Journal of Organometallic Chemistry, 125 (1977) 253—271
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THE REACTION OF ALLENE WITH β-DIKETONATOIRIDIUM(I) COMPLEXES: SYNTHESIS, PROPERTIES AND CRYSTAL STRUCTURES OF BIS(η^3-ALLYLIC) COMPLEXES OF IRIDIUM(III) AND OF IRIDOCYCLOPENTANE DERIVATIVES

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(Received July 23rd, 1976)

Summary

Allene reacts with compounds of the type (β-diketonato)Ir(η-C_8H_{14})$_2$ (I) to give iridium(III) derivatives of formula (β-diketonato)Ir$C_{12}H_{16}$ (II) in which an allene tetramer, i.e. the 2,3,6,7-tetramethyleneoctane-1,8-diyl group, is bonded to the iridium atom by two η^3-allylic groups. The molecular structures of these complexes were deduced by ^{1}H NMR studies and by single-crystal X-ray analysis of (hfacac)Ir$C_{12}H_{16}$ (IIb). The reactions of the complexes II with hydrogen and with CO are described.

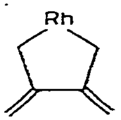
The reaction of (acac)Ir(η-C_8H_{14})$_2$ with allene, at —78°C, gives a thermally unstable compound of probable stoichiometry (acac)Ir(C_3H_4)$_4$ (VI). Its low-temperature IR spectrum and its reaction with bromine indicate that VI contains two η^2-bonded allene molecules and the 3,4-dimethyleneiridocyclopentane moiety. VI reacts with pyridine with loss of an allene molecule to give an iridium(III) derivative of formula (acac)Ir(C_6H_8)(C_3H_4)py (IX). Complex IX was shown by single-crystal X-ray analysis to contain the 3,4-dimethyleneiridocyclopentane moiety and one η^2-bonded allene molecule.

The role of irido cycles as precursors of the bis(allylic) complexes II is discussed.

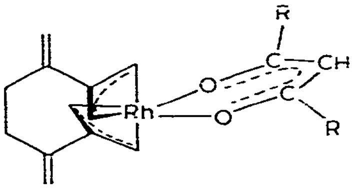
Introduction

The reaction of allene with transition metal compounds has attracted considerable attention in recent years, and in consequence many organometallic complexes showing unusual structural features have been made available [1], and information has accumulated about the role of transition metals in some catalytic or stoichiometric reactions of allene.

Many of these reactions have been postulated to occur via dimethylenemetallocyclopentane intermediates [2—5]. Recently compounds containing the 3,4-dimethylenerhodacyclopentane moiety (A) have been isolated [6,7]. Their intermediacy in the formation of the bis(η^3-allylic) complexes of rhodium(III) (B) [7], as well as in the polymerization and oligomerization of allene catalyzed by some rhodium(I) derivatives [13], has been established.



(A)



(B)

However the details of the A → B transformation are still not fully understood.

In order to extend knowledge on the oxidative addition of allene to d^8 metals we have investigated the reactions of propadiene with some iridium(I) derivatives of general formula (β-diketonato)Ir(η-C_8H_{14})$_2$. (There have previously been only a few reports dealing with the iridium—allene chemistry [1,8].) We have now isolated new bis(η^3-allylic) and iridocyclopentane complexes of iridium(III), of which the preparation, properties and X-ray structures we report in this paper *.

Our study shows the substantial similarity of β-diketonato derivatives of rhodium(I) and iridium(I) as far as the reaction with allene is concerned. Moreover the isolation and structure determination of an iridium(III) complex, whose rhodium-analogue has not so far been prepared, enables us to suggest a plausible mechanism for the transformation leading to bis(η^3-allylic) complexes from metallocyclopentane compounds.

Results and discussion

Preparation and properties of bis(η^3-allylic) derivatives of iridium(III)

When allene is bubbled through a pentane solution of (hfacac)Ir(η-C_8H_{14})$_2$ (Ib), a fast reaction takes place as indicated by a rapid change in the colour of the solution from reddish-violet to light-red. From this solution an orange-red crystalline diamagnetic product of stoichiometry (hfacac)Ir$C_{12}H_{16}$ (IIb), is obtained in good yields, on cooling to —30°C. Analogously from the reaction of Ic with allene, a compound of stoichiometry (dbm)Ir$C_{12}H_{16}$ (IIa) is formed.

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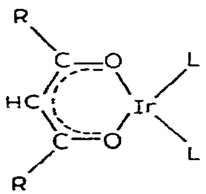
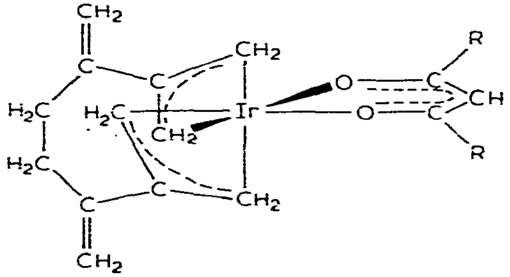
* Preliminary accounts have appeared [9,10].

The presence of the expected (acac)Ir$C_{12}H_{16}$ (IIa) was demonstrated by ^1H NMR spectroscopy in the crude products obtained by treating Ia with allene under a range of experimental conditions, but we could not isolate IIa in pure form.



(I)



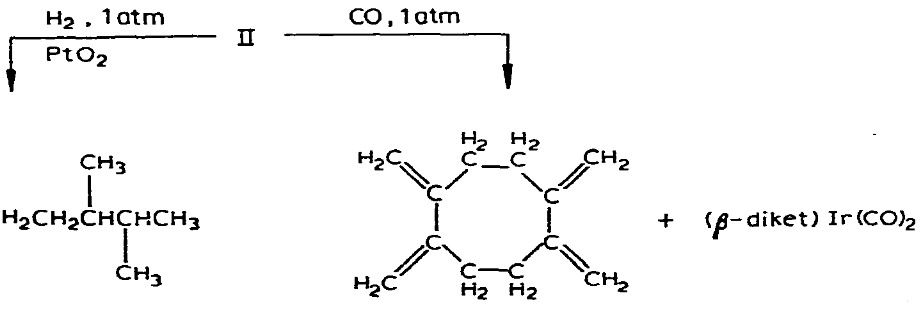
(II)

(L = cyclooctene ; a, R = CH_3 ; b, R = CF_3 ; c, R = C_6H_5)

In the solid state IIb and IIc are stable at room temperature and remain unchanged in air for a long time. IIb is very soluble in most organic solvents and it can be easily purified by low-temperature crystallization from pentane. IIc is markedly less soluble in hydrocarbon solvents.

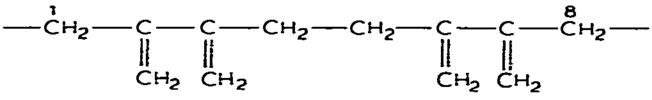
The structural assignment to these complexes is based upon their chemical behaviour, their IR and ^1H NMR spectra, and for IIb also upon single-crystal X-ray diffraction studies. Both IIb and IIc react with hydrogen at room temperature and atmospheric pressure in the presence of PtO_2 to give metallic iridium and a mixture of products which, on distillation from Na gives a mixture containing 2,3,6,7-tetramethyloctane (III) as the major product (95%, by GLC) (Scheme 1). III was identified by comparison of its properties with those of an authentic sample.

SCHEME 1



(III) (IV)

Treatment of a pentane solution of IIc with CO at room temperature and at atmospheric pressure leads to 1,2,5,6-tetramethylenecyclooctane (IV) and (dbm)Ir$(CO)_2$ (Scheme 1). IIb reacts similarly with CO, but the reaction is more complicated, since (hfacac)Ir$(CO)_2$ further reacts with IV to give unidentified products. These results suggest that the complexes II contain the 2,3,6,7-tetramethyleneoctane-1,8-dyil group (V) bonded to iridium by carbon atoms 1 and 8. The observed reaction pattern is characteristic of transition metal compounds



$$-\overset{1}{C}H_2-\underset{\underset{CH_2}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-\underset{\underset{CH_2}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-\overset{8}{C}H_2-$$

(V)

containing two σ- or η-allylic metal—carbon bonds [7,11,12].

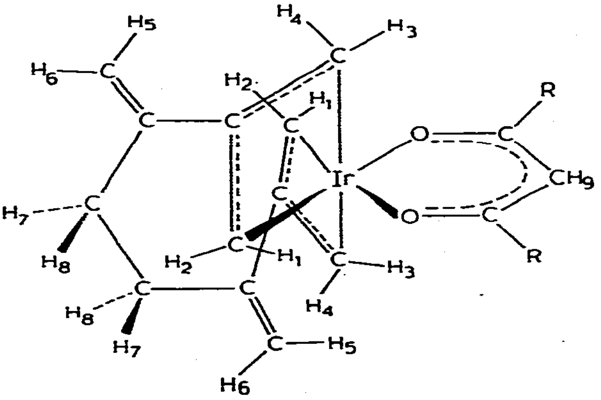
IR spectra (see Experimental) reveal that in complexes II the β-diketonato group is bonded by the two oxygen atoms to iridium which is then assigned a formal oxidation state of III with the low-spin electron configuration $5d^6$. If the ligand V is bonded to iridium in a bis(η^3-allylic) fashion, the iridium(III) attains hexacoordination and has 18 valence electrons.

These conclusions were confirmed by X-ray examination of IIa and are also in agreement with the ^{1}H NMR spectra of the complexes II (see Table 1).

Because of the similarity of the NMR spectra of complexes IIb and IIc, our discussion is confined to the ^{1}H NMR spectrum of IIb. This spectrum shows the

TABLE 1

^{1}H NMR DATA FOR BIS(η^3-ALLYLIC) COMPLEXES II [a]



Protons	IIb (R = CF_3)	IIc (R = C_6H_5)
1	1.53 ud	1.61 ud
2	1.95 ud	1.97 ud
7,8	2.37 s	2.39 s
4	3.00 m	3.05 m
3	4.31 m	4.31 m
5 or 6	5.20 ud	5.16 ud
6 or 5	5.50 d	5.49 d
9	5.97 s	6.61 s
Phenyl	—	8.00—7.35 bm

[a] Measured in $CDCl_3$, at 37°C. Chemical shifts (δ values) refer to TMS as internal standard; s, singlet, d, doublet, m, multiplet, ud, unresolved doublet, bm, broad multiplet.

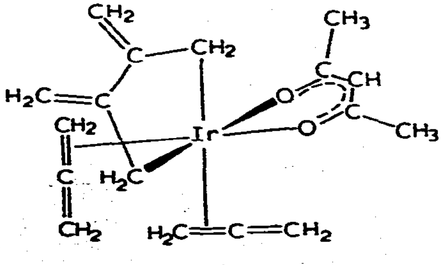
following resonances: δ 1.53 (2H), 1.95 (2H), 2.37 (4H), 3.00 (2H), 4.31 (2H), 5.20 (2H), 5.50 (2H), 5.97 (1H) ppm. These data together with the results of double irradiation experiments are consistent with the bis(η^3-allylic) structure II. The singlet at δ 5.97 ppm is attributed to the methine proton of the β-diketonato group. The resonances at δ 5.50 and 5.16 ppm are assigned to vinylidenic protons 5 and 6. The singlet at δ 2.37 ppm is attributed to the four protons 7 and 8. The signals at δ 3.00 and at 3.41 ppm have been found by double irradiation experiments to be coupled. They are assigned to protons 3 and 4 attached to the carbon atoms of the allylic groups *trans* to each other. The signals at δ 1.93 and 1.51 ppm are assigned to allylic protons 1 and 2. Double irradiation could not be carried out on the δ 1.93 resonance because of the proximity to the signal at δ 1.51 ppm. However, these signals may be assumed to be coupled since the 1.51 resonance is not coupled to any other resonance in the spectrum and the coupling constants are the same for the splittings in the two resonances.

This assignment is consistent with a bis(η^3-allylic) complex in which the two equivalent allylic groups are asymmetrically bonded to the iridium atom; that is the two terminal carbon atoms in each allylic group are at different distances from the iridium atom. Such a situation can arise only if the terminal carbon atoms in each allylic group "see" different ligands in the *trans* position. The proposed structure satisfies these geometrical requirements. A similar behaviour has been previously observed for complexes of the type $Rh_2X_2(C_3H_5)_4$ [11] and (β-diketonato)$RhC_{12}H_{16}$ [7]. The X-ray structure of IIb accounts for this asymmetry (see X-ray results for discussion).

IIb and IIc react at 70°C with allene in hydrocarbon solutions to give highly crystalline polymers of regular constitution $\text{+}CH_2C(=CH_2)\text{+}_n$ along with a mixture of oligomers. The polymers appear to be identical with those obtained in the presence of other transition metal-based catalysts [21,28].

Preparation and properties of 3,4-dimethyleneiridocyclopentane derivatives

The reaction between (acac)Ir(η-C_8H_{14})$_2$ (Ia) and allene has been investigated with a view to preparing a bis(η^3-allylic) complex analogous to IIb and to IIc. It was found that Ia reacts with allene at −78°C to give cyclooctene and a microcrystalline pale yellow product (VI) which is slightly soluble in cold pentane (Scheme 2). VI is thermally very unstable and in the solid state must be stored below −20°C. Its instability precluded elemental analysis or molecular weight measurement. VI was then tentatively assigned the following structure on the basis of the IR spectrum (measured at −30°C) and its chemical behaviour (Scheme 2).

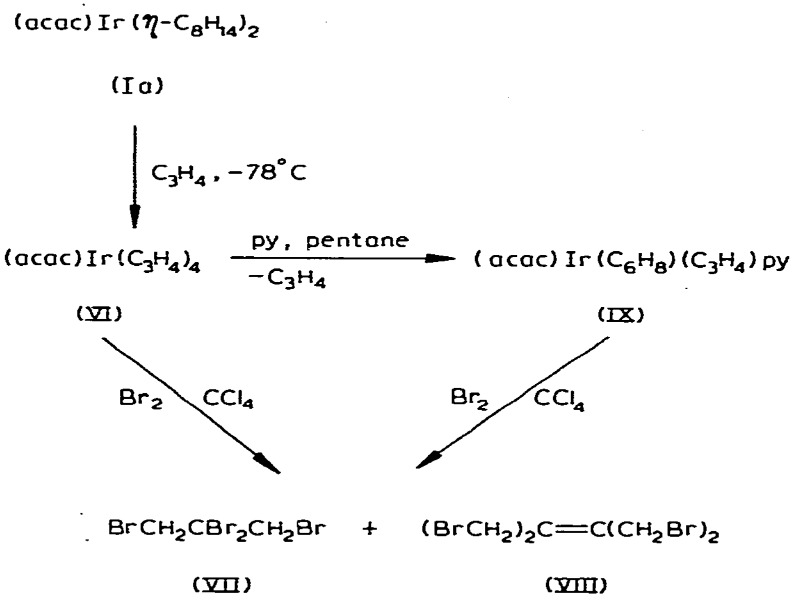


(VI)

The IR spectrum reveals that the acetylacetonate group is bonded to iridium by the two oxygen atoms (ν(C $\doteq$ O)1580; ν(C $\doteq$ C) 1510 cm^{-1}). Furthermore two bands at 1710 and 1690 cm^{-1} in addition to a very strong broad band centered at 865 cm^{-1} indicate [8] the presence at least of two allene molecules η^2-bonded to iridium.

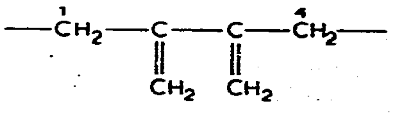
On reaction with pyridine, VI gives allene and a very stable yellow-greenish compound of formula (acac)Ir(C_6H_8) (C_3H_4)py (IX) (Scheme 2).

SCHEME 2



The allene molecule present in IX is η^2-bonded to iridium as revealed by two bands at 1770 and at 855 cm^{-1} in the IR spectrum (see Experimental). Both VI and IX react with bromine in carbon tetrachloride to give unidentified water-soluble iridium compounds and a mixture of 1,2,2,3-tetrabromopropane (VII) and tetrabromomethylethylene (VIII) (Scheme 2). The ^{1}H NMR spectra showed the mixtures obtained from VI and IX to contain VII and VIII in the molar ratios of 2 : 1 and 1 : 1, respectively.

The formation of 1,2,2,3-tetrabromopropane confirms the presence of coordinated allene in the complexes VI and IX [19]. On the other hand, assuming that no coupling between allene molecules occurs during the reaction with bromine, the presence of tetrabromoethylethylene implies that both VI and IX contain an allene dimer of the structure C in which carbon atoms 1 and 4 may

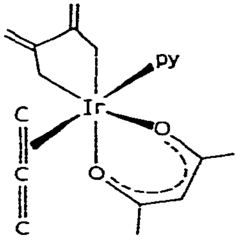


(C)

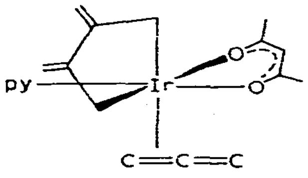
be σ-bonded to one or to two iridium atoms.

Similar results were observed for the reaction of 3,4-dimethylenerhodacyclopentane compounds with bromine [6,7].

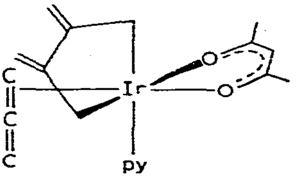
IX has a molecular weight consistent with a monomeric structure, it seems probable that IX contains the 3,4-dimethylenerhodacyclopentane moiety. Three diastereoisomeric structures are then to be expected:



(IXa)



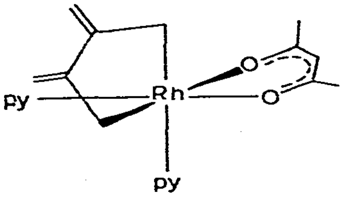
(IXb)



(IXb)

The ^{1}H NMR spectrum of IX is quite complicated; Table 2 lists the proton resonances and tentative assignments. However the presence of the two singlets at δ 1.88 ppm and at δ 1.91 ppm attributable to the acetylacetonate group rules out the structure IXa (in which the two methyls would be equivalent).

Moreover the magnitude of the separation between the two singlets (0.03 ppm) favours structure IXb. A larger difference (0.15 ppm) has been noticed in the ^{1}H NMR spectrum of the following rhodium compound, whose structure was confirmed by X-ray analysis [6,7].



This tentative assignment was confirmed by X-ray diffraction study of single crystals of IX (see below). Finally, assuming that no rearrangement occurs in the reaction of VI with pyridine, we tend to regard as correct the suggested structure of VI; the thermal instability of VI can be associated with ready loss of the coordinated allene molecules and formation of coordinatively unsaturated complexes.

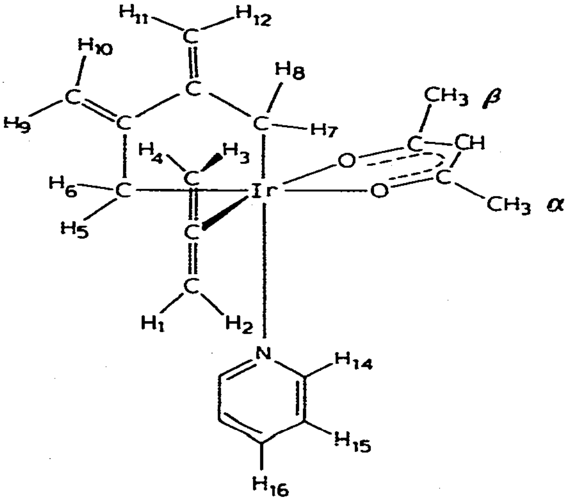
VI and IX appear to be the first examples of compounds in which an allene molecule is η^2-bonded to a transition metal which is also σ-bonded to two carbon atoms.

X-ray results

The molecular structures of IIb and IX are given in the computer drawings of Fig. 1 (for labeling see the schematic inserts) and the results of the X-ray analysis for both complexes are summarized in Tables 3 (atomic fractional coordinates) and 4 (anisotropic thermal vibration parameters). The most significant

TABLE 2

^{1}H NMR DATA FOR COMPOUND IX [a]



Protons	Chemical shifts
14	8.3 m
16	7.6 m
15	7.3 m
13	5.14 s
1 or 2	5.4 m
2 or 1	4.84 m
3 or 4	3.66 m
4 or 3	2.82 m
5,6,7,8	2.06—2.66
9,10,11,12	4.4—5.0
methyl α or β	1.91 s
methyl β or α	1.88 s

[a] Measured in $CDCl_3$, at 37°C. Chemical shifts (δ values) refer to TMS as internal standard; s, singlet, m, multiplet.

bond distances and angles are listed in Tables 5 and 6.

In complex IIb the tetrameric allene ligand V is present with the structure and mode of bonding already observed in (dbm)$RhC_{12}H_{16}$ [7,29] and (acac)-$RhC_{12}H_{16}$ [32].

In the crystal the C_2 molecular symmetry of IIb is retained, and the coordination polyhedron around the iridium atom can be described as a very distorted octahedron if the η^3-allylic groups are regarded as bidentate ligands.

The *b* and *b'* Ir—C bond axes deviate by about 21° from the axial direction and form an angle of 168.7°.

From Table 5 it can be easily verified that the two equivalent η^3-allylic groups are asymmetrically bonded to iridium, as previously observed for some bis-(η^3-allylic) complexes of rhodium(III) with C_2 symmetry [7,29—31].

C(4) and C(4'), which are *trans* to each other, show a longer Ir—C distance

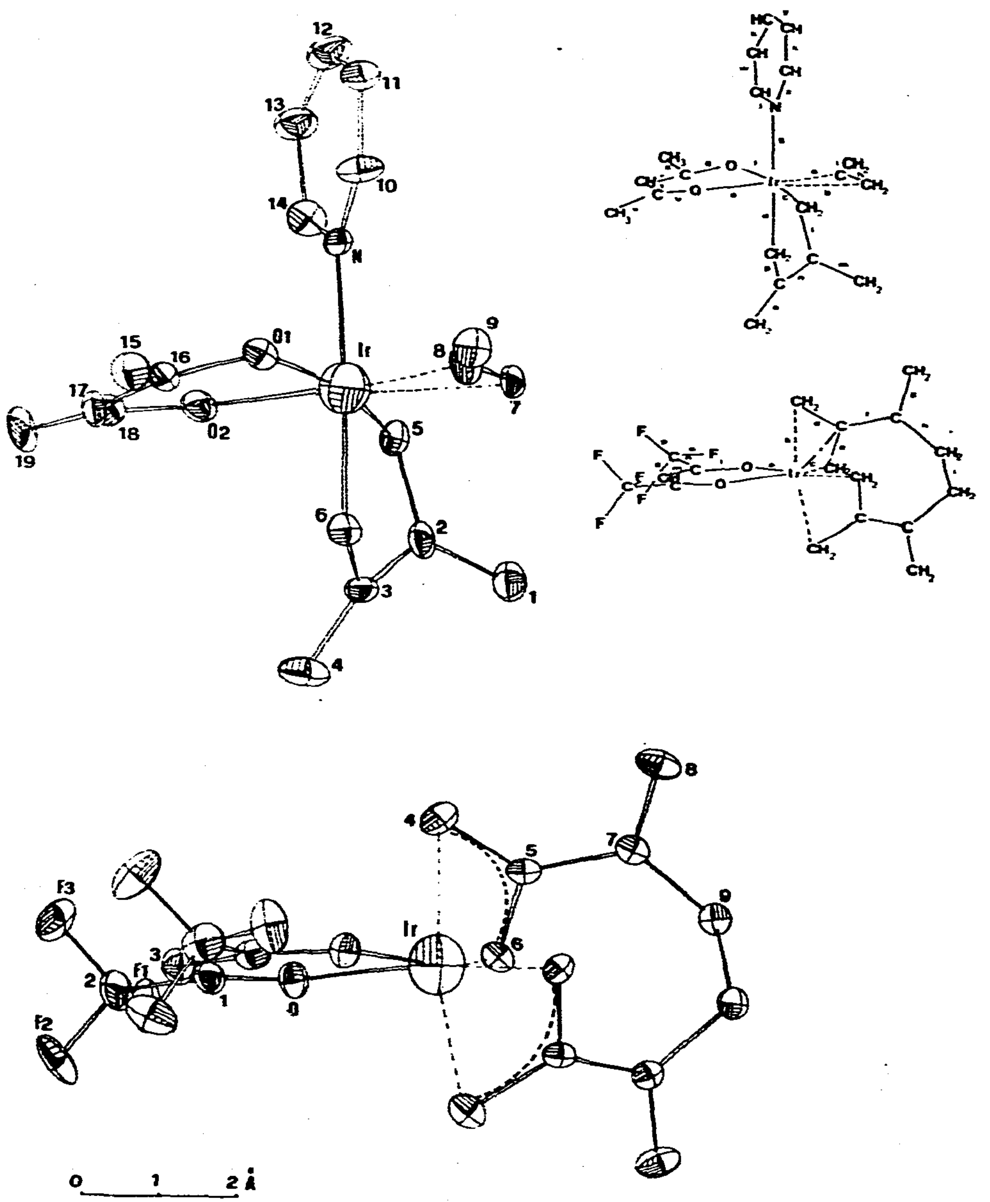


Fig. 1. Computer drawings of the molecular structures of IIb (bottom) and IX (top). Corresponding schematic inserts for labeling are given at the top-right.

(2.21 Å), while *C*(6) and *C*(6′) which are *trans* to oxygen atoms are at a shorter distance (2.11 Å) from iridium. The lengths of the three bonds f, h and i viz., 1.47, 1.51 and 1.54 Å, respectively, increase in the expected order [though the standard deviations are fairly large (0.02 Å)] in terms of the hybridization states

TABLE 3

ATOMIC FRACTIONAL COORDINATES (X 10^4) AND ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*
Complex IIb			
Ir	5000(0)	3413(3)	2500(0)
F(1)	1411(11)	4834(6)	1481(22)
F(2)	2388(16)	5521(7)	2856(21)
F(3)	2598(14)	5479(7)	549(18)
O	3524(8)	4142(4)	2056(10)
C(1)	3753(13)	4689(6)	2108(15)
C(2)	2493(18)	5128(8)	1719(20)
C(3)	5000(0)	5016(10)	2500(0)
C(4)	4884(13)	3312(7)	−76(16)
C(5)	4422(10)	2760(6)	630(12)
C(6)	3335(9)	2845(5)	1606(13)
C(7)	5076(10)	2145(6)	588(13)
C(8)	5900(13)	2031(8)	−520(16)
C(9)	4688(11)	1622(6)	1629(14)
Complex IX			
Ir	−1377(1)	1410(1)	1786(1)
O(1)	−2841(18)	1198(9)	3123(16)
O(2)	−679(19)	354(10)	2121(18)
N	−2996(22)	1011(10)	359(20)
C(1)	2530(33)	2287(18)	865(36)
C(2)	1657(32)	1775(14)	1353(28)
C(3)	1683(30)	1698(16)	2738(24)
C(4)	2927(30)	1413(21)	3453(30)
C(5)	354(27)	1414(14)	674(22)
C(6)	207(26)	1745(13)	3174(25)
C(7)	−1479(30)	2476(13)	919(25)
C(8)	−2448(32)	2414(16)	1841(30)
C(9)	−3380(35)	2698(17)	2541(30)
C(10)	−4330(29)	1177(18)	160(27)
C(11)	−5344(31)	950(17)	−771(29)
C(12)	−4938(40)	462(20)	−1584(30)
C(13)	−3489(36)	184(18)	−1465(29)
C(14)	−2567(32)	509(16)	−505(26)
C(15)	−3613(33)	765(19)	5032(24)
C(16)	−2692(27)	680(15)	3951(24)
C(17)	−1770(32)	105(14)	3948(26)
C(18)	−979(32)	−80(15)	3003(27)
C(19)	−229(40)	−777(15)	3011(33)

of carbon atoms C(5), C(7), C(9), and C(9′), i.e. sp^2, sp^2, sp^3, and sp^3, respectively.

The conformation of the hydrocarbon ligand is very close to that in a similar rhodium complex [29], with values of 20°, 168°, 168° and 4°, for the torsion angles dfg, dfh, efg and efh, respectively.

The geometry of IX is approximately octahedral, with the allene dimer and the acetylacetonate group acting as a chelating ligand and having a pseudo-*fac* configuration relative to each other. Pyridine and one of the double bonds of the allene molecule complete the coordination around the iridium atom, occupying the two remaining mutually *cis* positions.

TABLE 4

ANISOTROPIC THERMAL PARAMETERS (× 10^2 FOR Ir AND × 10 FOR THE LIGHTER ATOMS)

Thermal function is $T = \exp - (U_{11}h^2a^{*2} + U_{22}k^2b^2 + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)/4$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Complex IIb						
Ir	223(2)	334(2)	387(3)	0(0)	−106(4)	0(0)
F(1)	43(5)	74(7)	229(15)	51(9)	−2(14)	44(17)
F(2)	114(10)	126(11)	160(13)	166(17)	−48(18)	−125(19)
F(3)	94(8)	132(11)	133(11)	120(15)	24(15)	152(18)
O	35(3)	32(3)	46(4)	8(6)	−10(6)	−3(6)
C(1)	44(6)	41(6)	37(5)	28(9)	9(9)	2(9)
C(2)	66(9)	52(8)	58(8)	64(14)	9(13)	10(13)
C(3)	53(10)	36(8)	66(12)	0(0)	39(18)	0(0)
C(4)	34(5)	51(7)	40(5)	−9(9)	−6(8)	22(9)
C(5)	20(3)	44(5)	24(4)	−9(7)	−7(6)	−3(7)
C(6)	16(3)	37(5)	35(4)	−5(6)	−8(6)	−18(7)
C(7)	23(4)	40(5)	32(4)	−6(7)	−7(6)	−11(8)
C(8)	33(5)	74(9)	40(6)	8(11)	7(9)	−27(12)
C(9)	31(4)	37(5)	40(5)	−10(8)	−0(7)	−5(9)
Complex IX						
Ir	308(3)	237(3)	320(3)	33(9)	46(5)	−20(9)
O(1)	38(8)	39(8)	38(8)	20(12)	12(12)	−11(12)
O(2)	39(8)	40(9)	54(10)	21(14)	−4(15)	−3(15)
N	35(10)	17(8)	51(11)	11(13)	−8(16)	−12(15)
C(1)	41(14)	51(17)	95(23)	7(24)	24(29)	48(32)
C(2)	50(14)	29(11)	60(16)	23(21)	15(24)	26(22)
C(3)	43(13)	55(15)	36(12)	−37(23)	−16(20)	23(22)
C(4)	37(13)	76(19)	67(17)	26(30)	−24(23)	−48(35)
C(5)	47(11)	20(8)	44(11)	10(20)	26(18)	−15(20)
C(6)	32(11)	29(10)	50(13)	31(17)	7(19)	−19(20)
C(7)	52(14)	18(9)	45(13)	5(19)	−8(21)	6(18)
C(8)	54(15)	39(13)	62(17)	29(23)	50(26)	15(24)
C(9)	59(16)	47(15)	55(16)	14(25)	39(27)	−9(25)
C(10)	31(12)	75(19)	49(14)	−21(23)	6(21)	−32(26)
C(11)	36(13)	58(17)	59(16)	−11(23)	1(23)	5(27)
C(12)	78(20)	70(20)	44(15)	−65(33)	−6(28)	−27(28)
C(13)	59(18)	61(17)	51(17)	−22(29)	−10(28)	−24(26)
C(14)	53(15)	47(14)	42(13)	21(23)	22(22)	−23(22)
C(15)	59(16)	75(19)	29(12)	−29(29)	40(22)	24(25)
C(16)	53(11)	40(12)	40(12)	−6(19)	−4(19)	20(20)
C(17)	59(15)	27(11)	45(13)	2(21)	1(23)	24(20)
C(18)	50(14)	41(13)	53(13)	−19(22)	−7(22)	7(22)
C(19)	90(22)	22(12)	85(21)	55(27)	−7(34)	20(27)

TABLE 5

BOND LENGTHS (Å). ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Complex IIb					
b	2.21(1)	d	1.43(2)	g	1.35(2)
r	2.15(1)	e	1.45(1)	h	1.51(2)
a	2.14(1)	f	1.47(2)	i	1.54(2)
c	2.11(1)				
Complex IX					
f	2.13(2)	b	2.19(3)	o	1.42(4)
e	2.08(2)	a	2.11(3)	p	1.50(4)
g	2.16(2)	m	1.39(4)	h	1.42(4)
c	2.11(2)	n	1.51(4)	i	1.32(4)
d	2.07(3)	l	1.50(4)		

TABLE 6

BOND ANGLES (°). ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Complex IIb					
rd	73.0(5)	br	38(1)	df	124.8(5)
bd	68.7(5)	bc	68.7(5)	fg	118.9(5)
ce	71.7(5)	rc	40(1)	fh	120.7(5)
re	68.6(5)	de	115.9(5)	gh	119.9(5)
fe	118.8(5)				
Complex IX					
cl	110(1)	fc	166(3)	gc	95.8(5)
dp	110(1)	fd	90.6(5)	gb	90.5(5)
ah	74(1)	fb	117.4(5)	ga	91.9(5)
bh	68(1)	fa	78.9(5)	cd	84.0(5)
ai	135(2)	eg	88.8(5)	cb	75.5(5)
gz	128(2)	ec	82.1(5)	ca	113.7(5)
gi	119(1)	ed	88.6(5)	db	92.0(5)
fe	85.2(5)	eb	157(2)	da	90.6(5)
fg	89.0(5)	ea	164(3)	ba	39(2)

The fact that the pyridine ligand is *trans* to C(6) is evidence for the structure attributed to VI. In the latter compound, substitution of pyridine for allene should be easier for the ligand *trans* to C(6) than for that *trans* to O(2). In this respect it is noteworthy that in the similar rhodium complex (acac)Rh(C_3H_4)$_2$py$_2$ [33], in which these mutually *cis* positions are both occupied by pyridine molecules, the two Rh—N distances are significantly different, the longer distance being that *trans* to a σ-bonded C atom of the allene dimer ligand.

In IX the monomeric allene ligand has a non-linear skeleton geometry, with C_s symmetry for the C_3H_4Ir group. Recently [34] it was proposed that the geometry and the charge distribution of the allene ligand of C_s symmetry are virtually identical with those in the isolated molecule in the first excited triplet state. Since the deviation from linearity of this ligand and the corresponding charge transfer are an obvious consequence of an electron back-donation from the metal, these considerations are relevant also to recent attempts [35,36] to correlate the structural details of the allene ligand with the stability of the corresponding complexes and with their catalytic activity.

From this point of view it is also noteworthy that the small but significant difference between the angles ah (74°) and bh (68°) is indicative of the coordination asymmetry of the allene ligand and makes more significant the difference between the values of 2.11(3) Å and 2.19(3) Å for the distances a and b.

Two complexes containing the 3,4-dimethylenerhodacyclopentane moiety have already been reported [7,33].

The allene dimer, which in the complexes of the cited references shows the ability to coordinate both as a chelate σ,σ'-bonded ligand and as a μ-bonded diene, has a conformation which depends on the particular coordination geometry and molecular packing. In the case of IX the torsion angles lnp and mno are 37.5° and 69.8°, respectively, while the corresponding torsion angles in the similar rhodium complex [33] are 39.85° and 47.57°.

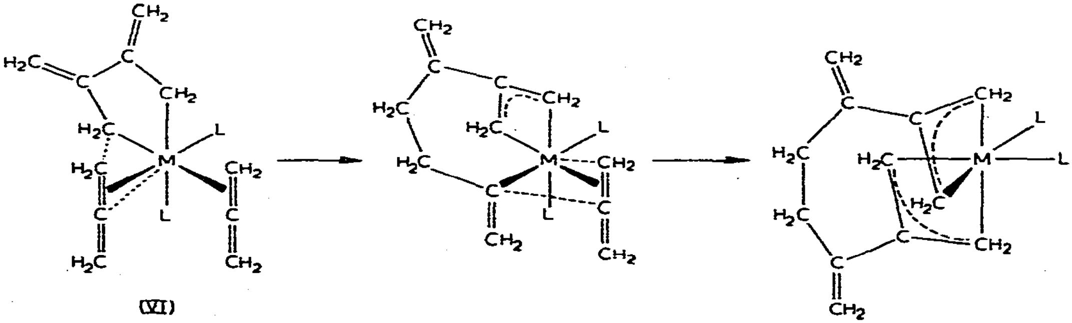
How do the bis(η^3-allylic) complexes II form

As noted in the Introduction, the intermediacy of the compounds containing the 3,4-dimethylenerhodacyclopentane moiety (A) in the formation of the rhodium(III) bis(allylic) complexes (B) has been firmly established [7]. On the basis of our results, which show the substantial similarity between β-diketonato derivatives of iridium(I) and rhodium(I) as far as their reactivities with allene are concerned, we are inclined to regard the iridocyclic compounds of the type VI as the precursors of the bis(allylic) complexes II.

A critical point remians to be clarified, namely what is the mechanism of formation of rhodium(III) and iridium(III) bis(allylic) compounds from an intermediate species containing the 3,4-dimethylenemetallocyclopentane moiety?

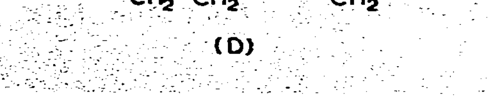
A plausible two-step mechanism is outlined in Scheme 3. The first step is an alkyl migration to the CH_2 of a coordinated allene molecule to form a new metal—carbon σ-bond, which in its turn migrates to the central carbon atom of the second coordinated allene molecule. The occurence of the first step can be explained as a consequence of the structural features of VI, which can be inferred from the known structure of IX. In this compound in fact a very short non-bonding distance (2.61 Å) between C(5) of the allene dimer and C(7) of the monomeric ligand is observed (Fig. 1), while all the other C ··· C non-bonding distances between the two hydrocarbon ligands are normal, being larger than 3.10 Å. This feature, if also present in VI, should determine the alkyl migration to a CH_2 of the coordinated allene.

SCHEME 3



It is interesting to note that this process is different from that which probably occurs in the formation of some iron [37] and nickel [40] complexes containing an allene trimer of structure D. Assuming that in this case also a dimethylenemetallocyclopentane intermediate is involved, the above trimer must form through an alkyl migration to the central carbon atom of a coordinated allene molecule.

The second step of Scheme 3 obviously requires that allene inserts into a metal—carbon σ-bond in different way from that involved in the first step. It is



$$-CH_2-\underset{\underset{CH_2}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2-$$

(D)

not easy to explain this difference; examination of the products which would be formed by all the possible insertion reactions of allene into each of the two reactive metal—carbon bonds present in the trimer intermediate (Scheme 3), shows that the only route to bis(η^3-allylic) compounds is that depicted above. It may be that this is essentially a thermodynamically controlled process, i.e., the bis(η^3-allylic) complexes are more stable than all the other possible products.

Experimental

Allene (Matheson, purity ca. 98.7%), hexafluoroacetylacetone and dibenzoylmethane (Fluka), Tl(acac) (Alfa Products) were used without further purification. $(NH_4)_2IrCl_6$ [1], $[ClIr(\eta\text{-}C_8H_{14})_2]_2$ [2] and Tl(hfacac) [7] were prepared as described in the references cited. Na(dbm) was prepared by treating dibenzoylmethane with $NaOC_2H_5$ in absolute ethanol. Solvents were used after dehydration and distillation. All operations were carried out under dry dinitrogen.

^{1}H NMR spectra were obtained with a Varian T 60 spectrometer, IR spectra with a 225 Perkin—Elmer instrument. Melting or decomposition points were determined with a Kofler hot-stage apparatus and are uncorrected. GLC analyses were carried out with a Carlo Erba Fractovap Mod. GT with a 2 m, 20% SE-30 on 68-80 Chromosorb W column. Molecular weights were determined at 37°C by a Mechrolab vapor-pressure Osmometer Mod. 3019.

Microanalyses were performed by the Laboratorio di Microanalisi of Istituto di Chimica Organica (Facoltà di Farmacia, Università di Pisa).

Preparation of (acac)Ir(η-C_8H_{14})$_2$ (Ia)

Tl(acac) (850 mg) was added at room temperature to a suspension of $[ClIr(\eta\text{-}C_8H_{14})_2]_2$ (1.18 g) in pentane (100 ml). The suspension was stirred for 3 h and then filtered. The resulting yellow solution was concentrated to 10 ml and then kept at —30°C to give in ca. 24 h (acac)Ir(η-C_8H_{14})$_2$ (977 mg, yield 86%), as orange-yellow crystals, m.p. 114—115°C. (Found: C, 49.56; H, 7.08. Mol.wt., 502 (benzene). $C_{21}H_{35}O_2Ir$ calcd.: C, 49.2; H, 6.88%. Mol.wt., 512.6.) ^{1}H NMR ($CDCl_3$) (δ from TMS): 5.43(s, 1H); 1.92(s, 6H); 2.4—1.7(bm, 8H); 1.7—1.0(bm, 20H) ppm. IR (KBr): 2970s, 2910s, 2890s, 2830s, 1570s, 1540m, 1510s, 1460s, 1440m, 1410w, 1370m, 1340w, 1310w, 1270w, 1185w, 1140w, 1015s, 970w, 930w, 910w cm^{-1}.

Preparation of (hfacac)Ir(η-C_8H_{14})$_2$ (Ib)

Tl(hfacac) (600 mg) was added at room temperature to a suspension of $[ClIr(\eta\text{-}C_8H_{14})_2]_2$ (920 mg) in pentane (100 ml). The suspension was stirred for 3 h and then filtered. The resulting red solution was concentrated to 10 ml and then kept at —30°C to give in about 24 h (hfacac)Ir(η-C_8H_{14})$_2$ (786.5 mg, yield 70%) as red crystals, m.p. 96—97°C. (Found: C, 41.53; H, 4.58. Mol.wt., 604 (benzene). $C_{24}H_{29}F_6O_2Ir$ calcd.: C, 40.70; H, 4.68%. Mol.wt., 620.5.) ^{1}H NMR ($CDCl_3$) (δ from TMS): 6.26(s, 1H); 2.8—2.4(bm, 4H); 2.3—1.8(bm, 8H); 1.7—1.3(bm, 16H) ppm. IR (KBr): 2960m, 2910s, 2840s, 2660w, 1620m, 1580s, 1540s, 1500w, 1440s, 1340s, 1310w, 1250s, 1210w, 1140s, 1040w, 1015w, 970w, 950m, 945w, 910s, 895w, 875w, 860w, 850w, 810m, 795s, 740m, 680s, 630m, 590s, 570m, 545s, 435m cm^{-1}.

Preparation of (dbm)Ir(η-C_8H_{14})$_2$ (Ic)

Na(dbm) (234 mg) and [ClIr(η-C_8H_{14})$_2$]$_2$ (425 mg) were suspended in dry Et_2O (100 ml). The suspension was stirred for 3 h at room temperature and then filtered. The resulting deep red solution was evaporated in vacuo to give a red-orange microcrystalline solid which was washed with acetone and dried under vacuum. 630 mg of Ic (75% yield) were obtained, m.p. 193°C (dec.). (Found: C, 56.72; H, 6.52. Mol.wt., 635 (benzene). $C_{41}H_{39}O_2Ir$ calcd.: C, 57.49; H, 6.17%. Mol.wt., 636.6.) ^{1}H NMR ($CDCl_3$) (δ from TMS): 8.0—7.3(bm, 10H); 6.7(s, 1H); 2.5—1.9(bm, 12H); 1.9—1.2(bm, 16 H) ppm. IR (KBr): 2970w, 2950w, 2910s, 2895s, 2840m, 1590m, 1530m, 1470m, 1440m, 1370m, 1350w, 1315w, 1250w, 1270w, 1225s, 1175m, 1150w, 1140w, 1120w, 1065m, 1060m, 1020m, 995w, 910m, 830w, 804m, 770s, 760s, 725w, 720s, 690s, 685s, 645s, 570m, 550m, 535m, 455m cm^{-1}.

Reaction of (hfacac)Ir(η-C_8H_{14})$_2$ (Ib) with allene: formation of (hfacac)Ir-($C_{12}H_{16}$) (IIb)

Allene was bubbled at room temperature for 5 min through a solution of Ib (372 mg) in pentane (15 ml). The colour changed quickly from deep to bright red. The solution was filtered, concentrated up 3 ml and kept at —30°C to give IIb (206 mg, 65% yield) as red-orange crystals, which were further purified by sublimation (75°C/0.2 mmHg). M.p. 118—119°C. (Found: C, 37.42; H, 3.14. Mol.wt., 568 (benzene). $C_{17}H_{17}F_6O_2Ir$ calcd.: C, 36.5; H, 3.04%. Mol.wt., 560.4.) IR (KBr): 3250w, 3090w, 3070m, 3060w, 2990m, 2950s, 1840s, 1810m, 1640s, 1570m, 1550s, 1510m, 1470s, 1420s, 1350s, 1265s, 1215s, 1155s, 1120s, 1000s, 955w, 945m, 915s, 905s, 885w, 865w, 850m, 820w, 805w, 780s, 760s, 750s, 735s, 695s, 685s, 595m, 550m, 530w, 515m, 490w, 455m, 440m cm^{-1}.

Hydrogenolysis of (hfacac)Ir$C_{12}H_{16}$ (IIb)

A well stirred solution of IIb (40 mg) in pentane (30 ml), containing PtO_2 (10 mg) as catalyst, was kept under hydrogen atmosphere, at room temperature. After 144 h, the colourless mixture was filtered and distilled on Na. Analytical GLC of the distillate indicated the presence of one predominant compound (97%), which was identified as 2,3,6,7-tetramethyloctane (III) by comparison with an authentic specimen prepared from 2,3-dimethylbut-1-ene by Brown and Snyder's method [16].

Reaction of (hfacac)Ir$C_{12}H_{16}$ (IIb) with CO

A solution of IIb (60 mg) in pentane (20 ml) was kept under CO atmosphere at room temperature for 10 h. The solution was then cooled to —78°C to give a greenish-brown precipitate, which on sublimation at 30—40°C/0.2 mmHg on to an ice-cooled probe gave a small quantity of green needles of (hfacac)Ir(CO)$_2$. The filtered solution was eluted on silica gel and the solvent distilled off. Analytical GLC of the residue indicated the presence of one component, which was identified as 1,2,5,6-tetramethylenecyclooctane (IV) by comparison of its ^{1}H NMR with that previously reported [5].

Reaction of (dbm)Ir(η-C_8H_{14})$_2$ (Ic) with allene: formation of (dbm)Ir$C_{12}H_{16}$ (IIc)

Ic (426 mg) was suspended in liquid allene (5 ml) at —78°C. The suspension was kept at this temperature for 30 min and then, after the addition of pentane (80 ml), was heated at room temperature and filtered. A yellow solution was obtained which was concentrated up to 50 ml and then kept at —30°C. During 20 days (dbm)Ir$C_{12}H_{16}$ (IIc) (92 mg, 24% yield) precipitated as orange-yellow crystals, m.p. 191—193°C (dec.). (Found: C, 56.25; H, 4.86. Mol.wt., 594 (benzene). $C_{27}H_{27}O_2Ir$ calcd.: C, 56.25; H, 4.72%. Mol.wt., 576.5.) IR (KBr): 3040w, 2970w, 2910w, 1680w, 1650m, 1600w, 1580s, 1530s, 1500s, 1470s, 1380s, 1300s, 1255m, 1225s, 1180m, 1155w, 1090w, 1060m, 1020m, 995w, 940w, 910s, 895s, 845w, 785w, 745w, 730m, 705s, 680s, 640m, 585w, 535m, 505w cm^{-1}.

Hydrogenolysis of (dbm)Ir$C_{12}H_{16}$ (IIc)

This reaction was carried out as reported for the hydrogenolysis of IIb. Analytical GLC of the reaction mixture indicated the presence of 2,3,6,7-tetramethyloctane (III) as the major component (95%).

Reaction of (dbm)Ir$C_{12}H_{16}$ (IIc) with CO

A solution of IIc (50 mg) in benzene (15 ml) was kept under CO atmosphere at room temperature for 22 h. After evaporation of the solvent a solid red residue was obtained, and this was washed twice with pentane (2 ml) at —78°C then dried. Analytical GLC of the pentane extracts of the residue indicated the presence of one component, which was identified as 1,2,5,6-tetramethylenecyclooctane (IV) by comparison of its ^1H NMR spectrum with that previously reported [17]. On sublimation of the above solid residue at 130°C/0.1 mmHg, orange crystals of (Dbm)Ir$(CO)_2$ [18] were obtained. The yield was almost quantitative.

Reaction of (acac)Ir(η-C_8H_{14})$_2$ (Ia) with allene: formation of [(acac)Ir(C_3H_4)$_x$]$_n$ (VI)

(acac)Ir(η-C_8H_{14})$_2$ (Ia) (246.2 mg) was suspended in liquid allene (5 ml) at —78°C. The mixture was kept at this temperature for 30 min, then pentane (10 ml) precooled at —78°C was added. This caused the precipitation of a microcrystalline pale-yellow solid, which was separated from the mother liquor, washed twice with pentane (10 ml) precooled at —78°C and then dried at —50°C by evaporation of solvent under high vacuum. The product was stored at —30°C, since it decomposes above —20°C. IR (Nujol mull, —60°C): 1717s, 1695s, 1650s, 1613m, 1580s, 1515s, 1505s, 1285m, 1270m, 1230w, 1167w, 1146m, 1062s, 1040w 1018w, 930s, 866vs, 765m, 750m, 728s, 720m, 673w, 630m, 587m, 526m, 448m, 425s, 415 cm^{-1}.

Reaction of [(acac)Ir(C_3H_4)$_x$]$_n$ (VI) with bromine

To a suspension of VI (200 mg) in CCl_4 (50 ml) at —78°C, bromine (2 ml) was added. The temperature was slowly raised to 20°C and the mixture was stirred for 90 min at this temperature. The mixture was washed with water, then with a dilute solution of $Na_2S_2O_3$, and again with water. The organic layer was dried over molecular sieves and concentrated to 3 ml by carefull distillation of CCl_4. The ^1H NMR spectrum of the crude residue showed two singlets, at δ 4.30 and at δ 4.18 ppm (from TMS) (areas ratio, 1 : 1), which were respectively attributed to 1,2,2,3-tetrabromopropane (VII) and tetrabromomethylethylene (VIII) by comparison with the ^{1}H NMR spectra of authentic samples [19,20].

Reaction of $[(acac)Ir(C_3H_4)_x]_n$ *(VI) with pyridine: formation of* $(acac)Ir(C_6H_8)(C_3H_4)py$ *(IX)*

To a suspension of VI (300 mg) in heptane (50 ml) at −78°C, pyridine (0.2 ml) was added. The temperature was slowly raised to 30°C and the mixture was kept at this temperature for 2 h. Evolution of allene was observed. A greenish-yellow solution was obtained which was concentrated up to 25 ml, filtered and cooled at −30°C. During 24 h IX (40% yield) precipitated as yellow crystals, m.p. 118—119°C (dec.). (Found: C, 47.83; H, 5.01; N, 2.97. Mol.wt., 476 (benzene). $C_{19}H_{24}NO_2Ir$ calcd.: C, 46.43; H, 4.88; N, 2.85%. Mol.wt., 491.47.) IR (KBr): 3060m, 2990w, 2960, 2925m, 2885m, 2850w, 1770s, 1700w, 1615s, 1602s, 1585s, 1520s, 1480m, 1450s, 1425w, 1405w, 1381s, 1375s, 1355s, 1287w, 1270s, 1237w, 1218s, 1198m, 1145w, 1135m, 1075s, 1068s, 1042m, 1020m, 1012m, 938w, 887s, 870s, 853s, 815m, 770s, 757s, 720m, 695s, 673w, 657w, 648w, 640w, 631w, 582s, 550w, 533w, 512w, 490w, 458m, 440m, 432m, 385w, 345w, 310w cm^{-1}.

Reaction of $(acac)Ir(C_6H_8)(C_3H_4)py$ *(IX) with bromine*

To a suspension of IX (150 mg) in CCl_4 (30 ml) at −78°C, bromine (1 ml) was added. The temperature was then raised to 20°C and the mixture was stirred for 90 min at this temperature. The mixture was washed with water, with a diluted solution of $Na_2S_2O_3$, and again with water. The organic layer was dried over molecular sieves and concentrated to 2 ml by carefull distillation of CCl_4. The crude residue was examined by ^{1}H NMR, which showed two singlets at δ 4.30 ppm and at δ 4.18 ppm (from TMS) (areas ratio, 1 : 2) which were respectively attributed to 1,2,2,3-tetrabromopropane (VII) and tetrabromomethylethylene (VIII) by comparison with ^{1}H NMR spectra of authentic samples [19,20].

Polymerization of allene

All the polymerization runs were carried out in a stirred stainless steel autoclave (150 ml) using an allene/catalyst (compounds I and II) molar ratio, 500 : 1, in benzene (10 ml), at 70°C. The polymer, which was insoluble in cold benzene, was separated and washed with benzene, then with methanol, and dried. IR and ^{1}H NMR spectra of polymer samples were identical to those reported [21—28] for a polyallene of high regular constitution, $\left[\!-CH_2C(=CH_2)-\!\right]_n$. X-ray powder spectra revealed ca. 75% crystallinity.

X-ray diffraction experiments

Crystals suitable for diffraction measurements were obtained by low-temperature crystallization of complexes IIb and IX from pentane.

X-ray diffraction intensities were measured with a Philips PW-1100 single crystal diffractometer, using a graphite monochromator and Mo-K_α radiation. Unit cells and crystal symmetries were determined using the standard control program of the PW-1100 system [38] with randomly oriented crystals. For accurate lattice parameter determination the Bragg positions of 71 (complex

IX) and 18 (complex IIb) strong reflections with $10° < \theta < 20°$ (λ 0.71069 Å) were measured and for maximum precision the angular positions were evaluated as centers of gravity of the diffraction profiles $I = f(\theta)$, averaging over positive and negative θ values. A least-squares refinement, minimizing $\Sigma(\sin\theta_{obs} - \sin\theta_{calcd})^2$ for the above reflections, with the constraint $\alpha = \gamma = 90°$, gave the below-listed parameters.

Crystal data: complex IX, $C_{19}H_{24}O_2NIr$; mol.wt., 490.60; a 9.248(1), b 18.547(5), c 10.853(1) Å; β 96.53(1)°, D_c 1.761 g cm^{-3}, Z 4, $F(000)$ 952, space group $P2_1/c$, μ 76.63 cm^{-1}; complex IIb, $C_{17}H_{17}O_2F_6Ir$, mol.wt., 559.51; a 9.850(2), b 21.452(8), c 8.583(2) Å, β 96.91(1)°, D_c 2.063 g cm^{-3}, Z 4, $F(000)$ 1064, space group $C2/c$, μ 79.24 cm^{-1}.

For the two complexes the working conditions are shown in Table 7.

Structure determination and refinement

After correction for the Lorentz and polarization effects, (no absorption correction applied), the atomic positions were determined by the heavy-atom method and refined by the least-squares method, minimizing $\Sigma w(F_o - F_c)^2$ with unitary weight factors, and using anisotropic thermal vibration parameters. For complex IX the 9 × 9 block-diagonal approximation was used, while for complex IIb a full-matrix refinement was carried out. The atomic scattering factors given in [39] were used with a constant correction of -2.06 e for the iridium atom in order to account for the anomalous scattering. (No imaginary part was included in the correction in view of the presence of centers of symmetry in both cases.) In the last refinement cycle the positional and thermal shifts were all less than 0.1σ in the case of IX and 0.5σ in the case of IIb.

In the difference electron-density maps, calculated at the end of the refinement, several residuals of 1.5—2.5 e Å^{-3} (for IX) and of 1.5—4.3 e Å^{-3} (for IIb) were found at a distance of 0.8—0.9 Å from the metal which were attributed to series truncation effects. Scattered residuals of lower weight (less than 1.1 e Å^{-3}) were also observed, but no easy interpretation in terms of hydrogen atoms was found for them and no further attempt was made to analyze these maps.

TABLE 7

WORKING CONDITIONS FOR THE COMPLEXES IX AND IIb

	IX	IIb
Scan method	$\omega - 2\theta$	$\omega - 2\theta$
Scan speed	2.4 deg/min	1.8 deg/min
Scan width	1.0°	1.3°
Background time (half-peak time)	2 × 12.5 sec	2 × 21.6 sec
θ range (d_{min})	3—26° (0.81)	3—30° (0.71)
Reciprocal space explored	$k,l \geqslant 0$	$k,l \geqslant 0$
Measured reflections	4403	2570
'Observed' reflections (I 2.5σ, σ^2 = peak-counts + total background-counts)	2263	2223
Approximate crystal size	0.2 × 0.2 × 0.1 mm	0.1 × 0.12 × 0.04 mm

Acknowledgements

We acknowledge financial support by the "Consiglio Nazionale delle Ricerche". We are also grateful to Mr. A. Girola for measurement of many ^{1}H NMR spectra, and to Mr. G. Vergamini for assistance in obtaining the IR spectra. We also thank Mr. P. Zambelli for technical help in measuring the X-ray intensities and performing the crystallographic calculations.

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