hydride should react with fluoroolefins to give vinyl compounds through the intermediacy of a π complex, whereas the metal carbonyl hydrides give only fluoroalkyl derivatives. The explanation that can be offered at present is that the platinum(II) hydride has a square-planar geometry and so can readily form a π-olefinic complex which functions as the reaction intermediate. The carbonyl hydrides are generally five- or six-coordinate and can less readily increase their coordination shell. The latter hydrides, therefore, are more likely to react with olefins *via* a four-center- or free-radical-type mechanism.

Acknowledgments. The financial support of the National Research Council is gratefully acknowledged and also the award of a Commonwealth Scholarship to W. S. T.

Chemistry of Metal Hydrides. II. Spectroscopic Studies of Fluorovinylplatinum(II) Derivatives

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Contribution from the Department of Chemistry, University of Western Ontario, London, Canada. *Received September 8, 1966*

Abstract: Infrared and nuclear magnetic resonance (^{1}H and ^{19}F) spectroscopic data are presented for some new fluorovinyl derivatives of platinum(II). Some features of the infrared spectra are examined in the light of current evidence of π bonding between fluorocarbon groups and transition metals. These are the first organoplatinum(II) compounds in which spin-spin coupling is observed between ^{19}F and ^{195}Pt, and also between ^{19}F and the ^{31}P nuclei of the tertiary phosphine ligands. The stereochemistries of the products are established, and results pertinent to the concept of "through-space coupling" are described.

In the previous paper[1] the reactions of some platinum(II) hydrides, principally $[(C_2H_5)_3P]_2PtHCl$, with a number of unsaturated fluorocarbons were described, the principal products being fluorovinyl derivatives. These are among the first of a new class of organometallic compounds, although others were reported while our work was in progress,[2] obtained from reactions between metal carbonyl anions and fluoroolefins. The spectroscopic properties of these new Pt(II) compounds not only enabled detailed characterizations to be made, but also provide valuable information concerning the bonding of fluorocarbon groups to transition metals. This has considerable interest at present, since recent studies[3-6] provide clear evidence of π-type interactions between fluorocarbon groups and transition metal atoms. In fluorovinyl derivatives, the presence of the C=C π system may enhance such interaction, and the data described in this paper have been examined with this in mind.

Experimental Section

The preparation of all the compounds has been described in the previous paper, together with the analytical data. Infrared spectra were recorded with a Beckman IR-10 double-beam spectrophotommeter, using Nujol or halocarbon oil mulls; spectra were calibrated against polystyrene. Nmr spectra were obtained with Varian A-60 (proton spectra) and DP-60 (^{19}F spectra) spectrometers. Proton chemical shifts are reported in ppm with respect to tetramethylsilane as external standard, and ^{19}F spectra with respect to trifluoroacetic acid as external standard; unless otherwise stated, deuteriochloroform was used as solvent.

Discussion

Infrared Spectra. The observed infrared absorption frequencies of the new fluorovinylplatinum(II) compounds are listed in Table I. Many of these bands arise from vibrations of the triethylphosphine groups, and assignments have been made by comparison with those given for the free phosphine.[7] No detailed consideration will be given to vibrations other than the P–C stretching and Pt–P stretching modes, since absorptions due to the hydrocarbon portions of the molecules are fairly standard and show no unique features. The suggested range[8] for P–C stretching vibrations in a series of phosphonium compounds is 650–750 cm^{-1}, and it has also been pointed out[8] that the presence of a $P-C_2H_5$ group in a molecule is characterized by two bands in the 1227–1282-cm^{-1} region. Chatt, *et al.*,[9] have studied the infrared spectra of a series of alkylplatinum(II) complexes stabilized by tertiary phosphines. For trimethylphosphine complexes, they assigned bands in the 669–689- and 720–743-cm^{-1} regions to the symmetrical and asymmetrical P–C stretching vibrations, respectively. Triethylphosphine complexes gave more complicated spectra, but it was possible to assign bands in the 625–643-cm^{-1} region to the P–C symmetrical stretching mode. In the spectra of the present investigation, generally only one band was found in the region 625–643 cm^{-1}, and this is therefore attributed to the same vibration. Moreover, usually

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[1] H. C. Clark and W. S. Tsang, *J. Am. Chem. Soc.*, **89**, 529 (1967).

[2] (a) P. W. Jolly and F. G. A. Stone, *Chem. Commun.*, 85 (1965); (b) P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 5830 (1965).

[3] F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.* (Amsterdam), **4**, 490 (1965).

[4] M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965).

[5] R. Mason and D. R. Russell, *Chem. Commun.*, 182 (1965).

[6] H. C. Clark and J. H. Tsai, *J. Organometal. Chem.* (Amsterdam), in press.

[7] H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, **15**, 366 (1959).

[8] L. C. Thomas and R. A. Chittenden, *ibid.*, **21**, 1905 (1965).

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Table I. Infrared Frequencies (cm^{-1}) of Fluorovinylplatinum(II) Compounds[a,b]

	A	B	C	D	E	F	G
C—H str	2972 m	2970 m	2970 s	2970 m	2972 m	2980 m	2972 m
	2940 m	2940 m	2940 s	2940 m	2940 m	2940 m	2940 m
	2920 m	2918 m	2910 s	2910 m	2920 m	2920 m	2922 m
	2884 m	2880 m	2880 s	2880 m	2884 m	2880 m	2884 m
C═C str	1724 s	1643 vs	1644 s	1640 m	1634 m	1680 m	1603 m
CH_3 deform and CH_2 scissor	1445 m	1444 m	1455 s	1454 m	1452 m	1450 m	1458 m
	1405 m	1405 m	1417 s	1416 m	1416 m	1418 m	1420 m
	1370 m	1370 m	1380 s	1380 m	1380 m	1381 m	1380 m
CH_2 wag		1344 m			1266 m	1265 m	
	1257 m	1336 m	1257 m	1235 m	1254 m	1251 m	. . .[c]
		1258 m	1240 m	1237 m	1233 m		
		1245 m					
C—C str and C—CH_3 rock	1082 m	1037 s		1030 s			1029 s
	1052 m		. . .[c]		1016 s	1005 s	1003 m, sh
	1022 s	1010 m		1000 sh			969 w, sh
C—F str	1233 s	1114 m	1350 vs	1380 s			1333 s
	1037 vs	1075 s	1326 vs	1353 s			1258 s, br
			1300 m, sh	1274 s	1096 m	1080 m	
	980 vs	952 m	1180 vs	1172 m	1034 vs	1030 vs	1207 m
			1113 vs	1110 m			1150 s
			1035 vs	1063 s	990 s	990 s	113 vs, br
			898 vs	927 s		902 m	903 m
			830 s	800 s			815 m
Skeletal modes of PEt_3 and CH_2 rock	767 vs	786 m	767 vs	758 s	788 s	788 s	761 s
	736 s	766 s	735 s	727 s	764 vs	760 vs	727 s
	715 m	735 s	713 m	702 m, sh	728 s	729 s	705 m, sh
	680 w	712 m	691 s		708 s, sh	708 m	668 w
		678 w			678 vs	673 w	
P—C str	635 m	630 m	635 m	636 w			643 m
			612 m	621 w	633 m	630 m	627 m
Pt—C str	537 w	594 w	565 w		575 w		611 m
				554 m		550 w	532 vw
	540 m	507 m	542 w				486 w
Pt—P str	420 w, sh	420 m	458 w	430 vw			
	413 m	415 m	415 w	408 w	409 m	408 m	413 w
Incl Pt—Cl str	383 w	380 w	382 w	270 vw	382 w	380 w	374 w
	305 m, sh	283 w, sh	330 w, sh	290 m, br	277 w	316 w	323 w
	298 m	268 m	309 m			275 w	294 w
							271 w, br

[a] A = $[(C_2H_5)_3P]_2PtCl(CF{=}CF_2)$, B = $[(C_2H_5)_3P]_2PtCl[C(CJ_2F){=}CF_2]$, C = $[(C_2H_5)_3P]_2PtCl(C_3F_5)$, D = $[(C_2H_5)_3P]_2PtCl(C_4F_5)$, E = $[(C_2H_5)_3P]_2PtCl($*cis*-$CF{=}CFH)$, F = *trans* isomer of E, G = $[(C_2H_5)_3P]_2PtCl[C(CF_3){=}C(CF_3)H]$. [b] s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder. [c] Bands hidden by intense C–F absorptions.

two bands were also observed in the 1227–1282-cm^{-1} region. The asymmetric P–C stretching vibration could not be readily distinguished.

The C–F stretching vibrations generally cause strong absorption in the 800–1400-cm^{-1} region, although in these compounds vibrations involving CH_2 wagging, C–C stretching, and C–CH_3 rocking modes also occur within this range. However, in most cases, the C–F absorptions are of characteristically high intensity and can readily be assigned utilizing previous assignments and spectral differences in comparison with that of *trans*-$[(C_2H_5)_3P]_2PtHCl$. For the perfluorovinyl compound, $[(C_2H_5)_3P]_2PtCl(CF{=}CF_2)$, assignments of the strong C–F absorptions can be made, since there is much published data[10,11] on the spectra of $CF_2{=}CFM$ groups, where M = H_1, a metal, or metalloid (Table II). These data hold considerable interest, since it is clear from Table II that the C–F stretching frequencies for the transition metal compounds are much lower than those of either the analogous main group metallic derivatives or of trifluoroethylenes. This is consistent with Cotton and McCleverty's[3] observation that the C–F frequencies in transition metal–perfluoroalkyl compounds are lowered by around 100 cm^{-1} owing to π interaction, and with our previous discussion[6] of fluorocarbon π bonding. The distinction between main group metal- and transition metal–fluorovinyl compounds is further supported, as well as the conclusion that the C–F bonds are weakened. For the 1,2-difluorovinyl compounds, direct comparison with the analogous trimethyltin[12] and pentacarbonylmanganese[13] derivatives is difficult, owing to the uncertainty of the assignments caused by overlapping with other bands. This is unfortunate in view of the detailed structural information[14] available for *cis*-$CFH{=}CFMn(CO)_5$. For the *cis*-olefinic isomer of *trans*-$[(C_2H_5)_3P]_2PtCl(CF{=}CFH)$, C–F stretching vibrations are observed at 1034 and 990 cm^{-1} [compare[13] with 1045 and 968 cm^{-1} for *cis*-$CFH{=}CFMn(CO)_5$], but the assignment of a third band at 1096 cm^{-1} to either a C–F stretching, C–C stretching, or C–CH_3 rocking mode is less certain. For the perfluorocyclobutenylplatinum-

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(10) S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta*, 17, 412 (1961).

(11) D. E. Mann, N. Acquista and E. K. Plyler, *J. Chem. Phys.*, 22, 1586 (1954).

(12) A. D. Beveridge, H. C. Clark, and J. T. Kwon, *Can. J. Chem.*, 44, 179 (1966).

(13) H. C. Clark and J. H. Tsai, *Inorg. Chem.*, 5, 1407 (1966).

(14) F. W. B. Einstein, H. Luth, and J. Trotter, *J. Chem. Soc.*, in press.

(II) compound and for $[(C_2H_5)_3P]_2PtCl[C(CF_3){=}CH(CF_3)]$, the C–F stretching frequencies are in good agreement with those reported for analogous compounds.[2b,15] For the perfluoropropenyl derivatives, there are some variations in the literature[16–18] concerning the expected frequencies, largely because of uncertainties as to the exact isomeric form involved. For none of the last three classes of compounds have detailed assignments yet been suggested.

Table II. Assignments for the $CF_2{=}CFM$ Group

Compound	$CF_2{=}$ (asym)	—CF=	$CF_2{=}$ (sym)	Ref
$CF_2{=}CFPtCl[P(C_2H_5)_3]_2$	1233	1037	(8)	This work
$CF_2{=}CFRe(CO)_5$	1242	1050	970	2b
$CF_2{=}CFFe(CO)_2(\pi\text{-}C_5H_5)$	1235	1040	960	2b
$CF_2{=}CFM^a$	1274–1327	1121–1178	1004–1049	10
$CF_2{=}CFH$	1326	1264	927	11
$CF_2{=}CFBr$	1330	1203	1027	11

[a] M = B, Sn, Ge, Si, As, and Hg.

The C=C stretching vibrations cause absorption in the range 1603–1724 cm^{-1} for these platinum(II) compounds. This is a surprisingly wide range and must result from a combination of at least two factors. First, it is well known[19] that the C=C stretching frequency decreases from 1788 cm^{-1} in $CF_2{=}CFH$ to 1654 cm^{-1} in $CH_2{=}CHF$ with progressive replacement of fluorine. Second, for some perfluorovinyl metallic compounds,[10] the C=C frequencies are usually low in comparison with free olefins (*e.g.*, for $(CF_2{=}CF)_2BCl$ at 1678 cm^{-1}) owing to π interactions with the metallic atom. That the platinum(II) compound containing the $PtC(CF_3){=}CH(CF_3)$ grouping should have a C=C stretching frequency of 1603 cm^{-1} must be largely due to this latter factor, since $(CF_3)CF{=}CH(CF_3)$ shows this absorption at 1740 cm^{-1}, and this argument must extend to the other compounds described here. Thus, structures of the type Pt=C=C must make reasonable contributions to the over-all structure, with some consequent weakening of the C=C bonds.

Below 600 cm^{-1}, absorptions due to the Pt–C, Pt–P, and Pt–Cl vibrations, as well as skeletal vibrations of the unsaturated fluorocarbon groups, may occur. Because of the resultant complexity of the spectra, the assignments shown in Table I are, at best, only tentative. Chatt, *et al.*,[9] have reported that monoalkyl platinum(II) complexes usually show only one band in the 500–600-cm^{-1} region associated with the Pt–C stretching vibration. Most of the new Pt(II) compounds showed (Table I) at least two absorptions in this region; only one of these is probably associated with a vibration of the corresponding fluorocarbon grouping and another with the Pt–C stretching vibration, but no attempt can be made to distinguish between them. For Pt–P vibrations, Coates and Parkin[20] have suggested the frequency range 340–400 cm^{-1} for Pt–P stretching vibrations, while Rosevear and Stone[21] give the ranges as 416–442 and 410–419 cm^{-1} for the Pt–P stretching frequencies in *cis* and *trans* isomers, respectively. Our own results with $[(C_2H_5)_3P]_2PtCl_2$ are in agreement with those of Rosevear and Stone. For these new fluorovinylplatinum(II) complexes, two bands were generally observed in the 408–450-cm^{-1} region, and we have arbitrarily assigned the 408–415-cm^{-1} band to the Pt–P stretching vibration. Clearly, for a *trans* complex, there should be only one infrared-active Pt–P stretching vibration. The Pt–Cl stretching vibrations occur[9] in the region 269–340 cm^{-1}, with the frequency being dependent on the *trans* effect of the group *trans* to chloride. Since, for these Pt(II) compounds, other absorptions are also observed in the 250–400-cm^{-1} region, assignments cannot readily be made, so that the relative *trans* effects of the fluorocarbon groups cannot be meaningfully discussed.

Nmr Spectra. The data are summarized in Table III.

(a) Proton Nmr Spectra of the Ethyl Protons. Previous authors[22] have shown that because of virtual coupling, the resonance of the methyl protons for two dimethylphenylphosphine molecules *trans* to each other in a square-planar complex is a 1:2:1 triplet. Since the *cis* complex gives a symmetrical doublet, the splitting pattern of the methyl resonances can be used to determine the configuration[12] of many phosphine complexes. For these Pt(II) fluorovinyl complexes, the methyl resonance was always a 1:4:6:4:1 quintet, due to spin–spin coupling of the methyl protons with the methylene protons (J_{H-H} = 8 cps) to give a triplet which is further split by coupling with the two phosphorus atoms (J_{P-H} = 7.8 cps) to give the quintet. This confirms the *trans* configuration for compounds A–G. The value for J_{P-H} of 7.8 cps is large in comparison with values of 4–8 cps for dimethylphenylphosphine complexes[22] where the phosphorus atom and methyl proton are only two bonds distant, but comparable values have recently been reported for compounds where the phosphorus atom and protons are similarly four bonds distant.[23] The quintet for the methyl protons does not show any resolvable fine structure, so that coupling with ^{195}Pt is essentially zero. For all the compounds, the methylene resonance was complex and consisted of more than eight peaks; coupling with methyl protons, phosphorus, and ^{195}Pt was clearly involved and no detailed analyses were attempted.

Detailed characterizations were made on the basis of the proton and ^{19}F spectra arising from the organic groups attached to platinum, and the results are now described for individual compounds.

(b) $[(C_2H_5)_3P]_2PtCl(CF{=}CF_2)$ (Compound A). The ^{19}F spectrum of this compound consisted of three sets of multiplets of equal intensity centered at +24, +58.7, and +77 ppm, in which the pattern of splittings is essentially a 1:1:1:1 quartet, a 1:2:1 triplet, and a 1:1:1:1 quartet, respectively. Satellite bands, having one-fourth the intensity of the main peaks, appear

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(15) W. R. Cullen, D. S. Dawson, and G. E. Styan, *Can. J. Chem.*, **43**, 3392 (1965).

(16) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, 17, 1244 (1961).

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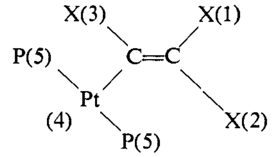
(21) D. T. Rosevear and F. G. A. Stone, *ibid.*, 5275 (1965).

(22) (a) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963); (b) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc., A*, 770 (1966).

(23) E. J. Boros, K. J. Corkran, R. W. King, and J. G. Verkade, *J. Am. Chem. Soc.*, **88**, 1140 (1966).

Table III. Nmr Data for Fluorovinylplatinum(II) Derivatives

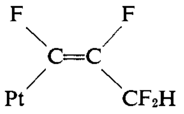


		A	B	C (*cis*)	C (*trans*)	E	F	G
	X_1	F	F	F	CF_3	F	H	CF_3
	X_2	F	F	CF_3	F	H	F	H
	X_3	F	CF_2H	F	F	F	F	CF_3
	δ_{CH_3}	−1.21	-0.58^{9}	−1.7	−1.7	-1.23^{b}	-1.23^{b}	−1.8
	δ_{CH_2}	−1.95	−1.31	−2.5	−2.5	-1.97^{b}	-1.97^{b}	−2.4
	δ_1	...	...	...	...	...	−7.58	−6.50
	δ_2	...	...	...	...	-5.54^{b}	...	...
	δ_3	...	−4.58 for CF_2H^{b}	...	...	...	...	...
^{1}H nmr	J_{12}	...	...	...	...	82.3	84	9.62
	J_{13}	...	...	...	...	...	7.8	...
	J_{14}	...	...	...	...	...	4.2	...
	J_{23}	...	...	...	...	24	...	...
	J_{24}	...	...	...	...	4	...	...
	$J_{H\text{-}CF_2}$	...	57	...	...	...	...	...
	$J_{CH_2H\text{-}Pt}$	...	7.5	...	...	...	...	...
	δ_1	24	46.4	75.1	−12.22	...	...	−20.7
	δ_2	58.7	47.7	−13.2	97.1	...	...	...
	δ_3	77	47.0	8.27	22.8	...	...	−25.7
^{19}F nmr	J_{12}	120	26.5	15.3	13.3			9.6
	J_{13}	35.6	...	12.8	21.3			12.2
	J_{14}	59.7	...	12.8	5.82			5.82
	J_{15}	4.8	...	...	...			...
	J_{23}	120	...	9.29	124			0
	J_{24}	62.4	...	13.45	186.1			...
	J_{34}	574	240	479	501			142.3
	$J_{CF_2\text{-}H}$		55	...	...			...
	J_{25}			3.17	3.5			

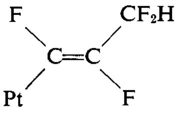
[a] Benzene solution. [b] CCl_4 solution.

symmetrically on either side of each of the three sets, and these must arise from coupling with ^{195}Pt. Since the largest Pt–F coupling constant (574 cps) is observed in the multiplet at +77 ppm, this multiplet is assigned to F(3), as this is closest to the Pt atom. The multiplets at +58.7 and +24 ppm are then assigned to F(2) and F(1), respectively. These assignments place the chemical shifts in the order $\delta(F1) < \delta(F2) < \delta(F3)$, and the coupling constants in the order $J_{cis} < J_{gem} = J_{trans}$, in agreement with results for other perfluorovinyl metallic compounds.[24] The large J_{gem} (120 cps) observed here is unusual, and, since it is equal to J_{trans}, the triplet is observed for F(2). It will be noted that, in the multiplet at +24 ppm, each main and satellite peak possesses hyperfine structure in the form of a 1:2:1 triplet, apparently due to spin–spin coupling of F(1) with the two phosphorus atoms (J = 4.8 cps). Since this triplet structure is not observed for F(2) and F(3), F(1) must be in a special environment with respect to the phosphorus nuclei. The explanation is not clear, since "through-space coupling"[25] might apply between F(2) and phosphorus, allowing for suitable rotation of the Pt–C bond, but certainly not between F(1) and phosphorus.

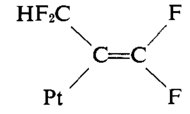
(c) $[(C_2H_5)_3P]_2PtCl[C(CH_2F)\!=\!CF_2]$ (Compound B). Structures I–III are consistent with the analytical data and with the presence of a C=C bond, based on the infrared spectrum. The ^{19}F nmr spectrum showed a doublet at +47 ppm and two doublets at +46.4 and +47.4 ppm which overlap to form a 1:2:1 triplet of area equal to that of the doublet. Since no coupling constant of around 110 cps was observed, a *trans* isomer such as II can be excluded. In structure i, coupling between $-CF_2H$ and the geminal F, separated by three bonds, is expected, whereas in III the separation between $-CF_2H$ and F is four bonds and there may be no coupling. The simplicity of the spectrum supports structure III.



I



II



III

In the ^{1}H spectrum, a 1:2:1 triplet at −4.58 ppm (J = 57 cps), of which each component is split into a 1:4:1 triplet (J = 7.5 cps), is observed. The 1:2:1 triplet shows the presence of a $-CF_2H$ group in the molecule,[26,27] although the chemical shift of the $-CF_2H$ proton is higher than usual in this case. The satellite peaks result from spin–spin coupling with ^{195}Pt, the magnitude of the coupling constant being more consistent with structure III than with structure I where the separation of Pt and the $-CF_2H$ proton is increased to four bonds.

(d) $[(C_2H_5)_3P]_2PtCl(CFCFCF_3)$ (Compound C). The following structures, IV–VII, are possible for the

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(24) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta*, 17, 968 (1961).

(25) S. Ng and C. H. Sederholm, *J. Chem. Phys.*, 40, 2090 (1964).

(26) H. C. Clark, J. T. Kwon, L. W. Reeves, and E. J. Wells, *Can. J. Chem.*, 41, 3005 (1963).

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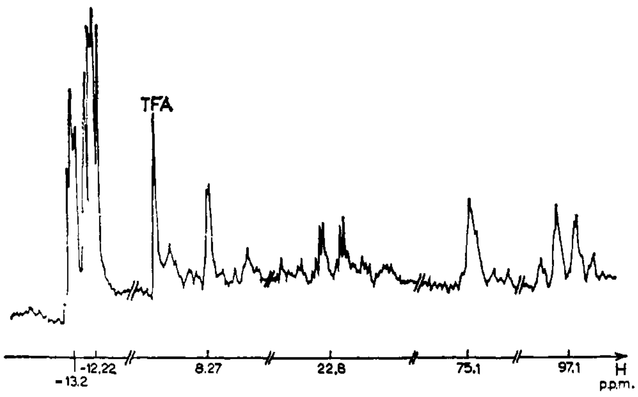


Figure 1. ^{19}F nmr spectrum of *trans*-[(C$_2$H$_5$)$_3$P]$_2$PtCl(C$_3$F$_5$).

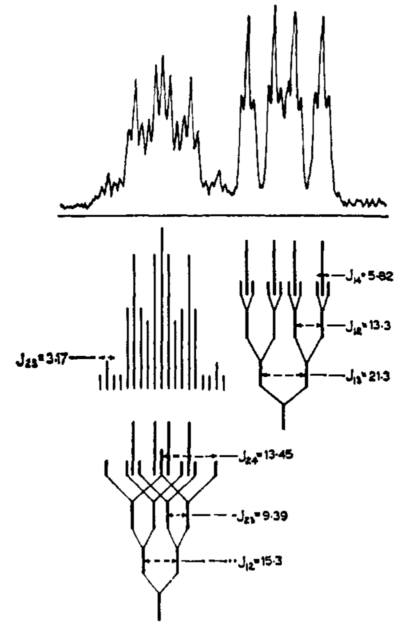


Figure 2. Absorptions at −13.2 and −12.22 ppm in the ^{19}F nmr spectrum of *trans*-[(C$_2$H$_5$)$_3$P]$_2$PtCl(C$_3$F$_5$).

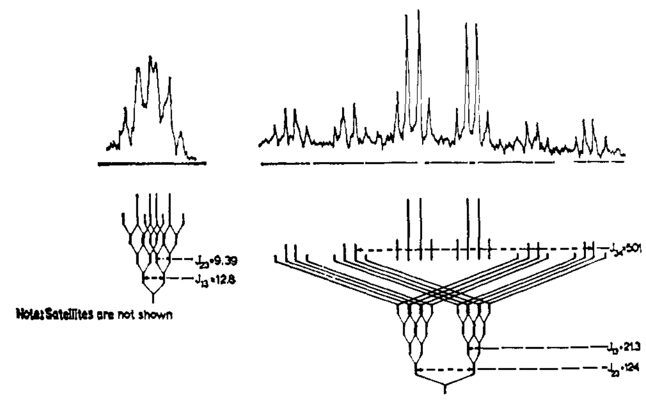


Figure 3. Absorptions at +8.27 and +22.8 ppm in the ^{19}F nmr spectrum of *trans*-[(C$_2$H$_5$)$_3$P]$_2$PtCl(C$_3$F$_5$).

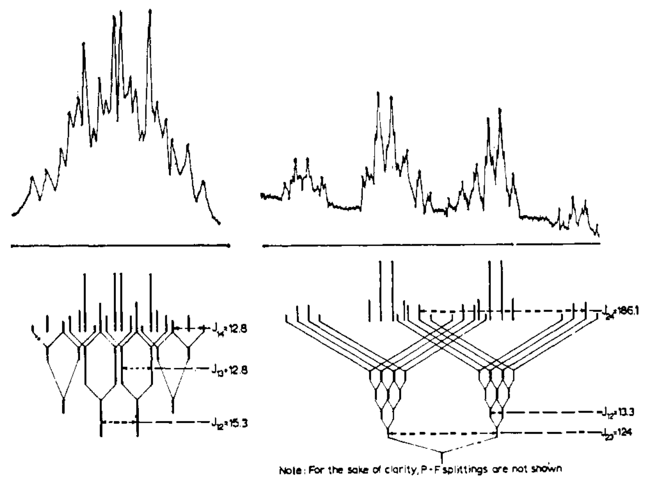
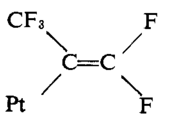


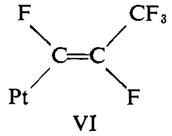
Figure 4. Absorptions at +75.1 and +97.1 ppm in the ^{19}F nmr spectrum of *trans*-[(C$_2$H$_5$)$_3$P]$_2$PtCl(C$_3$F$_5$).

Pt—CF$_2$—CF=CF$_2$

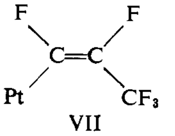
IV



V



VI



VII

Pt-C$_3$F$_5$ grouping. The ^{19}F nmr spectrum (Figures 1–4) consisted of four rather weak absorptions to high field at +8.27, +22.8, +75.1, and +97.1 ppm, and two complex signals of higher intensity at −12.22 and −13.2 ppm. Since the characteristic shift to low field for a CF$_2$ group bonded to a transition metal[28] is not observed, and since the C=C frequency in the infrared spectrum is too low for consistency with a -CF$_2$CF=CF$_2$ grouping, the ^{19}F spectrum has been examined in terms of a -CF=CFCF$_3$ structure. The peaks at −1222 and −13.2 ppm were three times the intensity of each of the remaining peaks, and detailed analysis, in order to determine coupling constants, showed unambiguously that the peaks at +75.1, +8.27, and −13.2 ppm belonged to one component, and those at +97.1, +22.8, and −12.22 ppm to another. Clearly, the sample was a mixture of the *cis* and *trans* isomers in the ratio of 2:3. This explains the complexity of the infrared spectrum, particularly of the C–F stretching vibrations, although it is surprising that only one C=C stretching frequency is observed. This may be due to a lack of resolution or to coincidence of the two bands. On the above basis, analysis of the ^{19}F spectrum was possible to give the coupling constants shown in Table III. These are completely self-consistent and correlate well with data for other propenyl compounds.[16] The configuration of the *trans* isomer is strongly supported by the large value (124 cps) for the two *trans* F atoms. Of particular interest are the large values, 450–550 cps, for the coupling constants between the α-fluorine atom and ^{195}Pt. It is also especially significant that coupling to ^{31}P is observed only for X(2), the values being 3.17 cps for X(2) = CF$_3$ (*cis* isomer) and 3.5 cps for X(2) = F (*trans* isomer). Since there is a separation of five and four bonds, respectively, and since such coupling is not seen to X(1) at four bonds distance, the most reasonable explanation is in terms of through-space coupling.[25] This has been proposed as an im-

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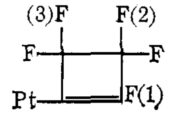
(28) E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, **36**, 124 (1962).

Table IV. Nmr Data for Difluorovinyl Derivatives

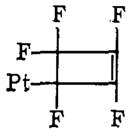
Compound	J_{H-F} cis	J_{H-F} trans	J_{H-F} gem	$\delta_{\text{vinyl H}}$	Ref
$(CH_3)_3SnCF{=}CFH$-*cis*	15	25.5	77	−5.93	12
$(CH_3)_3SnCF{=}CFH$-*trans*	9	...	78	−7.6	
$(CH_3)_3SnCH{=}CF_2$	...	46	...	−3.92	
$(CO)_5MnCF{=}CFH$-*cis*	10.2	25	80	−5.7	13
$(CO)_5MnCF{=}CFH$-*trans*	...	...	86.5	−8.1	
$[(C_2H_5)_3P]_2PtCl(CF{=}CFH$-*cis*$)$	7.8	24	82.3	−5.54	This work
$[(C_2H_5)_3P]_2PtCl(CF{=}CFH$-*trans*$)$		...	84	−7.58	

portant mechanism in F–F coupling, and the present data apparently support the suggestion[25] that it should be valid for coupling between other magnetic nuclei with non-s electrons, in this case $^{31}P-^{19}F$ coupling. Certainly, in the present compounds, X(2) is much closer to ^{31}P than is X(1).

(e) $[(C_2H_5)_3P]_2PtCl(C_4F_5)$ (Compound D). A Pt-cyclic-C_4H_5 grouping can have structure VIII or IX, each with additional isomeric possibilities. The ^{19}F



VIII



IX

spectrum showed a complex multiplet and a 1:3:3:1 quartet centered at +30 and +37.8 ppm (most intense peak) with a ratio of integrated areas of 3:2. The infrared spectrum showed the C=C stretching vibration at 1640 cm^{-1}, indicating that the Pt atom is attached directly to the double bond rather than to a carbon atom in the α position to the double bond.[10] Hence the ^{19}F nmr spectrum was interpreted on the basis of structure VIII. For perfluorocyclobutenyl-metal derivatives [except $C_4F_5Fe(CO)_2(\pi\text{-}C_5H_5)$], the fluorine atoms furthest from the metal have the highest chemical shift.[2b] This suggests that the two F(2) atoms produce the quartet which results from coupling with fluorine atoms (1 and 3), hence assuming J_{12} and J_{23} are equal. The multiplet spreads over a region of 200 cps and in addition to coupling of F(1) and F(3) to F(2), spin–spin coupling with ^{195}Pt must be involved. Since the multiplet could not be completely resolved, detailed analysis was not possible.

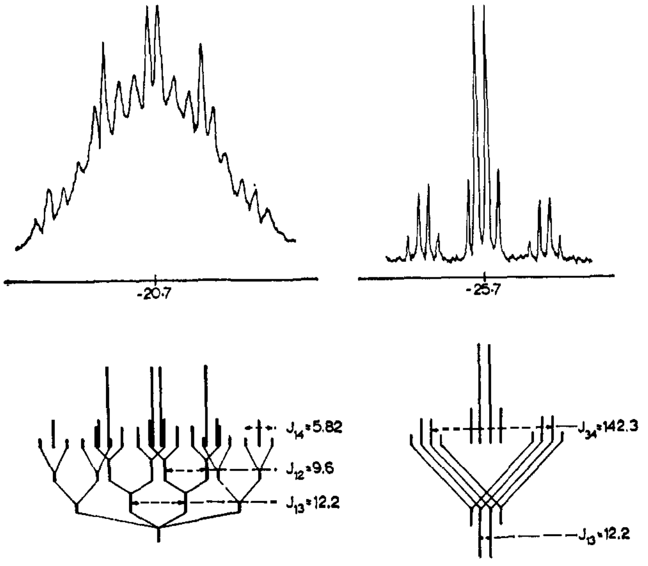
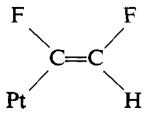
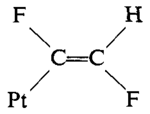


Figure 5. ^{19}F nmr spectrum of *trans*-$[(C_2H_5)_3P]_2PtCl[C(CF_3){=}C(CF_3)H]$.

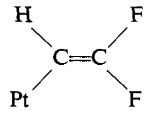
(f) *cis*- and *trans*-$[(C_2H_5)_3P]_2PtCl(CF{=}CFH)$ (Compounds E and F). The grouping Pt–C_2F_2H can adopt structures X–XII. Proton chemical shift and coupling



X



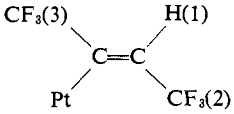
XI



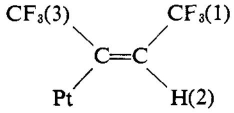
XII

constant data for such isomeric forms have been compiled,[12] and proton and ^{19}F spectra of related pentacarbonylmanganese derivatives have been described.[13] The data for these Pt(II) compounds are in full agreement with the earlier results, and, as indicated by Table IV, the analysis presents no difficulties.

(g) $[(C_2H_5)_3P]_2PtCl[C(CF_3){=}C(CF_3)H]$ (Compound G). The *cis* and *trans* olefinic isomers, represented by structures XIII and XIV, are again possible. The



XIII



XIV

proton spectrum showed a 1:3:3:1 quartet at −6.50 ppm. Cullen, *et al.*,[15] have found that the vinyl protons of the *cis* and *trans* isomers of $(CH_3)_2As(CF_3)C{=}C(CF_3)H$ are at −5.83 and −6.5 ppm, respectively, and on this basis our Pt(II) may be considered to have the *trans* configuration. This is not a convincing argument, however, since the extent to which the chemical shift depends on the substituents (in the case Pt(II) rather than $(CH_3)_2As$) is unknown. From the values of the coupling constants determined from the ^{19}F spectrum, it seems more likely that the *cis* configuration is correct. The ^{19}F spectrum (Figure 5) consisted essentially of a 1:3:3:1 quartet and a multiplet of equal intensity at −25.7 and −20.7 ppm, respectively. On either side of the principal quartet at −25.7 ppm was a satellite quartet of one-fourth the intensity of the main quartet, these being due to spin–spin coupling with ^{195}Pt. Since J_{Pt-F} has the high value of 142.3 cps, it seems reasonable to conclude that this resonance must be due to the CF_3 group geminal to platinum. No coupling between this CF_3 group and the vinylic proton was observed although the spectrum was well resolved. This argues in favor of the *cis* structure, since

Table V. Some H–F Coupling Constants of Vinylic Protons and CF_3 Groups

Compound	J_{12}	J_{13}	J_{23}	Ref
$[(C_2H_5)_3P]_2PtClC(CF_3){=}C(CF_3)H$	9.6	...	0	This work
$(CO)_5Re(CF_3)C{=}C(CF_3)H$-*trans*	9.1	2.5	..	29
$(CO)_5Mn(CF_3)C{=}C(CF_3)H$-*trans*	9.6	2.3	..	29
$(CH_3)_2As(CF_3)C{=}C(CF_3)H$-*trans*	8.3	2.0	..	15
$(CH_3)_2As(CF_3)C{=}C(CF_3)H$-*cis*	8.3	...	0	15
$CH_3(C_6H_5)_2As(CF_3)C{=}C(CF_3)H$-*cis*	8.5	...	0	15
$CH_3(C_6H_5)_2As(CF_3)C{=}C(CF_3)H$-*trans*	8.5	2	..	15

for *trans* isomers of related derivatives[29] the coupling constant is of the order of 1.5–2.5 cps and is zero for *cis* isomers (Table V). The multiplet at −20.7 ppm must be due to the CF_3 group geminal to the vinylic proton and consists of 18 peaks which are formed by coupling with the latter proton, fluorine atoms in the other CF_3 group, and to ^{195}Pt. The value of $J_{CF_3-CF_3}$ = 12.2 cps is in excellent agreement with those reported for other *cis* isomers,[15] whereas analogous *trans* isomers[15,29] give $J_{CF_3-CF_3}$ of the order of 1–3 cps. This high value of $J_{CF_3-CF_3}$ in the *cis* configuration has been attributed to through-space coupling.[29] The evidence therefore strongly favors the *cis*-olefinic confirmation for our Pt(II) compound, and, as final configuration, the excellent agreement of the $J_{Pt-C-C-CF_3}$ values for this compound and the *trans*-perfluoropropenyl derivative (both 5.82 cps) may be cited. It is interesting that there is no spectroscopic evidence for a *trans* isomer produced from this reaction of perfluorobut-2-yne.

Acknowledgment. The financial support of the National Research Council is gratefully acknowledged and also the award of a Commonwealth Scholarship to W. S. T.

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Organometallic Compounds with Metal–Metal Bonds. VI. Preparation and Infrared Spectra of the Carbonylmetalate Ions $[(OC)_5M\text{-}M'(CO)_5]^-$ (M = Mn, Re; M′ = Cr, Mo, W)[1]

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received July 21, 1966*

Abstract: Reaction of $NaM(CO)_5$ with $M'(CO)_6$ affords the six new anions $[(OC)_5M\text{-}M'(CO)_5]^-$ (M = Mn, Re; M′ = Cr, Mo, W), which were isolated as the yellow or orange tetraethylammonium salts. They are isoelectronic and isostructural with $Mn_2(CO)_{10}$. Their infrared spectra exhibit six terminal and no bridging carbonyl stretching frequencies, as expected for a C_{4v} structure. Attempts to isolate a neutral protonated derivative were not successful.

Manganese carbonyl, $Mn_2(CO)_{10}$, and the anion $[Cr_2(CO)_{10}]^{2-}$ constitute an isoelectronic pair. The manganese derivative is among the most fully characterized of all carbonyl compounds, both by infrared spectroscopy[3,4] and by X-ray diffraction.[5] By contrast, the structure of the chromium species must be regarded as unsettled. The salt $Na_2[Cr_2(CO)_{10}]$ was first obtained by Behrens and Haag,[6] from reaction of chromium hexacarbonyl with sodium borohydride in liquid ammonia at 60°. The first infrared results[7] favored a structure without bridging carbonyl groups, similar to that of manganese carbonyl. Very recently, it has been found by Hayter[8] that an ion of composition $[Cr_2(CO)_{10}]^{2-}$ is formed in the reduction of a tetrahydrofuran solution of chromium hexacarbonyl by sodium amalgum; however, bridging carbonyl groups are indicated by the infrared spectrum of Hayter's compound.

Additional interest in the nature of the $[Cr_2(CO)_{10}]^{2-}$ species arises from recent studies[8–10] of its protonated derivative $[HCr_2(CO)_{10}]^-$. The latter ion contains a linear, and probably symmetrical Cr–H–Cr unit, which has been described as a protonated metal–metal bond,[9] or, more generally, as a three-center–two-electron bond.[10]

Consideration of the isoelectronic pair $M_2(CO)_{10}$–$[M'_2(CO)_{10}]^{2-}$ (M = Mn, Re; M′ = Cr, Mo, W)[11] led us to believe that a third, intermediate member of the series should exist, namely $[(CO)_5M\text{-}M'(CO)_5]^-$. We describe in this paper the preparation and infrared spectra of these new anions.

Experimental Section

Reactions were carried out and products purified under a nitrogen atmosphere. Diglyme and THF[12] were freshly distilled from lith-

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[2] To whom correspondence should be addressed.

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[11] This symbolism is used throughout.

[12] Diglyme = diethylene glycol dimethyl ether; THF = tetrahydrofuran.