

Preliminary communication

SYNTHESIS OF HOMOLEPTIC TRIS(ORGANO-CHELATE)IRIDIUM(III) COMPLEXES BY SPONTANEOUS *ortho*-METALLATION OF ELECTRON-RICH OLEFIN-DERIVED *N,N'*-DIARYLCARBENE LIGANDS AND THE X-RAY STRUCTURES OF *fac*-[Ir{CN(C₆H₄Me-*p*)(CH₂)₂NC₆H₃Me-*p*}]₃] AND *mer*-[Ir{CN(C₆H₄Me-*p*)(CH₂)₂NC₆H₃Me-*p*}]₂{CN(C₆H₄Me-*p*)(CH₂)₂NC₆H₄Me-*p*}]Cl (A PRODUCT OF HCl CLEAVAGE)*

PETER B. HITCHCOCK, MICHAEL F. LAPPERT and PILAR TERREROS

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ
 (Great Britain)

(Received August 27th, 1982)

Summary

Treatment of [Ir(COD)(μ-Cl)]₂ with excess of the electron-rich olefin [CN(Ar)(CH₂)₂NAr]₂ (abbreviated as (L^{Ar})₂, Ar = C₆H₄Me-*p* or C₆H₄OMe-*p*) affords the *ortho*-metallated tricycle [Ir(L^{Ar})₃], which for Ar = C₆H₄Me-*p* (Ia) with HCl yields [Ir(L^{Ar})₂(L^{Ar})]Cl (IV); X-ray data show that in IV there is an unexpectedly close Ir...C(*o*-aryl) contact (2;52(1) Å) involving the "free" L^{Ar}, which compares with an Ir—C(*o*-aryl) distance of 2.09(3) Å in Ia or 2.07(3) Å in the *ortho*-metallated L^{Ar} ligand of complex IV.

We report the synthesis from an iridium(I) precursor of two homoleptic organoiridium(III) tricycles [Ir(X)₃] (I) and the X-ray characterisation of one of them (Ia, Fig. 1). Each of the bidentate ligands X⁻ (II) has two *sp*² carbon donor sites, one of which is formally an arylcarbanion and the other a neutral carbene, i.e., X⁻ is a mono-*ortho*-metallated bis(arylamino)carbene ligand. This is the first example of a neutral noble metal σ-complex in which each of the ligating atoms within the metal inner coordination sphere is carbon.

Surprisingly, this Ir^I → Ir^{III} transformation (see reaction i in Scheme 1) is effected by means of the electron-rich olefin III (abbreviated as (L^{Ar})₂ whence the complexes I may be written as [Ir(L^{Ar})₃]), normally an exceptionally powerful reducing agent. We further show that reaction of complex Ia with anhydrous HCl (reaction ii in Scheme 1) causes ring-scission of one of the Ir—C_{Aryl} bonds to afford the salt [Ir(L^{Ar})₂(L^{Ar})]⁺Cl⁻ (IV), the structure of which is established

*No reprints available.

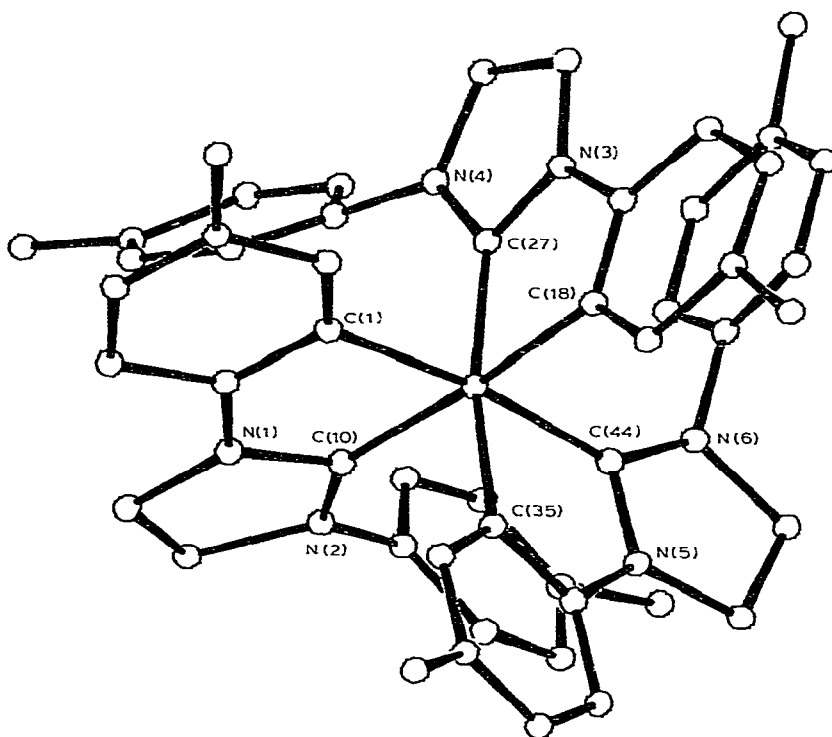
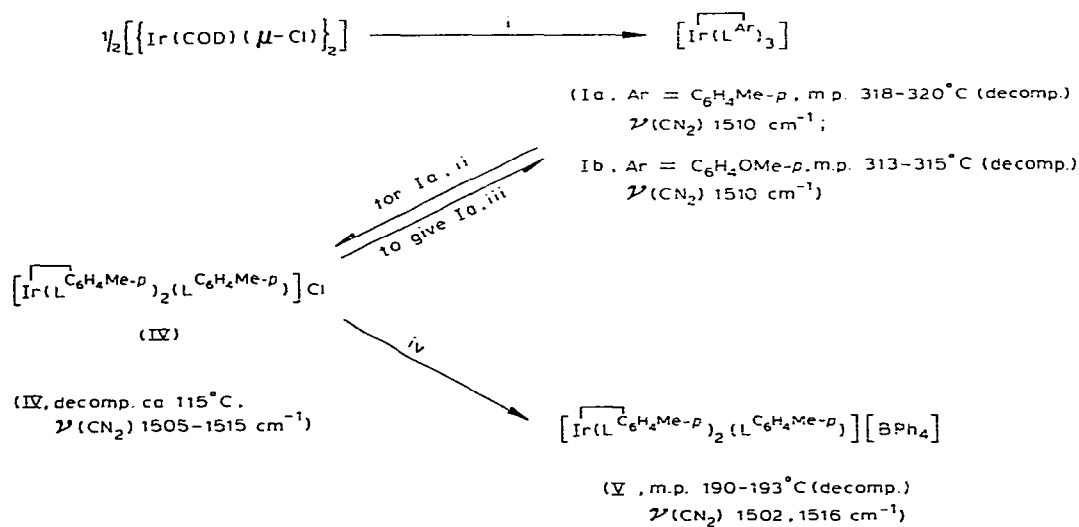


Fig. 1. The molecular structure of *fac*-[Ir{CN(C₆H₄Me-*p*)(CH₂)₂NC₆H₃Me-*p*}₃] (Ia).



SCHEME 1. Reagents and conditions (COD = cycloocta-1,5-diene): i, (L^{Ar})₂ (= III), PhMe, 120°C, 3 h, and successive filtration, addition of *n*-C₅H₁₂ to filtrate, and recrystallisation of I (CH₂Cl₂/OEt₂); ii, HCl gas into C₆H₆/OEt₂ solution of Ia, 20°C, ½ h, and successive filtration and recrystallisation of IV (CH₂Cl₂/PhMe); iii, NEt₃, C₆H₆, and successive precipitation with *n*-C₆H₁₄ and recrystallisation (CH₂Cl₂/OEt₂); iv, Na[BPh₄], EtOH, 2 h. Crystalline white Ia, Ib, or yellow IV and V yielded satisfactory microanalytical and ¹H and ¹³C NMR spectroscopic data.

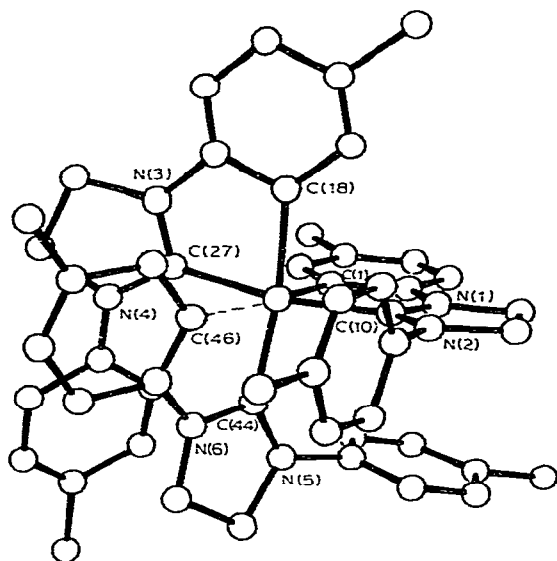
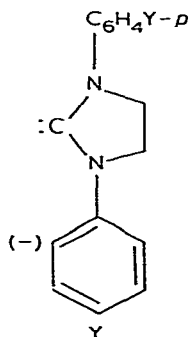
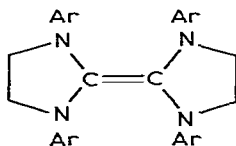


Fig. 2. The structure of the cation in $mer\text{-}[\text{Ir}\{\text{CN}(\text{C}_6\text{H}_4\text{Me-}p)(\text{CH}_2)_2\text{NC}_6\text{H}_4\text{Me-}p\}_2\{\text{CN}(\text{C}_6\text{H}_4\text{Me-}p)(\text{CH}_2)_2\text{N-C}_6\text{H}_4\text{Me-}p\}]\text{Cl}$ (IV). The lengths of the Ir—C “bonds” are: Ir—C(1) 2.02(1), Ir—C(10) 2.05(1), Ir—C(18) 2.08(2), Ir—C(27) 2.06(1), Ir—C(44) 2.02(1), Ir \cdots C(46) 2.52(1) Å.

by X-ray crystallography (Fig. 2, but see comments on structure). Dehydrochlorination of IV causes ring closure and reformation of the homoleptic complex Ia (reaction iii in Scheme 1). The chloride anion in IV is replaceable by $[\text{BPh}_4]^-$ to yield the salt V.

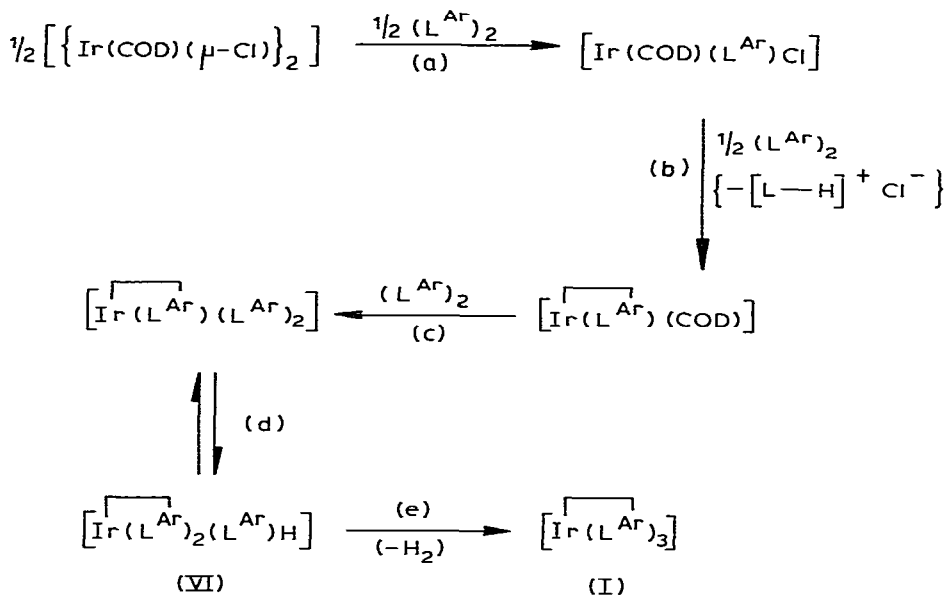


(IIa, Y = Me;
IIb, Y = OMe)



(III a, Ar = $\text{C}_6\text{H}_4\text{Me-}p$;
III b, Ar = $\text{C}_6\text{H}_4\text{OMe-}p$)

We suggest that the reaction sequence leading to the formation of complexes I is as shown in Scheme 2. Steps (a) and (c) are unexceptional [1]. Step (b), whereby the olefin III functions as a base, has precedent; cf. [2], the synthesis of $[\text{Ru}(\text{L}^{\text{Ar}})\text{Cl}(\text{PPh}_3)_2]$ from $[\text{RuCl}_2(\text{PPh}_3)_3]$ and III. The tautomerism of step (d) and subsequent dihydrogen elimination are believed to be caused by steric acceleration. The proposed intermediate VI is related to the cation of IV which, as shown by X-ray data (Fig. 2), is exceedingly crowded. The complexes $[\text{Ir}(\text{L}^{\text{Ar}})_3]$



SCHEME 2. Proposed reaction pathway to the tris(orthometallated-carbene)iridium(III) complexes (I).

may prove to be forerunners of a wider class of homoleptic compounds $[\overline{\text{M}}(\text{X}')_3]$, in which X' represents a bidentate *ortho*-metallated ligand; for example, $[\{\text{Ir}(\text{COD})\text{Cl}\}_2]$ may react with $\text{P}(\text{CH}_2\text{Ph})_3$ in the presence of a tertiary base to give $[\text{Ir}\{\text{P}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o)(\text{CH}_2\text{Ph})_2\}_3]$, cf. ref. 4.

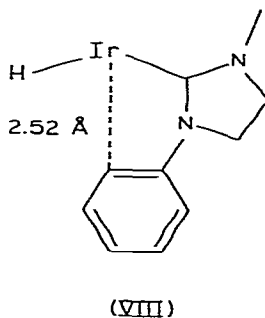
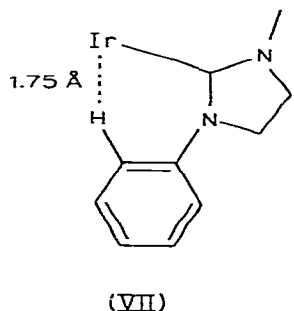
Crystal data: Ia, $\text{C}_{51}\text{H}_{51}\text{IrN}_6$, monoclinic, space group $P2_1/c$, $a = 23.227(9)$, $b = 19.846(3)$, $c = 18.313(7)$ Å, $\beta = 92.96(4)^\circ$, $Z = 8$. IV, $\text{C}_{51}\text{H}_{52}\text{ClIrN}_6$, triclinic, space group $P\bar{1}$, $a = 11.860(9)$, $b = 14.107(3)$, $c = 17.952(5)$ Å, $\alpha = 65.50(2)$, $\beta = 77.26(5)$, $\gamma = 70.51(4)^\circ$, $Z = 2$.

Diffraction data for both crystals were measured on an Enraf-Nonius CAD4 diffractometer. The structures were solved by routine heavy atom methods and refined by least squares using data with $I > \sigma(I)$. The final residuals were: for structure Ia, $R = 0.082$ for 5830 reflections, and for IV $R = 0.087$ for 3802 reflections.

In structure Ia both the two independent molecules have the *fac* arrangement, Fig. 1. The six carbene ligands have similar geometries with the following mean values and r.m.s. deviations; Ir—C(carbene) 2.03(3) Å, Ir—C(*o*-aryl) 2.09(3) Å.

In structure IV the chlorine atom has no apparent bonding contacts and is thus assumed to be Cl^- , indicating that the Ir complex has been protonated to form a cation. This cation has the *mer* configuration, Fig. 2. For two of the carbene ligands the Ir—C(carbene) and Ir—C(*o*-aryl) bonds are essentially the same as in Ia. However, the third carbene ligand shows an increase in the Ir—C(46) bond length to 2.52(1) Å. It was impossible to locate the hydrogen atoms from the X-ray data. If the extra H atom is actually bonded to C(46) as in VII then, assuming normal phenyl ring geometry with C—H 1.08 Å, the calculated Ir...H distance would be 1.75 Å, consistent with a two-electron, three-centre Ir...H...C interaction, as found for example in $(\eta^3\text{-cyclohexenyl})\text{tricarbonylmanganese(I)}$ [3]. An alternative hypothesis is that the protonation occurs

at the metal (VII), with an accompanying lengthening of one of the Ir—C(*o*-aryl) bonds. Against this are the following: (i) the observed Ir—C(46) distance of 2.52 Å corresponds to an extremely weakened bond which seems unlikely in the absence of any direct interaction with the added H⁺; (ii) structure VIII implies an Ir^{IV} *d*⁵ complex, but IV is diamagnetic; and (iii) there is no evidence for an Ir—H bond in IV either by IR or ¹H NMR spectroscopy.



Acknowledgment. We thank S.E.R.C. for support.

References

- 1 Cf., M.F. Lappert, *J. Organometal. Chem.*, **100** (1975) 139.
- 2 P.B. Hitchcock, M.F. Lappert, P.L. Pye, and S. Thomas, *J. Chem. Soc., Dalton Trans.*, (1979) 1929.
- 3 M.A. Brookhart, W. Lamanna, and M.B. Humphrey, *J. Am. Chem. Soc.*, **104** (1982) 2117; and refs. therein.
- 4 J.M. Duff and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1972) 2219.