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Tetrafluoroethylene Complexes of Iridium(I)

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The chlorobis(ethylene)iridium(I) dimer, $[IrCl(C_2H_4)_2]_2$ and acetylacetonatobis(ethylene)iridium(I), Ir(acac)-$(C_2H_4)_2$, react with C_2F_4 to give mixed ethylenetetrafluoroethylene complexes, in which the ethylene ligand may be replaced by alkenes such as cyclooctene and 1,5-cyclooctadiene. A number of neutral ligands can be added to these complexes with or without alkene substitution.

In several complexes a strong IR-absorption in the region 1350-1500 cm^{-1} is found and attributed to (C=C)-stretching vibration of the fluoro-alkene. From PMR-experiments with Ir(acac)$(C_2H_4)_2$ and Ir(acac)-$(C_2H_4)(C_2F_4)$ it could be concluded that the rate of associative ethylene exchange and the barrier to rotation around the metal-ethylene bond were related to the basicity of the metal substrate. The process of alkene addition is discussed in terms of nucleophilic attack of the metal on the empty antibonding alkene-orbitals.

Introduction

The coordination chemistry of tetrafluoroethylene is characterized by the relatively low addition rate of the alkene to transition metals and the rigid three-membered ring structure of the metal-tetrafluoroethylene moiety in the resulting complexes.[1-12] Generally the C_2F_4-complexes differ from their C_2H_4-analogues in the stronger metal-alkene bond, in the absence of alkene rotation around this bond together with better coordination properties towards Lewis bases.

In addition to the high basicity of iridium(I) and its ability to form penta-coordinated complexes, these features made a study of iridium(I)-tetrafluoroethylene complexes worthwhile. Some iridium-tetrafluoroethylene compounds have been reported earlier.[1,2,12,13] This paper deals with the preparation and characterization of chloro- and acetylacetonato-iridium(I)-alkene-tetrafluoroethylene complexes and their behaviour towards Lewis bases.

Experimental Section

IR-spectra were recorded on the Hitachi spectrometers EPI-G2 (4000-400 cm^{-1}) and EPI-L (700-200 cm^{-1}) in KBr disks and as Nujol mull between CsI disk respectively. PMR spectra were recorded on a Varian A-60 MC spectrometer and ^{19}F NMR spectra on a Varian HA-100 MC spectrometer adapted with a 94.1 MC external oscillator. The magnetic saturation measurements were performed at 60 MC on a Bruker Kernspinrezonanz-Impuls spektrometer B-KR 3045. Melting points were measured on a Reichert hot-stage microscope and are uncorrected. Microanalyses and molecular weight determinations were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany.

Materials. $(NH_4)_3IrCl_6$ was purchased from Messrs. Drijfhout, Amsterdam. $IrCl(C_2H_4)_4$ and $[IrCl(C_8H_{14})_2]_2$ were prepared by literature methods.[14] C_2F_4 was prepared by cracking teflon-fibres at 500-550°C under vacuum. Subsequently it was passed over KOH pellets and condensed in a nitrogen trap. Solid and gaseous reagents were used without purification; solvents were reagent-grade, degassed with nitrogen before use, and if required dried over sodium.

Reactions were carried out under nitrogen or ethylene. Whenever possible, working up of the products was done in air. The preparation and analytical data of the complexes prepared are given in Tables I and II.

Preparation and Characterization of Alkene-tetrafluoroethylene-iridium(I) Complexes. Chloro-complexes. Although C_2F_4 generally reacts rather slowly with transition metal complexes, its reaction with the bis(ethylene)-complex $[IrCl(C_2H_4)_2]_2$ (1a) (ref. 14) in ether or pentane at -20°C is complete within 20 min giving the yellow $[IrCl(C_2H_4)(C_2F_4)]_n$ (1b). At room temperature 1b degradates readily to ill-defined carbonyl-compounds under the influence of atmospheric moisture. A similar behaviour has also been found

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Table I. Preparation and analytical data of chloro-iridium(I)-alkene-tetrafluoroethylene complexes.

Compound	Starting from	Procedure	Yield (%)	Elementary analysis calculated found C	H	F	Cl/O/S	N/P/As	M.P. °C	Mol. wt. calculated found	Properties
1b $[IrCl(C_2H_4)(C_2F_4)]_n$	$IrCl(C_2H_4)_4$ (0.5 g) in 15 ml ethylene-saturated dry ether	Stir mixture at –20°C under C_2F_4 for 20 min, remove solvent under reduced pressure									Unstable, can be stored at –20°C under argon for 1 month
1c $[IrCl(C_8H_{14})(C_2F_4)]_n$	$[IrCl(C_8H_{14})_2]_2$ (1.0 g) in 25 ml dry ether	Pass ethylene through with simultaneous cooling to –70°C for 5 min, stir under C_2F_4 at –20°C for 20 min, remove solvent under reduced pressure, wash with cold alcohol, dry under xacuum	80	27.3 29.4	3.2 3.5	17.4 17.1	8.1 8.0		dec.	438 1110[b] 2450[a]	Yellow, store under vacuum at –20°C
3 $[IrCl(C_8H_{12})(C_2F_4)]_2$	$[IrCl(C_8H_{14})(C_2F_4)]_n$ (0.5 g) in 15 ml ether	Add 0.5 ml 1,5-cyclooctadiene and stir for a few minutes, filter off precipitate and wash with ether	90	27.6 29.3	2.8 3.5	17.5 17.0	8.2 7.9		143-147 (dec.)	436 756[c]	Yellow, airstable
5 $[IrCl(PPh_3)(C_2F_4)]_2$	$[IrCl(C_8H_{14})(C_2F_4)]_n$ (0.350 g) in 15 ml pentane	Add under vigorous stirring 0.208 g PPh_3 in 25 ml pentane, filter off precipitate and wash with pentane	88	40.7 40.3	2.5 3.1	12.9 12.5	6.0 5.8	5.3 5.0	dec.	1180 1150[a]	Yellow
6 $IrCl(PPh_3)_2(C_2F_4)$	$[IrCl(C_8H_{14})(C_2F_4)]_n$ in 25 ml pentane	Add under vigorous stirring 0.45 g PPh_3 in 25 ml CH_2Cl_2, filter solution, concentrate to 5 ml, cool to –70°C filter off precipitate, wash with pentane, recrystallize from a pentane-CH_2Cl_2 mixture	55	53.6 53.6	3.6 3.8	8.9 9.1	4.2 4.2	7.3 7.2	222-223 (dec.)	852 870[b]	Yellow
7 $IrCl(AsPh_3)_2(C_2F_4)$	See 6	See 6 but recrystallize twice	30	48.5 50.2	3.2 3.7	8.1 8.0	3.8 3.8	16.0 15.7	190-198	940 956[b]	Yellow
9a $[IrCl(C_2H_4)(C_2F_4)(CH_3CN)]_n$	Cold solution of 1b, prepared *in situ* from $IrCl(C_2H_4)_4$ and C_2F_2 in ether	Add CH_3CN dropwise, filter off precipitate, wash with ether and pentane	80	18.1 18.3	1.8 1.6	19.1 19.4	8.9 7.4	3.5 3.6	dec.		White
9b $[IrCl(C_8H_{14})(C_2F_4)(CH_3CN)]_n$	Solution of 1c ih pentane	Add CH_3CN dropwise, filter off precipitate, wash with pentane	75	30.1 30.2	3.6 3.7	15.9 16.0	7.4 7.5	2.9 3.1	dec.		Pale-yellow
10 $IrCl(C_8H_{14})(C_2F_4)(py)_2$	1c dissolved in minimum of pyridine	Add pentane after 30 min, filter off precipitate and wash with pentane	70	40.3 40.4	4.0 4.5	12.8 12.9	6.0 5.8	4.7 4.8	dec.	594 583[b]	White
11a $IrCl(C_2H_4)(C_2F_4)(dipy)$	Solution of 1b prepared *in stiu*	Add 2,2′-dipyridyl under vigorous stirring, filter off precipitate and wash with alcohol	76	32.8 33.0	2.3 2.4	14.9 15.0	6.9 7.1	5.5 5.3	dec.		White
11b $IrCl(C_8H_{14})(C_2F_4)(dipy)$	1c (0.350 g)	Stir with 2,2′-dipyridyl in either, filter off precipitate and wash with alcohol	85	40.4 40.4	3.7 3.9	12.8 12.9	6.0 5.8	4.7 4.8	dec.		White
12a $[Ir(NH_3)_3(C_2H_4)(C_2F_4)]^+Cl^-$	1b prepared *in situ*	Pass dry NH_3 through for 20 min, filter off precipitate and wash with ether	85	11.8 12.0	3.2 3.2	18.7 18.9	8.7 8.7	10.3 10.5	dec.	407 276[d]	White
12b $[Ir(NH_3)_3(C_8H_{14})(C_2F_4)]^+Cl^-$	Acetone solution of 1c	See 12a	89	24.6 26.1	4.7 4.9	15.5 15.3	7.3 7.2	8.6 8.3	92-96 (dec.)	489 260[d]	White
13 $IrCl(C_8H_{12})(C_2F_4)(py)$	3 dissolved in minimum of pyridine	See 10	72	35.0 36.2	3.3 3.5	14.8 14.6		2.7 2.8	dec.		White

[a] osm. in acetone; [b] osm. in benzene; [c] osm. in chloroform; [d] osm. in methanol.

Table II. Preparation and analytical data of acetylacetonato-iridium(I)-alkene-tetrafluoroethylene complexes.

Compound	Starting from	Procedure	Yield (%)	Elementary analysis calculated found C	H	F	Cl/O/S	N/P/As	M.P. °C	Mol. wt. calculated found	Properties
2a $Ir(acac)(C_2H_4)_2$	$IrCl(C_2H_4)_4$ (0.70 g) in 20 ml peroxide-free ethylene-saturated tetrahydrofuran	At –80°C add acetylacetone (0.3 g), add powdered KOH (0.2 g) and stir for 30 min on an ice-bath, add 30 ml H_2O, filter off precipitate and wash with water and alcohol	92	31.1 31.0	4.3 4.4		9.2 9.4		>120 (subl. dec.)	347 388[b]	Orange
2b $Ir(acac)(C_2H_4)(C_2F_4)$	2a (0.80 g) in 20 ml pentane	Treat with C_2F_4 for 20 min, concentrate solution under ethylene cool to –70C°, filter off precipitate, wash with pentane and recrystallize from ether	75	25.8 25.8	2.6 2.7	18.1 20.5			114-115 (dec.)	419 446[b]	Yellow
2c $Ir(acac)(C_8H_{14})(C_2F_4)$	2b (1.30 g) in pentane	Add C_8H_{14} (0.40 g), remove ethylene by a stream of nitrogen, concentrate, cool to –70°C, filter off precipitate in the cold and recrystallize from ether	80	35.9 38.4	4.2 4.4	15.2 15.4			131-133	501 541[b]	Yellow
4 $Ir(acac)(C_8H_{12})(C_2F_4)$	2b (0.40 g)	Add 2b to C_8H_{12} (0.120 g) in 10 ml pentane, cool after stirring to –70°C, collect crystals on filter	63	36.1 36.2	3.8 3.7	15.2 17.9			116-120[d]	499 515[c]	Yellow
14 $Ir(acac)(CO)(C_2F_4)$	2b in pentane	Pass CO through, replace after a few min CO by nitrogen till a few ml of solvent are left, filter off precipitate and wash with pentane	85	22.9 24.1	1.7 1.8	18.1 19.1			dec.	419 445[a]	Pale rose
15 $Ir(acac)(PPh_3)_2(C_2F_4)$	2b in pentane	Add excess PPh_3, filter off precipitate and wash with pentane	90	56.4 57.3	4.0 4.3	8.3 7.7		6.8 6.2	195-198	915 902[c]	Yellow
16 $[Ir(acac)(C_2F_4)(CH_3CN)]_n$	2b	Dissolve 2b in CH_3CN, filter off after 3 days the crystals and wash with acetone	30	25.0 26.2	2.3 2.3	17.6 18.6		3.2 3.5	dec.		Pale yellow
17a $Ir(acac)(C_2H_4)(C_2F_4)(py)$	2b in pentane	Add pyridine slowly filter off precipitate, wash with pentane and recrystallize from CH_2Cl_2	78	33.7 33.5	3.2 3.3	15.3 15.7		2.8 3.2	dec.		White
17b $Ir(acac)(C_8H_{14})(C_2F_4)(py)$	2c in pyridine	After standing overnight add pentane, filter off precipitate and wash with acetone	89	41.4 41.4	4.5 4.4	13.1 13.9		2.4 2.7	127-131	580 450[b]	White
18a $Ir(acac)(C_2H_4)(C_2F_4)(NH_3)$	2b in acetone	Pass through NH_3 filter off precipitate and wash with acetone	85	24.8 23.9	3.2 3.3	17.5 19.8			dec.		White
18b $Ir(acac)(C_8H_{14})(C_2F_4)(NH_3)$	2c in acetone	See 18a	82	34.8 34.6	4.6 4.8	14.6 15.7		2.7 3.0	81-86[e]	518 481[b]	White

[a] osm. in acetone; [b] osm in benzene; [c] osm. in chloroform; [d] second m.p. 155-157°C; [e] second m.p. 130-135°C.

Table III. PMR spectra of iridium(I)-C_2F_4 complexes; internal ref. TMS, 40°C, τ-values, number of protons in parentheses, solvent $CDCl_3$.

Compond	Alkene protons	Acac protons	Other ligands
C_2H_4	4.65		
2a $Ir(acac)(C_2H_4)_2$	7.42(8) broad	4.51(1), 8.00(6)	
idem at −50°C	6.86(4), 8.12(4) [d]	4.46(1), 7.99(6)	
2b $Ir(acac)(C_2H_4)(C_2F_4)$	6.23(4)	4.29(1), 7.79(3), 7.90(3)	
idem at −50°C	6.27(4)	4.27(1), 7.79(3), 7.93(3)	
17a $Ir(acac)(C_2H_4)(C_2F_4)(py)$	6.18(4)	4.97(1), 8.14(6)	1.39(2), 2.32(1) 2.72(2)
18a $Ir(acac)(C_2H_4)(C_2F_4)(NH_3)$	6.35(4)	4.85(1), 8.10(6)	
12a $[Ir(NH_3)_3(C_2H_4)(C_2F_4)]Cl$ [a]	6.53		
C_8H_{14}	4.45(2), 7.90(4), 8.48(8)		
1c $[IrCl(C_8H_{14})(C_2F_4)]_n$ [b]	5.9(2), 7.90(4), 8.50(8)		
12b $[Ir(NH_3)_3(C_8H_{14})(C_2F_4)]Cl$ [c]	6.1(2), 8.1, 8.50(12)		
2c $Ir(acac)(C_8H_{14})(C_2F_4)$	6.0(2) 7.8(4), 8.50(8)	4.43(1) 7.92, 7.94(6)	
17b $Ir(acac)(C_8H_{14})(C_2F_4)(py)$	5.5(2) 8.07(4), 8.48(8)	5.17(1), 8.25(6)	1.40(2), 2.33(1) 2.83(2)
18b $Ir(acac)(C_8H_{14})(C_2F_4)(NH_3)$	5.75(2), 8.2(4) 8.50(8)	4.80(1), 8.08(6)	
C_8H_{12}	4.54(4), 7.70(8)		
4 $Ir(acac)(C_8H_{12})(C_2F_4)$	4.40(1), 5.17(1) 5.76(1), 6.20(1) 7.40(4), 8.00(4)	4.75(1) 7.93(3), 8.20(3)	
15 $Ir(acac)(PPh_3)_2(C_2F_4)$		4.75(1) 8.26(3), 8.55(3)	2.82, 3.02(30)
14 $Ir(acac)(CO)(C_2F_4)$		4.27(1), 7.83(3), 7.90(3)	

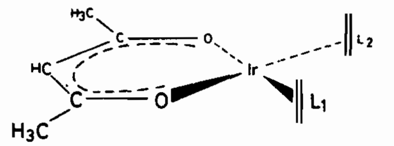
[a] solvent D_2O, internal ref. TSS; [b] solvent-acetone-d_6; [c] solvent CD_3OD; [d] AA'BB' pattern, at 8.12 partially hidden under methyl resonances.

with other C_2F_4-complexes.[12] The compound can be stored at −20°C under argon for over a month without much decomposition. Solutions are unstable, even at low temperature. Its instability obstructs normal analysis and molecular weight determination. A freshly prepared sample was destroyed with KOH and H_2O_2 and the Cl/F ratio in the resulting mixture was determined as 1.00:4.10. Magnetic saturation measurements at −50°C showed that 12.8±1.3 mmole H and 10.4±0.9 mmole F per g were present (theoretical 11.3 mmole H and F per g). The chemical behaviour of 1b towards Lewis bases, described in the next section, also confirmed its composition.

C_2F_4 does not react with the chlorobis(cyclooctene)-iridium(I)-dimer, $[IrCl(C_8H_{14})_2]_2$ (ref. 14), but cyclooctene displaces ethylene from 1b to give the yellow $[IrCl(C_8H_{14})(C_2F_4)]_n$ (1c). The reaction can be carried out *in situ,* by treating a suspension of $[IrCl(C_8H_{14})_2]_2$ in ether or pentane with C_2H_4 and C_2F_4 successively. 1c is very similar to 1b but is somewhat more stable. As indicated by molecular weight measurements, 1c is associated in solution, n being about 2½ in benzene and about 5½ in acetone.

Both 1b and 1c give with 1,5-cyclooctadiene in ether the yellow, airstable compound $[IrCl(C_8H_{12})(C_2F_4)]_2$ (3). This compound is only slightly soluble in methanol and chloroform. Its molecular weight in the latter solvent indicates a dimeric structure.

Acetylacetonato complexes. The monomeric acetylacetonatobis(ethylene)iridium(I), $Ir(acac)(C_2H_4)_2$, (2a) was prepared as an orange precipitate by treating a suspension of $IrCl(C_2H_4)_4$ (ref. 14) in tetrahydrofuran below 0°C with acetylacetone and KOH, after which water was added.



I (compounds: 2a $L_1 = L_2 = C_2H_4$
2b $L_1 = C_2H_4$, $L_2 = C_2F_4$;
2c $L_1 = C_8H_{14}$, $L_2 = C_2F_4$)

2a reacts with C_2F_4 at room temperature within 20 min to give the yellow $Ir(acac)(C_2H_4)(C_2F_4)$ (2b) which is more stable than the corresponding chloro-complex 1b. The ethylene ligand in 2b can be replaced by cyclooctene and 1,5-cyclooctadiene, giving $Ir(acac)(C_8H_{14})(C_2F_4)$ (2c) and $Ir(acac)(C_8H_{12})(C_2F_4)$ (4) respectively. C_2F_4 is loosely bound in 4; at the melting point this compound quickly loses all C_2F_4 and decomposes into $Ir(acac)(C_8H_{12})$ (ref. 15).

Depending on the molecular symmetry, in the PMR spectra of the acetylacetonato complexes one or two methyl-resonances may be present (see Table III). So the spectrum of 2a, showing only one methyl-resonance, indicates the presence of a plane of symmetry. As may be concluded from the presence of two methyl-resonances, such a plane is absent in the structure of the monomeric complexes 2b, 2c, and 4.

For the complexes $Ir(acac)(C_2H_4)_2$ (2a) and $Ir(acac)(C_2H_4)(C_2F_4)$ (2b) proton spectra, taken under various conditions are given in Figure 1.

Although structurally similar, the compounds show striking differences. At ambient temperature 2a shows a broad ethylene-resonance at τ = 7.42 (8). At low temperature this resonance is completely re-

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(15) S.D. Robinson and B.L. Shaw, *J. Chem. Soc.*, 4997 (1965).

solved into a sharp AA'BB' pattern, similar to that found at low temperatures for rhodium-ethylene compounds.[11,16] for which spectrum simulation proved the equivalence of the *cis*-proton of the C_2H_4-ligands and as a consequence the perpendicular orientation of the C=C bond to the coordination plane (Structure I).

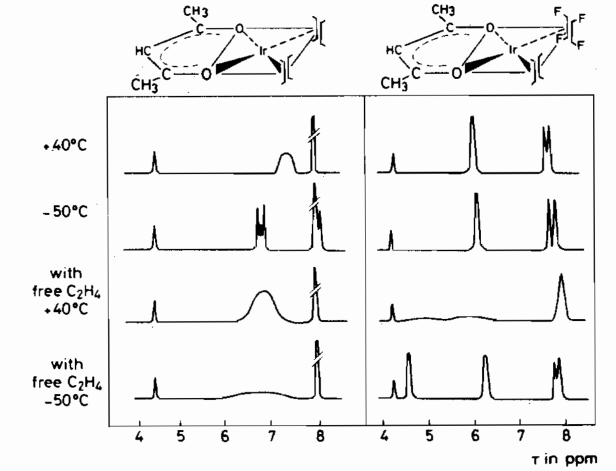


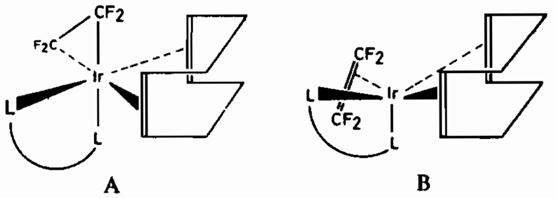
Figure 1. PMR-spectra (diagrammatic) at 60 MC in $CDCl_3$.

We may conclude that ethylene rotation in 2a is rather a slow process at ambient temperature and that at –50°C the 'frozen out' situation is obtained. On the other hand, 2b shows both at 40°C and –50°C a slightly broadened single ethyleneresonance at τ = 6.23 (4). We attribute this to a fast ethylene rotation, many times faster than in the bis-ethylene complex 2a. Since two distinct acetylacetonato-methyl-resonances are present in the spectrum of 2b, it is not likely that dissociation of ethylene is the cause of the fast C_2H_4-proton-equilibration. However, the latter process does occur to a certain extent in 2b as can be concluded from the sharpening at low temperature of the methyl-resonances which are slightly broadened at 40°C. Because of the stronger metal-ethylene bond in 2a, we think this process is absent in the case of this compound.

In the presence of free ethylene, 2a shows at 40°C a broad single absorption centred at τ = 6.79 (10.8), which at –50°C is further broadened, ranging from about τ = 6.0 to τ = 7.7. 2b shows in the presence of free ethylene at –50°C two completely separated and rather sharp absorptions at τ = 4.6 (3.4) for free and at τ = 6.3 (4) for coordinated ethylene. At 40°C, these absorptions are substantially broadened, but not yet completely collapsed into one broad absorption. At this temperature, ethylene-exchange causes equilibration of the methyl groups to such an extent that only one, although broad, methyl absorption is found. The exchange proceeds by both a dissociative and an associative mechanism, although the dissociative mechanism operates only slowly, as can be seen from the slight broadening of the methyl-resonances in the absence of free ethylene. The faster associative mechanism is, however, slow compared with the same process in 2a which even at –50° shows one very broad absorption due to free and coordinated ethylene.

Summarizing and comparing the properties of 2a and 2b deduced from the NMR spectra we find that 2a shows slow ethylene rotation and fast ethylene exchange, 2b on the contrary fast rotation and slow exchange.

The PMR spectrum of 4 not only shows two nonequivalent methyl-groups but also four distinct alkenic protons to be present. The ^{19}F NMR spectrum (Table IV) shows the nonequivalence of the four fluorine atoms. The structure of 4 may therefore be described either as distorted octahedral with a bidentate C_2F_4 ligand (Structure IIA) or alternatively, as tetragonal pyramidal with a monodentate C_2F_4 ligand, occupying one of the equatorial coordination sites (Structure IIB)*.



II (compound 4)

Behaviour of Alkene-Tetrafluoroethylene-Iridium(I)-Complexes Towards Lewis Bases. Chloro-complexes. In the reaction of triphenylphosphine with $[IrCl(alk)C_2F_4)]_n$ (1b, c) the first step is the replacement of the alkene ligand. The addition of the second phosphine involves breaking of the chlorine-bridge.

$$[IrCl(alk)(C_2F_4)]_n \text{ (1b, 1c)} \xrightarrow{PPh_3} [IrCl(C_2F_4)(PPh_3)]_2 \text{ (5)} \rightarrow$$

$$\xrightarrow{PPh_3} IrCl(C_2F_4)(PPh_3)_2 \text{ (6)} \xrightarrow{PPh_3} IrCl(C_2F_4)(PPh_3)_3 \text{ (ref. 12)}$$

In a similar manner $IrCl(C_2F_4)(AsPh_3)_2$ (7) was obtained. The behaviour of 1b and 1c towards triphenylphosphine mainly parallels the behaviour of $[IrCl(C_2H_4)_2]_2$ (1a). The difference lies in the last step, which in the case of 1a involves the slow formation of $IrCl(PPh_3)_3$ by replacement of ethylene from $IrCl(C_2H_4)(PPh_3)_2$ (ref. 17). In the reaction of $[IrCl(C_8H_{12})(C_2F_4)]_2$ (3) with triphenylphosphine, a product has been obtained which showed in its IR-spectrum C_2F_4-absorptions of varying intensity, indicating the formation of $IrCl(PPh_3)(C_8H_{12})(C_2F_4)$ (8) which slowly loses C_2F_4 A likewise unstable product has been obtained from the action of cyclooctadiene on 5.

The molecular weight of 5, which is only slightly soluble in alcohol and acetone, agrees with a dimeric formulation in the latter solvent. The *trans*-structure of 6 (see Structure III) which was described earlier by Stone et al.[12], may be concluded from its ^{19}F spec-

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(16) R. Cramer *J. Amer. Chem. Soc., 86,* 217 (1964).

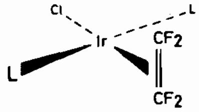
(*) The structure designs in this paper are for reasons of clarity based either on square planar or on octahedral coordination of the metal with C_2F_4 consequently acting as a mono- or bidentate ligand respectively; this choice does not intend to state the bonding mode of C_2F_4. For the determination of coordination numbers C_2F_4 is always referred to as a monodentate ligand.

(17) A. Van der Ent and A.L. Onderdelinden, *Inorg. Chim. Acta, 7,* 203 (1973).

Table IV. ^{19}F NMR spectra of iridium(I)-C_2F_4 complexes; 30°C , lock external CF_3COOH.

Compound	Shift δ (ppm)	Pattern	Solvent
C_2F_4	54.6	singlet	CH_2Cl_2
1c $[IrCl(C_8H_{14})(C_2F_4)]_n$	35.1		
	51.8	broadened AB	acetone
5 $IrCl(PPh_3)_2(C_2F_4)$	22.7	apparent triplet	CH_2Cl_2
7 $IrCl(AsPh_3)_2(C_2F_4)$	20.5	singlet	CH_2Cl_2
12a $[Ir(NH_3)_3(C_2H_4)(C_2F_4)]Cl$	53.1		
	55.5	broadened AB	CH_3OH
12b $[Ir(NH_3)_3(C_8H_{14})(C_2F_4)]Cl$	51.2	broadened AB	CH_3OH
	59.1	complex	CH_2Cl_2
2b $Ir(acac)(C_2H_4)(C_2F_4)$	44.5		
2c $Ir(acac)(C_8H_{14})(C_2F_4)$	42.5	AA'BB'	CH_2Cl_2
	50.6		
4 $Ir(acac)(C_8H_{12})(C_2F_4)$	43.1	complex	CH_2Cl_2
	50.7	complex	
	51.9	complex	
	57.0	complex	
14 $Ir(acac)(CO)(C_2F_4)$	34.4		
	52.5	AA'BB'	acetone
17b $Ir(acac)(C_8H_{14})(C_2F_4)(py)$	49.3		
	55.7	broadened AB	CH_2Cl_2
18a $Ir(acac)(C_2H_4)(C_2F_4)(NH_3)$	50.6		
	53.3	broadened AB	CH_2Cl_2
18b $Ir(acac)(C_8H_{14})(C_2F_4)(NH_3)$	48.7		
	58.2	broadened AB	acetone

trum (Table IV). This shows an apparent triplet due to coupling of the ^{19}F spins with two strongly coupled ^{31}P nuclei ($I = 1/2$). The ^{19}F spectrum of the corresponding arsine compound 7 shows, in agreement with the *trans*-structure, a single sharp resonance. The spectra of 6 and 7 are unaffected by temperature changes and by the presence of free C_2F_4 The latter indicates the absence of a C_2F_4-exchange process on the NMR time scale.



III (compounds: 6 L = PPh_3; 7 L = $AsPh_3$)

With nitrogen Lewis bases 1b and 1c generally yield addition compounds. Due to their insolubility or instability in solution these compounds, with the exception of the ammonia complexes, are not suitable for NMR investigations.

Consequently with methyl cyanide the white complex $[IrCl(C_2H_4)(C_2F_4)(CH_3CN)]_n$ (9a) and the pale-yellow complex $[IrCl(C_8H_{14})(C_2F_4)(CH_3CN]_n$ (9b) are formed. The presence of ethylene in 9a was demonstrated in the reaction with ammonia (see below).

During the reaction of 1b with a solution of pyridine ethylene is rapidly generated. The resulting product still showed C_2F_4-absorptions in the IR-spectrum, but could not be characterized. 1c yields with pyridine the penta-coordinated adduct $IrCl(C_8H_{14})(C_2F_4)(py)_2$ (10) The reaction of a pyridine solution with 1a resulted in the formation of the monomeric 1:1 adduct *cis*-$IrCl(C_2H_4)_2(py)$ (ref. 18).

Equimolar amounts of 2,2'-dipyridyl yields with 1b and 1c the adducts $IrCl(alk)(C_2F_4)(dipy)$ (11a alk = C_2H_4 and 11b alk = C_8H_{14}). With ammonia the ionic penta-coordinated compounds $[Ir(NH_3)_3(alk)(C_2F_4)]Cl^-$ (12a alk = C_2H_4 and 12b alk = C_8H_{14}) are obtained. The compounds are soluble in ionizing solvents such as alcohol and water. Their molecular weight as well as the conductivity in methanol are in agreement with their ionic character. 12a can also be prepared by substitution of the methyl cyanide ligand in 10, proving the presence of ethylene in the latter.

The cyclooctadiene compound 3 showed no reaction with methylcyanide and 2,2'-dipyridyl but with pyridine the 1 : 1 adduct $IrCl(C_8H_{12})(C_2F_4)(py)$ (13) was formed.

Acetylacetonato-complexes. The reaction of the acetylacetonato compounds 2b and 2c with carbonmonoxide yields a pale-rose coloured compound of composition $Ir(acac)(CO)(C_2F_4)$ (14). It turns yellow in various solvents, but can be recovered unchanged from $CHCl_3$ and acetone solutions by evaporating the solvent under a stream of nitrogen or CO. IR-spectra of 14 in solution and in the solid state are different (see Table V). In chloroform it shows two bands at 1530 cm^{-1} (s) and 1563 cm^{-1} (m) indicative of an oxygenbonded chelating acac-group. In KBr-pellet and as Nujol mull, however, instead of these two bands two new bands appeared at 1620 cm^{-1} (s) and 1520 cm^{-1} (m); the one at 1620 cm^{-1} may be indicative of a carbon-bridging acac-function[2]. Molecular weight measurements showed the compound to be monomeric in solution. These findings suggests that compound forms reversibly an iridium-carbon bond, being dimeric in the solid state with a carbon-bonded bridging acetylacetonato-group (Structure IV).

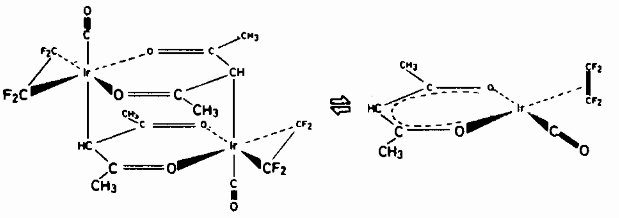
The PMR spectrum (Table III) of 14 in $CDCl_3$ shows two distinct CH_3–singlets of equal intensities, which should be expected for the monomer structure.

(18) A. Van der Ent, unpublished results.

Table V. Infrared data (cm^{-1}).

Compound	ν(C_2F_4)			ν(acac) and others
1c [IrCl(C_8H_{14})(C_2F_4)]$_n$	814s	1053s, 1157s	1475s	
3 [IrCl(C_8H_{12})(C_2F_4)$_2$]$_2$	785s	1053s, 1107s, 1183s	1377s, 1403s	
5 [IrCl(PPh_3)(C_2F_4)]$_2$	807s	1027s, 1096s		
6 IrCl(PPh_3)$_2$(C_2F_4)	817s	1030s, 1098		305m ν(Ir-Cl)
7 IrCl($AsPh_3$)$_2$(C_2F_4)	803s	1030s. 1110s		303m ν(Ir-Cl)
9a [IrCl(C_2H_4)(C_2F_4)(CH_3CN)]$_n$	822s	1060s, 1121s	1403s	2280w, 2320w ν(C≡N)
9b [IrCl(C_8H_{14})(C_2F_4)(CH_3CN)]$_n$	836s	1040s, 1107s	1375s	2280m, 2310m ν(C≡N)
10 IrCl(C_8H_{14})(C_2F_4)(py)$_2$	838s	1023s, 1045s, 1067s, 1080s	1348s	
13 IrCl(C_8H_{12})(C_2F_4)(py)	780s, 792sh	1037s, 1042s, 1116s	1350s	
11a IrCl(C_2H_4)(C_2F_4)(dipy)	851s	1037s, 1092s	1380s	
11b IrCl(C_8H_{14})(C_2F_4)(dipy)	840s	1022s, 1050s, 1083s	1370s	
12a [Ir(NH_3)$_3$(C_2H_4)(C_2F_4)]$^+$Cl$^-$	840s, 853sh	1037s, 1084s	1373s	
12b [Ir(NH_3)$_3$(C_8H_{14})(C_2F_4)]$^+$Cl$^-$	838s	1020s, 1052s, 1064s	1345s	
2a Ir(acac)(C_2H_4)$_2$				1536s, 1550sh, 1562sh, 1574sh
2b Ir(acac)(C_2H_4)(C_2F_4)	799s	1043s, 1134s	1497m	1537s, 1562s
2c Ir(acac)(C_8H_{14})(C_2F_4)	800s	1033s, 1050s, 1124s, 1140s	1481s	1534s, 1563s
4 Ir(acac)(C_8H_{12})(C_2F_4)	794s	1053s, 1086s, 1127s	1368s	1512s, 1573s, 1590s
14 Ir(acac)(CO)(C_2F_4)(KBr)	815s	1068s, 1135s	1393s	1520m, 1620s, 2051s, 2064sh ν(C≡O)
idem ($CHCl_3$)				1530s, 1563m, 2064s ν(C≡O)
15 Ir(acac)(C_2F_4)(PPh_3)$_2$	835s	1038s, 1080s	1356	1516s, 1584s
16 [Ir(acac)(C_2F_4)(CH_3CN)]$_2$	842s, 860s	1022s, 1035sh	1377s	1640s
17a Ir(acac)(C_2H_4)(C_2F_4)(py)	840s	1018s, 1036s, 1076s	1385s	1518s, 1575s
17b Ir(acac)(C_8H_{14})(C_2F_4)(py)	838s	1038s, 1083s	1364s	1518s, 1587s
18a Ir(acac)(C_2H_4)(C_2F_4)(NH_3)	850s	1003s, 1080s	1380s	1517s, 1572s, 1586s
18b Ir(acac)(C_8H_{14})(C_2F_4)(NH_3)	843s, 858s	1012s, 1065s, 1099s	1380s	1522s, 1573s

s = strong, m = medium, w = week, sh =shoulder.

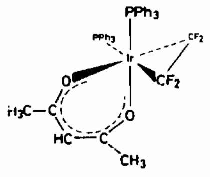


IV (compound 14)

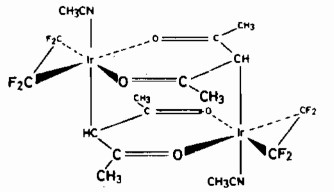
The ^{19}F NMR spectrum (Table IV) shows a complex pattern of the AA'BB' type.

Excess triphenylphosphine yielded with 2b and 2c the yellow complex Ir(acac)(PPh_3)$_2$(C_2F_4) (15) which, on account of the presence of two methyl-resonances of equal intensity in the PMR spectrum (Table III), has been attributed the *cis*-structure (Structure V). The corresponding Rh(acac)(PPh_3)$_2$(C_2F_4) has been attributted the *trans*-structure on account of the presence of only one methyl-resonance[2].

The structure of the reaction product of 2b or 2c with methyl cyanide [Ir(acac)(CH_3CN)(C_2F_4)]$_2$ (16) has been elucidated by X-ray investigation[19] by Dr van Soest of our laboratory (see Structure VI). The presence of a carbon-bridging acac-function was also indicated by a strong IR-absorption band at 1640 cm^{-1} (see Table V).

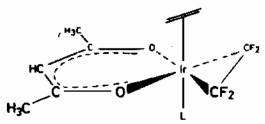


V (compound 15)



VI (compound 16)

With pyridine and ammonia 2b and 2c formed pentacoordinated 1: 1 adducts of the type Ir(acac)-(alk)(C_2F_4)L with alk = C_2H_4 or C_8H_{14} and L = pyridine (17) or NH_3 (18). The PMR spectra of these compounds showed only one methyl-resonance. Exchange experiments with free ethylene show that this is not caused by dissociative ethylene exchange in case of the ethylene compounds 17a and 18a. In agreement with this, the symmetrical structure VII is attributed to 17 and 18.



VII (compounds: 17a alkene = C_2H_4 and L = pyridine;
17b alkene = C_8H_{14} and L = pyridine;
18a alkene = C_2H_4 and L = NH_3;
18b alkene = C_8H_{14} and L = NH_3)

The bis(ethylene) complex Ir(acac)(C_2H_4)$_2$ (2a) shows a behaviour towards Lewis bases which is quite different from that of 2b. Ethylene replacement in 2a is complete with carbonmonoxide and 1,5-cyclooctadiene resulting in Ir(acac)(CO)$_2$ and Ir(acac) (diene) respectively, but no reaction with methyl cyanide and pyridine has been detected.

(19) E.C. Royers and T.C. Van Soest, to be published.

Ir-Spectra. In general three main regions of absorptions due to coordinated C_2F_4 are found (see Table V). Firstly, in all complexes there is a strong absorption at roughly 800 cm^{-1}, which is correlated with the symmetrical mode in free C_2F_4 at 778 cm^{-1}, which is mainly (C-F) stretching in character[20]. Secondly two or three strong absorptions are found between 1000 and 1170 cm^{-1}. Thirdly most complexes show a quite intense absorption between 1340 and 1500 cm^{-1}. We connect this absorption with the (C=C) stretching vibration, which in free C_2F_4 is found at 1872 cm^{-1} in the Raman spectrum[20]. Its position correlates with the basicity of the metal substrate. Thus Lewis base-adducts show this absorption 100 to 130 cm^{-1} lower than the parent complexes. Because of the electron-releasing alkyl substituents cyclooctene complexes show this absorption on an average some 15 cm^{-1} lower than the corresponding ethylene complexes. A similar lowering of the frequency on expansion of the coordination number from four to five has recently been reported for the carbonyl stretching vibration in iridium(I) and rhodium(I) complexes[21].

Rate of bond-formation and stability of the Metal-Alkene Bond. It is known that C_2F_4-coordination enhances the ability of rhodium(I) to form pentacoordinate complexes with donating ligands[1,2]. The same, even to a greater extent is found with iridium(I) complexes. This influence of C_2F_4 is in agreement with the dualistic nature of the metal by which it acts as a base towards accepting or acidic ligands and as an acid towards donating or basic ligands[17].

The transition metal-alkene bond is generally described on the basis of the Dewar-Chatt-Duncanson model[22] in which the filled bonding σ and π orbitals of the alkene show σ-donor capacity towards empty metal orbitals and in which the empty antibonding σ^* and π^* alkenic orbitals can accept electron density from a filled metal orbital by overlap of π symmetry. Electronegative substituents on the alkene should increase its acceptor properties at the expense of its donor-properties and leads to an increase in metal-alkene bond stability for complexes of electron rich metals. The influence of electronegative substituents on the rate of alkene-addition, is, however, not unambiguous. So, substitution of cyanide for hydrogen increases both the stability of the formed bond and the rate of alkene addition[23], whereas substitution by fluorine or chlorine increases the stability but decreases the rate of addition. Since C_2F_4 was supposed to be a good π-acid, it was concluded that π-interactions played a minor role in the initial stage of the alkene addition process[24]. Molecular orbital calculations (Hückel[25] and Extended Hückel[26]) indicate, however, that interactions of the carbon p_z-orbitals with the fluor π electrons result in higher energies of the π and π^* orbitals in C_2F_4 than in ethylene (Table VI). This would lead to higher C_2F_4-reactivities towards electrophilic and lower C_2F_4-reactivities towards nucleophilic reagents. So the low reactivity of C_2F_4 towards transition metals can only be accounted for by a nucleophilic attack of the metal on the alkenic π^* antibonding orbitals. The higher reactivity of tetracyanoethylene with its low lying empty π^* antibonding orbital can likewise be accounted for by the same mechanism. Also the ethylene-exchange experiments with $Ir(acac)(C_2H_4)_2$ (*2a*) and $Ir(acac)(C_2H_4)(C_2F_4)$ (2b) combined with their chemical behaviour towards nitrogen bases contain evidence for the influence of metal-basicity on the rate of alkene-addition. The slow ethylene rotation in 2a as compared with 2b reflects the higher amount of π back bonding from the metal to the alkene and the higher electron density on the metal. Although 2a has as a consequence a low affinity towards σ-bases, whereas 2b forms fairly stable adducts with the donor-molecules, ethylene-exchange is much faster in 2a than in 2b. So it may be concluded that nucleophilic attack of the metal on the alkene is a general feature in the addition of alkenes to transition metals.

Table VI. Energies of π and π^* orbitals in alkenes.

Alkene	Found		Calculated[a]		
	IP (eV)	$\pi \rightarrow \pi^*$ (cm^{-1})	π^* (eV)	π (eV)	$\pi \rightarrow \pi^*$ (cm^{-1})
C_2F_4	10.1	71650[b]	−11.4	−3.7	62200
C_2H_4	10.5	60170[b]	−13.2	−6.3	55700
$C_2(CN)_4$		40733[c]	−13.4	−10.0	27400

[a] Ref. 26; [b] Ref. 27; [c] Ref. 28.

In spite of the high π and π^* energies in C_2F_4 the direction of bond polarity is metal → C_2F_4, as may be concluded from the enormous increase in acidity of the metal in comparison with similar ethylene complexes and from the lowering of $\nu(C=C)$ on adduct formation with Lewis bases. This may be rationalised by the consideration that the alkene loses its planarity during the coordination process. As a consequence mixing of the alkenic π and σ orbitals occurs and the σ-inductive influence of the fluorine atoms gains importance and may become a dominant factor in determining the stability of the metal-C_2F_4 bond.

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