, hexafluoropropene reacted with *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ only on heating to 100° for 72 hr; the product decomposed on recrystallization from methanol to *cis*-$PtCl_2[P(CH_3)_2C_6H_5]_2$ and an unidentified fluoroalkylplatinum compound. Similarly, chlorotrifluoroethylene gave only *cis*-$PtCl_2[P(CH_3)_2C_6H_5]_2$, while trifluoroethylene and perfluorocyclobutene did not react with *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ at 90° in benzene solution.

Nmr Spectra of Insertion Products. (a) ^{1}H Nmr Spectra.—The nmr data are given in Tables II and III. The characteristic resonances of the methyl groups in

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[3] C. M. Mitchell and F. G. A. Stone, Proceedings of the 4th International Conference on Organometallic Chemistry, F. G. A. Stone and M. I. Bruce, Ed., E5, 1969.

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TABLE II

^{1}H AND ^{19}F NMR SPECTRAL DATA FOR $PtX(CF_2{}^1CF_2{}^2CH_3{}^1)L_2$[a]

Compound			^2J +										
X	L	$\delta(CH_3Y)$[b]	^4J(PH)	^3J(PtH)	$\delta(CH_3{}^1)$	$^3J(H^1F^2)$	$^4J(PtH^1)$	$\delta(CF_2{}^1)$	$^3J(PF^1)$	$^2J(PtF^1)$	$^3J(F^1F^2)$	$\delta(CF_2{}^2)$	$^3J(PtF^2)$
Cl	$P(CH_3)_2C_6H_5$	−1.84	7.0	29.0	−1.52	19.0	3	68.3	29.2	480	6.5	94.5	66
Br	$P(CH_3)_2C_6H_5$	−1.94	7.2	28.0	−1.64	18.5	3.5	68.2	29.8	487.5	7.0	94.1	74
I	$P(CH_3)_2C_6H_5$	−2.11	7.3	27.7	−1.80	18.5	4	68.3	28.4	484	4.0	93.8	62
Cl	$As(CH_3)_2C_6H_5$	−1.67	...	19.5	−1.49	18.5	3	66.7	...	467	3.0	95.1	98
Cl	$As(CH_3)_3$	−1.35	...	20.8	−1.69	18.7	4.5	67.4	...	474	3.1	95.3	106.5
CH_3	$P(CH_3)_2C_6H_5$[c]	−1.7	*d*	*d*	−1.72	19.0	*d*	69.0	28.7	475	*d*	95.8	*d*
$CH_3CF_2CF_2$	$As(CH_3)_2C_6H_5$[e]	−1.76	...	*f*	−1.65	18.5	*d*	78.0	...	454	3.0	97.1	76
$CH_3CF_2CF_2$	$As(CH_3)_2C_6H_5$[e,g]	−1.26	...	*f*	−1.65	18.5	*d*	78.0	...	264	3	93.7	55

[a] Trans isomer in chloroform unless otherwise stated; δ in ppm; *J* in Hz. [b] Y = P or As. [c] Stereochemistry unknown (recorded as mixture with $Pt(CF_2CF_2CH_3)_2L_2$, $\delta(CF_2{}^1)$ 69 ppm, $\delta(CF_2{}^2)$ 94.7 ppm, unresolved peaks). [d] Values obscured. [e] Solvent benzene. [f] Coupling not observed due to rapid exchange between isomers. [g] Cis geometry.

TABLE III

^{1}H AND ^{19}F NMR SPECTRAL DATA FOR *trans*-$PtX[C(CF_3{}^1){=}C(CF_3{}^2)CH_3{}^1]L_2$[a]

Compound			^2J +										
X	L	$\delta(CH_3Y)$[b]	^4J(PH)	^3J(PtH)	$\delta(CH_3{}^1)$	$^5J(H^1F^1)$	^4J(PtH)	$\delta(CF_3{}^1)$	$^5J(F^1F^2)$	$^3J(PtF^1)$	$\delta(CF_3{}^2)$	$^5J(PtF^2)$
Cl	$P(CH_3)_2C_6H_5$	−1.76, −1.73	6.8	30.2	−1.95	1.7	15	50.8	15.0	128.3	61.0	6.2
Br	$P(CH_3)_2C_6H_5$	−1.91, −1.84	6.7	29.6	−2.10	2.0	14.5	50.8	15.0	140.3	61.2	6.3
I	$P(CH_3)_2C_6H_5$	−2.00, −1.94	7.3	30.2	−2.20	1.8	15	50.9	14.8	136.6	61.2	...
Cl	$As(CH_3)_2C_6H_5$	−1.74, −1.73	...	21.8	−2.05	2.0	12.5	51.5	15.0	128.5	60.6	3.5
Cl	$As(CH_3)_3$	−1.19	...	22.1	−2.35	1.9	14.6	51.5	15.1	135.4	59.7	...

[a] Solvent chloroform; δ in ppm; *J* in Hz. [b] Y = P or As.

dimethylphenylphosphine complexes of platinum(II) give much information about the stereochemistry of these complexes.[10-12] For complexes of the type *trans*-$PtXY[P(CH_3)_2C_6H_5]_2$, the methyl groups give an apparent 1:2:1 triplet, by coupling with ^{31}P, with triplet satellites due to coupling with ^{195}Pt (33% natural abundance). This pattern was observed for the C_2F_4 insertion products of *trans*-$PtXCH_3[P(CH_3)_2C_6H_5]_2$, confirming their structures as *trans*-$PtX(CF_2CF_2CH_3)[P(CH_3)_2C_6H_5]_2$. However, the spectra of the C_4F_6 insertion products showed *two* overlapping triplets of equal intensity, indicating a structure in which there is no plane of symmetry containing the P–Pt–P axis.[12] This is consistent with the products having structure II, L = $P(CH_3)_2C_6H_5$, in which the plane of the vinyl group is perpendicular to the molecular plane, a configuration which facilitates back-bonding from filled d orbitals of platinum into antibonding orbitals of the vinyl group. A similar effect has been observed previously in some *o*-tolylnickel complexes.[12] Similarly complexes II, L = $As(CH_3)_2C_6H_5$, give *two* singlets of equal intensity for the methylarsine resonance, while the complexes *trans*-$PtX(CF_2CF_2CH_3)[As(CH_3)_2C_6H_5]_2$ give only one singlet.

(b) **^{19}F Nmr Spectra.**—The ^{19}F nmr spectra of complexes I are consistent with those expected for tetrafluoropropylplatinum compounds and do not merit further discussion. The ^{1}H and ^{19}F nmr spectra of $Pt(CF_2CF_2CH_3)_2[As(CH_3)_2C_6H_5]_2$ in benzene (Table II) contain more peaks than expected for either the cis or trans isomer alone and are interpreted in terms of an almost equimolar mixture of both isomers. In this sense the behavior is like that of dichloroplatinum(II) complexes[13] rather than the dialkylplatinum(II) complexes which normally exist as the cis isomers only.[9,10] The apparently anomalous behavior in this case is probably due to the high electronegativity of the fluoroalkyl group. The stereochemistry of the crystalline, solid complex is not known.

The ^{19}F nmr spectrum of the α-CF_2 group in $PtCH_3(CF_2CF_2CH_3)L_2$, L = $P(CH_3)_2C_6H_5$, appeared as a quartet with platinum side bands, rather than the triplet pair of doublets expected by coupling with two ^{31}P nuclei in the trans or cis isomer, respectively. Unfortunately, the resonances of the methylphosphine groups in the ^{1}H nmr spectrum were obscured by those due to the other methyl groups, and we are unable to determine the stereochemistry of this complex. On standing in chloroform, the complex slowly reacted to give I [X = Cl, L = $P(CH_3)_2C_6H_5$] by cleavage of the remaining platinum–methyl bond.

The large coupling constant (∼15 Hz) between the ^{19}F nuclei of the two trifluoromethyl groups in the ^{19}F nmr spectra of complexes II confirm that only cis addition of the methylplatinum bond across the triple bond of C_4F_6 occurred. A similar situation has been demonstrated[5] for the platinum hydride additions to C_4F_6.

Reactivity of Methylplatinum Compounds toward Insertion Reactions.—From a qualitative study of the reaction temperature, pressure, and time required for insertion of C_2F_4 or C_4F_6 into several methylplatinum compounds, we have determined the factors affecting the reactivity of methylplatinum compounds. Thus from the conditions required (see Experimental Section) for insertion of C_2F_4 into *trans*-$PtXCH_3L_2$ and *cis*-$Pt(CH_3)_2L_2$ the order of reactivity L = $As(CH_3)_2C_6H_5$ > $P(CH_3)_2C_6H_5$ > $P(C_6H_5)_3$ has been established. There was little difference in reactivity when X = Cl, Br, or I. Compounds *cis*-$Pt(CH_3)_2L_2$ were slightly less reactive than *trans*-$PtXCH_3L_2$ toward C_2F_4 though the opposite trend has been observed[14] for C_4F_6. The

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(12) J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, 1793 (1966).

(13) J. Chatt and R. G. Wilkins, *ibid.*, 2532 (1951).

(14) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970), and unpublished results.

methylplatinum compounds undergo insertion reactions less readily than platinum hydrides.[4,13]

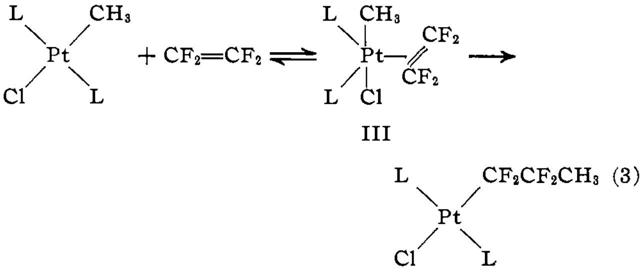
Surprisingly, *trans*-$PdClCH_3L_2$, L = $P(CH_3)_2C_6H_5$ [$\nu(PdCH_3)$ 515 cm^{-1}], was less reactive than the corresponding platinum complex [$\nu(PtCH_3)$ 550 cm^{-1}] toward C_2F_4 insertion, though the former has the weaker metal–carbon bond.

The rates of reaction were not particularly sensitive to variation of the solvent. However, if moist solvents were used, a different reaction occurred with C_2F_4. Thus in moist methanol the reaction of *trans*-$PtClCH_3L_2$, L = $P(CH_3)_2C_6H_5$, with C_2F_4 gave a mixture of *trans*-$PtCl(CF{=}CF_2)L_2$ and a compound containing the *trans*-$PtCl(CO)L_2^+$ cation, instead of the insertion product I obtained from the same reaction in dry methanol. A mechanism explaining the formation of such products from platinum hydrides and C_2F_4 has been discussed previously.[6]

Reaction of $Pt(C_2F_4)[P(C_6H_5)_3]_2$ and CH_3I.—The reaction of $Pt(C_2F_4)[P(C_6H_5)_3]_2$ with methyl iodide gave $PtI_2(CH_3)_2[P(C_6H_5)_3]_2$ and none of the insertion compound I (L = $P(C_6H_5)_3$, X = I) which might have been expected.[15] Curiously, Chatt and Shaw found[9] that the reaction of methyl iodide with $Pt[P(C_6H_5)_3]_3$ gave only *trans*-$PtI\,CH_3[P(C_6H_5)_3]_2$.

Discussion

The insertion reactions described here are believed to proceed by way of intermediate π complexes (III) of C_2F_4 (or C_4F_6) with the methylplatinum compounds (*e.g.*, eq 3). Complexes of type III have recently been isolated.[14] They may be considered as oxidative adducts of C_2F_4 or C_4F_6 with the initial methylplatinum(II) compounds, analogous to those formed with Vaska's compound $IrCl(CO)[P(C_6H_5)_3]_2$.[16] It is known that the ligands used here promote oxidative additions in the order $As(CH_3)_2C_6H_5 > P(CH_3)_2C_6H_5 > P(C_6H_5)_3$[17] and that oxidative additions to platinum(II) take place more readily than to palladium(II).[18] The more stable complexes (III) have greater back-bonding from platinum into antibonding orbitals of C_2F_4 and so weaken the C=C bond more. The fact that the same factors which promote oxidative addition also increase the rate of insertion strongly suggests that the rate of insertion is largely determined by the stability of the intermediate complex and by the extent of the weakening of the C=C or C≡C bond in the complex.



III

(3)

It is particularly interesting that insertion of C_2F_4 into the methylplatinum bond takes place more readily than insertion into the methylpalladium bond, whereas carbonylation takes place more readily with organopalladium compounds[19] in keeping with their greater lability over square-planar organoplatinum compounds.[20]

Experimental Section

Standard high-vacuum techniques were used throughout. Reactions with fluoroolefins and -acetylenes were performed in thick-walled Pyrex tubes having volumes of about 25 ml or in a stainless steel autoclave (100 ml). Infrared spectra were recorded using a Beckman IR 10 spectrophotometer. Samples were prepared as Nujol or Halocarbon oil mulls between cesium iodide plates. The ^1H and ^{19}F nmr spectra were recorded on Varian A-60 or HA 100 spectrometers; chemical shifts are given in parts per million relative to TMS or $CFCl_3$ as internal standard. Molecular weights were measured using a Hitachi Perkin-Elmer Model 115 molecular weight apparatus. Microanalyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Tetrafluoroethylene was prepared and purified as described previously.[4] Other fluoroolefins were obtained commercially and were used without further purification. Solvents were reagent grade unless otherwise specified. Benzene was dried by distillation from potassium. Dry samples of other solvents were obtained by standard methods.

Preparation of Methylplatinum Compounds.—*cis*-$Pt(CH_3)_2[P(CH_3)_2C_6H_5]_2$, *cis*-$Pt(CH_3)_2[As(CH_3)_2C_6H_5]_2$, *trans*-$PtXCH_3[P(CH_3)_2C_6H_5]_2$ (X = Cl, Br, I), and *trans*-$PtClCH_3[As(CH_3)_2C_6H_5]_2$ were prepared by the methods of Ruddick and Shaw.[10]

trans-**$PtBrCH_3[P(C_6H_5)_3]_2$**.—A solution of $Pt[P(C_6H_5)_3]_4$ in CH_2Cl_2 (10 ml) was stirred under CH_3Br (1 atm) for 3 hr. Methanol (10 ml) was added to precipitate the product (0.65 g), mp 275–277° (methanol). *Anal.* Calcd for $C_{37}H_{33}BrP_2Pt$: C, 54.6; H, 4.1. Found: C, 54.1; H, 4.0.

cis-**$Pt(CH_3)_2[As(CH_3)_3]_2$**.—This compound has been briefly mentioned previously.[21] It was obtained by the action of methyllithium on *cis*-$PtCl_2[As(CH_3)_3]_2$ in dry ether; yield 93%; mp 127–129° (petroleum ether). $\nu(PtC)$ 542 (m), 532 cm^{-1} (ms). Nmr in C_6H_6: $\delta(CH_3Pt)$ −1.33 ppm, $^2J(PtH)$ = 77.5 Hz; $\delta(CH_3As)$ −1.16 ppm, $^3J(PtH)$ = 11.3 Hz. *Anal.* Calcd for $C_8H_{24}As_2Pt$: C, 20.7; H, 5.2. Found: C, 20.95; H, 5.3.

trans-**$PtClCH_3[As(CH_3)_3]_2$**.—To *cis*-$Pt(CH_3)_2[As(CH_3]_2$ (1.00 g) in dry ether (10 ml) was added HCl in ether (3.1 ml, 0.80 *M*). The solvent was evaporated and the product extracted with C_6H_6, followed by recrystallization from petroleum ether (bp 60–100°); yield 0.63 g (60%); mp 159–160°. $\nu(PtC)$ 565 (m) cm^{-1}. Nmr in C_6H_6: $\delta(CH_3Pt)$ −0.88 ppm, $^2J(PtH)$ = 81.4 Hz; $\delta(CH_3As)$ −1.26 ppm, $^3J(PtH)$ = 21.3 Hz. *Anal.* Calcd for $C_7H_{21}ClAs_2Pt$: C, 17.3; H, 4.4. Found: C, 17.1; H, 4.4.

trans-**$PdClCH_3[P(CH_3)_2C_6H_5]_2$**.—Methyllithium (12.0 mmol) in ether (8 ml) was added to a suspension of *cis*-$PdCl_2[P(CH_3)_2C_6H_5]_2$ (1.16 g, 2.56 mmol) in dry benzene (10 ml) at 0°. After hydrolysis with ice water, the solvent was removed from the dried organic layer, leaving an oil which rapidly blackened. To a solution of the oil in dry ether (10 ml) was added HCl in ether (3.25 ml, 0.6 *M*, 1.95 mmol). The white precipitate was washed with ether and recrystallized rapidly from methanol; yield 0.88 g (2.03 mmol, 79%); mp 129–130° dec. $\nu(PdC)$ 515 cm^{-1}. Nmr in

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$CHCl_3$: $\delta(CH_3Pd)$ -0.08 ppm, $^3J(PH) = 6.6$ Hz; $\delta(CH_3P)$ -1.75 ppm, $^2J + {}^3J(PH) = 6.1$ Hz. *Anal.* Calcd for $C_{17}H_{25}ClP_2Pd$: C, 47.1; H, 5.8. Found: C, 47.0; H, 5.5. The compound blackened slowly on storage.

Reactions with C_2F_4.—Representative examples are given below. Analyses, yields, and physical and spectroscopic data are included in Tables I and II.

(a) **With *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ in Dry Acetone.**—*trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.404 g, 0.77 mmol) in dry acetone (6 ml) was heated with C_2F_4 (3.7 mmol) at 60° for 24 hr in a sealed tube. The gas phase was identified as C_2F_4 by its infrared spectrum. The solvent was evaporated and the product recrystallized from cyclohexane–chloroform, giving *trans*-$PtCl(CF_2CF_2CH_3)[P(CH_3)_2C_6H_5]_2$ (0.382 g, 79%). Similar reactions in dry benzene or dry methanol gave yields of 76 and 47%, respectively.

(b) **With *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ in Moist Methanol.**—*trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.165 g, 0.315 mmol) in methanol (3 ml, reagent grade) was heated with C_2F_4 (4.8 mmol) at 65° for 24 hr in a sealed tube. The solvent was evaporated leaving a pale yellow oil, whose infrared spectrum showed the characteristic peaks of a platinum carbonyl [$\nu(C\equiv O)$ 2075 cm^{-1}] and a perfluorovinylplatinum compound [$\nu(C{=}C)$ 1750 cm^{-1}]. The oil was chromatographed over Florisil, with pentane–chloroform (1:1 v/v eluent) and gave *trans*-$PtCl(CF{=}CF_2)[P(CH_3)_2C_6H_5]_2$ (0.083 g, 0.142 mmol); mp 110–113° ($CHCl_3$–petroleum ether). $\nu(C{=}C)$ 1748 (m), $\nu(CF)$ 1040 (s), 1000 (s), 970 cm^{-1} (s). *Anal.* Calcd for $C_{18}H_{22}F_3ClP_2Pt$: C, 36.8; H, 3.8; F, 9.7. Found: C, 36.5; H, 4.0; F, 10.1. Further elution of the column with $CHCl_3$ gave no other products.

(c) **With *trans*-$PtBrCH_3[P(C_6H_5)_3]_2$.**—*trans*-$PtBrCH_3[P(C_6H_5)_3]_2$ (0.162 g) in C_6H_6 (10 ml) was heated with C_2F_4 (1.8 mmol) at 90° for 48 hr in a sealed tube. Evaporation of the solvent gave a mixture of the *trans*-$PbBr(CO)[P(C_6H_4)_3]_2$ cation, $\nu(C\equiv O)$ 2090 cm^{-1} (s), and *trans*-$PtBr(CF{=}CF_2)[P(C_6H_5)_3]_2$, $\nu(C{=}C)$ 1730 cm^{-1} (m). Recrystallization from methanol gave pale yellow crystals (0.128 g) identified as a mixture of *trans*-$PtBr(CO_2CH_3)[P(C_6H_5)_3]_2$, $\nu(C{=}O)$ 1660 cm^{-1}, $\delta(CH_3O)$ in CH_2Cl_2 -2.37 ppm, and *trans*-$PtBr(CF{=}CF_2)[P(C_6H_5)_3]_2$, $\nu(C{=}C)$ 1737 cm^{-1}, by comparison with the authentic compounds.[22,23] Starting material was recovered in good yield from a similar reaction conducted at 75°.

(d) **With *trans*-$PdClCH_3[P(CH_3)_2C_6H_5]_2$.**—*trans*-$PdClCH_3[P(CH_3)_2C_6H_5]_2$ (0.162 g) in C_6H_6 (4 ml) was heated with C_2F_4 (8.3 mmol) at 75° for 24 hr in a sealed tube. Starting material was recovered in quantitative yield. Extensive decomposition and blackening took place during a similar reaction at 90°. Again no insertion product was isolated.

(e) **With *cis*-$Pt(CH_3)_2[As(CH_3)_2C_6H_5]_2$.**—*cis*-$Pt(CH_3)_2[As(CH_3)_2C_6H_5]_2$ (0.348 g, 0.590 mmol) in C_6H_6 (5 ml) was heated with C_2F_4 (2.5 mmol) at 70° for 24 hr in a sealed tube. Evaporation of the solvent and recrystallization from petroleum ether (bp 60–80°) gave $Pt(CF_2CF_2CH_3)_2[As(CH_3)_2C_6H_5]_2$ (0.272 g, 58%).

(f) **With *cis*-$Pt(CH_3)_2[P(CH_3)_2C_6H_5]_2$.**—*cis*-$Pt(CH_3)_2[P(CH_3)_2C_6H_5]_2$ (0.325 g, 0.64 mmol) in C_6H_6 (10 ml) was heated with C_2F_4 (1.7 mmol) at 80° for 48 hr in a sealed tube. Evaporation of the solvent gave a pale yellow oil which was purified by vacuum sublimation onto a cold finger at −78°, subl pt 130–150°. The product was a colorless viscous oil which was identified (analysis, molecular weight, ^{19}F nmr) as a mixture (0.112 g) of $PtCH_3(CF_2CF_2CH_3)[P(CH_3)_2C_6H_5]_2$ and probably a little $Pt(CF_2CF_2CH_3)_2[P(CH_3)_2C_6H_5]_2$. On standing in $CHCl_3$–$CFCl_3$ the product decomposed to *trans*-$PtCl(CF_2CF_2CH_3)[P(CH_3)_2C_6H_5]_2$, identical (ir, melting point, mixture melting point) with an authentic sample.

(g) **With *cis*-$Pt(CH_3)_2[P(C_6H_5)_3]_2$.**—*cis*-$Pt(CH_3)_2[P(C_6H_5)_3]_2$ (0.330 g) in C_6H_6 (15 ml) was heated with C_2F_4 (5 mmol) at 80° for 48 hr in a stainless steel autoclave. There was no reaction and starting material was recovered in good yield. A similar reaction at 90° led to extensive decomposition to Pt metal.

Reactions with Hexafluorobut-2-yne, C_4F_6.—Representative examples are given below. Yields and analytical, physical, and spectroscopic data are given in Tables I and III.

(a) **With *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$.**—*trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.336 g, 0.64 mmol) in C_6H_6 (4 ml) was heated with C_4F_6 (5.1 mmol) at 70° for 24 hr in a sealed tube. The gas phase was identified as unchanged C_4F_6 by its infrared spectrum. Evaporation of the solvent followed by chromatography of the product over Florisil with pentane–chloroform (1:1 v/v) eluent and then recrystallization from methanol gave *trans*-$PtCl[C(CF_3){=}C(CF_3)CH_3][P(CH_3)_2C_6H_5]_2$ (0.198 g, 45%). The infrared spectrum of the crude product indicated the presence of some $Pt(C_4F_6)[P(CH_3)_2C_6H_5]_2$.[24] A similar reaction in methanol at 85° gave the same compound in 36% yield, along with other uncharacterized products.

(b) **With *trans*-$PtClCH_3[As(CH_3)_2C_6H_5]_2$.**—*trans*-$PtClCH_3[As(CH_3)_2C_6H_5]_2$ (0.402 g) in C_6H_6 (10 ml) was heated with C_4F_6 (7.5 mmol) at 70° for 24 hr in a sealed tube. Evaporation of the solvent and recrystallization from methanol gave *trans*-$PtCl[C(CF_3){=}C(CF_3)CH_3][As(CH_3)_2C_6H_5]_2$ (0.336 g, 66%).

Reactions of *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ with Other Fluoroolefins. (a) **C_2F_3Cl.**—*trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.210 g, 0.40 mmol) in C_6H_6 (4 ml) was heated with C_2F_3Cl (4.7 mmol) at 90° for 24 hr in a sealed tube. The white precipitate formed was filtered off and recrystallized from methanol giving *cis*-$PtCl_2[P(CH_3)_2C_6H_5]_2$ (0.081 g, 40%), identical with an authentic sample. *Anal.* Calcd for $C_{16}H_{22}Cl_2P_2Pt$: C, 35.4; H, 4.1. Found: C, 35.5; H, 3.9.

(b) **$CF_3CF{=}CF_2$.**—*trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.36 g, 0.69 mmol) in C_6H_6 (10 ml) was heated with $CF_3CF{=}CF_2$ (12.9 mmol) at 100° for 72 hr in a stainless steel autoclave. Evaporation of the solvent gave an oil, whose infrared spectrum was consistent with that expected for an insertion product. Recrystallization from benzene–pentane was unsuccessful, and chromatography over Florisil led to complete decomposition. Recrystallization from methanol gave a mixture of orange and yellow crystals. The orange crystals, mp 198° dec, were identified as $PtCl_2[P(CH_3)_2C_6H_5]_2$ (0.074 g, 0.14 mmol). *Anal.* Calcd for $C_{16}H_{22}Cl_2P_2Pt$: C, 35.4; H, 4.1; Cl, 13.1; P, 11.4; Pt, 36.0. Found: C, 35.6; H, 4.7; Cl, 12.4; F, 0.0; P, 10.7; Pt (by difference), 36.6. The yellow crystals (0.030 g) were not identified, mp 123–124°. $\nu(CF)$ 1000, 976, 940 cm^{-1}. *Anal.* Found: C, 35.3; H, 4.1; F, 5.15. Similar reactions at 70–90° in C_6H_6, acetone or methanol gave only starting materials.

(c) **Perfluorocyclobutene.**—No reaction took place on heating with *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ in C_6H_6 at 90° for 48 hr.

***trans*-$PtI(CF_2CF_2CH_3)[P(CH_3)_2C_6H_5]_2$.**—NaI in acetone (10 ml of saturated solution) was added to *trans*-$PtCl(CF_2CF_2CH_3)[P(CH_3)_2C_6H_5]_2$ (0.162 g) in acetone (10 ml). After 5 min the solvent was evaporated, the product extracted with C_6H_6, the C_6H_6 evaporated, and the product recrystallized from methanol, giving *trans*-$PtI(CF_2CF_2CH_3)[P(CH_3)_2C_6H_5]_2$ (0.140 g, 75%) identical with the product obtained by direct insertion.

$Pt(C_2F_4)[P(C_6H_5)_3]_2$ and Methyl Iodide.—Methyl iodide (1 ml) was added to $Pt(C_2F_4)[P(C_6H_5)_3]_2$[22] (0.190 g) in CH_2Cl_2 (2 ml). After 48 hr, the solvent was evaporated giving $PtI_2(CH_3)_2[P(C_6H_5)_3]_2$ (0.131 g, 56%) which decrepitated at 130–140°, mp 274–276° dec. Nmr in $CHCl_3$: $\delta(CH_3Pt)$ -0.11 ppm (triplet), $^3J(PH) = 7.0$ Hz; δ -1.30 ppm (triplet), $^3J(PH) = 7.5$ Hz. The compound was insufficiently soluble to observe the ^{195}Pt coupling. *Anal.* Calcd for $C_{38}H_{36}I_2P_2Pt$: C, 45.5; H, 3.6. Found: C, 45.8; H, 3.4. This compound did not react with C_2F_4 when heated at 75° for 72 hr in benzene.

Reactions with Carbon Monoxide.—(a) *trans*-$PdClCH_3[P(CH_3)_2C_6H_5]_2$ (0.246 g) in dry C_6H_6 (3 ml) was shaken with CO (3 atm) for 12 hr at room temperature. The solvent was evaporated and the product was recrystallized quickly from

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methanol, giving *trans*-$PdCl(COCH_3)[P(CH_3)_2C_6H_5]_2$ (0.104 g, 40%), mp 129–130° dec. $\nu(C{=}O)$ 1675 (s), 1654 cm^{-1} (sh). Nmr in $CHCl_3$: $\delta(CH_3P)$ -1.73 ppm, $^2J + {}^4J(PH) = 7.3$ Hz; $\delta(CH_3CO)$ -1.78 ppm. *Anal.* Calcd for $C_{18}H_{25}ClOP_2Pd$: C, 46.9; H, 5.5. Found: C, 46.7; H, 5.85. The compound blackened slowly on storage.

(b) *trans*-$PtClCH_3[P(CH_3)_2C_6H_5]_2$ (0.102 g) in methanol (3 ml) was heated with CO (5 atm) at 80° for 4 hr in a sealed tube. The solvent was evaporated and the product was recrystallized from methanol giving *trans*-$PtCl(COCH_3)[P(CH_3)_2C_6H_5]_2$ (0.073 g, 68%), mp 153–157° dec. $\nu(C{=}O)$ 1632 cm^{-1} (s). Nmr in $CHCl_3$: $\delta(CH_3P)$ -1.44 ppm; $^2J + {}^4J(PH) = 7.5$ Hz, $^3J(PtH) = 37$ Hz; $\delta(CH_3CO)$ -1.73 ppm, $^3J(PtH) = 13.5$ Hz. *Anal.* Calcd for $C_{18}H_{25}ClOP_2Pt$: C, 39.3; H, 4.6. Found: C, 39.4; H, 4.8.

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Low-Frequency Infrared Spectra of Planar and Tetrahedral Nickel Bromide Complexes of Diphenylalkylphosphines[1a]

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The Ni–Br and Ni–P stretching bands characteristic of the planar and tetrahedral forms have been established for a series of compounds of the type $Ni(P(C_6H_5)_2R)_2Br_2$ where R is an alkyl group. The results of metal isotope studies showed that the Ni–Br and Ni–P stretching frequencies are located at *ca.* 330 and 260 cm^{-1}, respectively, for the planar form, and *ca.* 270–230 and 200–160 cm^{-1}, respectively, for the tetrahedral form.

Introduction

Complexes of the type $Ni(P(C_6H_5)_2R)_2Br_2$ (R, alkyl) exist in two isomeric forms: tetrahedral (green) and trans planar (brown).[2] Hayter and Humic[3] have isolated a number of pairs of these isomeric forms and determined their structures by electronic spectra, magnetic moments, and X-ray powder patterns. However, no systematic far-infrared studies have yet been made to distinguish these two forms. The purpose of this work was to prepare several pairs of these isomers and to assign the bands characteristic of each form. It is anticipated that the main spectral differences between the two forms will occur for the skeletal vibrations such as the Ni–P and Ni–Br stretching modes. In a previous communication,[4] it was demonstrated that the use of metal isotopes provided a clear-cut band assignment for these metal–ligand vibrations. This technique was therefore applied to several typical complexes of the aforementioned type. Spectral differences between the two isomers are not only useful for identification purposes, but are also of theoretical interest since these isomers differ only in the configuration around the central metal.

Experimental Section

Preparation of Compounds. Ligands.—The diphenylalkylphosphines were prepared by the method of Davies and Jones,[5] from chlorodiphenylphosphine and alkylmagnesium bromide.

Complexes.—The tetrahedral (green) complexes were prepared by the addition of the phosphine to a concentrated solution of nickel bromide in ethanol.[3] The trans-planar (brown) forms were obtained by recrystallization of the corresponding green forms from the solvents listed in Table I.

The trans-planar $Ni(P(C_6H_5)_2C_2H_5)_2Br_2$ complex could not be obtained by recrystallization from CS_2 solution at room temperature. It was prepared by the process of lyophilization. First, the tetrahedral isomer was dissolved in CS_2 by the gradual addition of CS_2 to a steam-heated flask. The green color changed to brown-purple and the flask was then immediately cooled in liquid nitrogen. The frozen sample was transferred to a Dry Ice–isopropyl alcohol slush bath and the solvent was removed with a high-vacuum system.

The solvents used for recrystallization of the products, magnetic moments, and microanalysis are tabulated in Table I.

Complexes containing metal isotopes were prepared on a milligram scale by the methods used for the preparation of the natural abundance species. The ^{58}Ni (99.98% pure) and ^{62}Ni (99.02% pure) isotopes were purchased from Oak Ridge National Laboratory. The purity of each complex was checked by comparing the spectrum with that of the corresponding complex containing the metal of natural abundance.

Magnetic Moment Measurements.—The magnetic moments were determined by using the Faraday technique.[6] Ferrous ammonium sulfate was used as the standard.

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[2] This terminology will be used throughout this paper and follows the terminology used by previous workers. It is understood that the angles around the nickel atom are ~109° in the tetrahedral form, while they are ~90° in the trans-planar form.

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