New Iridium(I)–Ethylene Compounds

By A. VAN DER ENT* and T. C. VAN SOEST

(*Unilever Research Laboratory, Vlaardingen, The Netherlands*)

Summary A five-co-ordinated iridium(I)-ethylene compound, $IrCl(C_2H_4)_4$, has been isolated from a suspension of $[IrCl(C_8H_{14})_2]_2$ in heptane after treatment with ethylene.

THE occurrence of five-co-ordinated complexes of transition metals and their role as intermediates or transition states in many inorganic reactions, is now well established. N.m.r. investigations of pentaco-ordinated compounds, such as $Fe(CO)_5$,[1] PF_5,[2] RPF_4,[3] and AsF_5,[4] have shown that fast intramolecular exchange between axial and equatorial ligands is 'a quite common process in trigonal bipyramidal structures'.[3] As Muetterties and his co-workers[3] pointed out, such a process may be described as the result of concerted bending vibrations, causing transitions between the two idealised geometric configurations, *i.e.* the trigonal bipyramid and the tetragonal pyramid.

We have now prepared the five-co-ordinated chlorotetrakis(ethylene)iridium(I), $IrCl(C_2H_4)_4$, in which this fast intramolecular exchange process between ethylene ligands at non-equivalent co-ordination sites is absent. The n.m.r. spectrum at −20° of a chloroform solution of $IrCl(C_2H_4)_4$ is shown in the Figure (a). The four ethylene ligands give rise to the sharp resonance A at τ 8·39 p.p.m. and a slightly broadened resonance B at τ 6·48 p.p.m., with intensity ratio 1 : 3. On addition of free ethylene (C) a substantial broadening of B is shown, while A remains unaffected [Figure (b)], even if the temperature is raised to 0° [Figure (c)]. At 30°, where some decomposition is noted, B and C are merged into D, and A is broadened [Figure (d)]. These results show that at low temperatures (⩽ 0°) three of the four ethylene ligands are spectroscopically equivalent and, we suppose, are the equatorial ligands in a trigonal bipyramidal structure (I). Their (slow) exchange with free ethylene molecules, demonstrated by the broadened resonances B and C in the Figure (b) and (c) may well be caused by an associative mechanism. This would involve a six-co-ordinated intermediate, like (II), in which the axial ethylene ligand has to preserve its distinct character. A six-co-ordinated intermediate is postulated[5] in the exchange reaction of PCl_5 with isotopic Cl_2. Wilkinson[6] also suggested the existence of a short-lived six-co-ordinated species in the hydroformylation of alkenes by $RhH(CO)_2(PPh_3)_2$.

Preliminary results of *X*-ray investigations show that $IrCl(C_2H_4)_4$ crystallizes in the tetragonal system ($a = b = 11{\cdot}2$, $c = 7{\cdot}1$ Å). Intensity measurements by means of a Pailred diffractometer at *ca.* −150° were obstructed by the breaking of the crystal after the measurement of 120 independent *hk*0 reflections. Some information was obtained from these zero-layer reflections. The two-dimensional space group is *p*4*g*. The iridium as well as the chlorine atom are in special positions; 4*c* with $x_{Ir} = 0{\cdot}275$ and $x_{Cl} = 0{\cdot}131$. The distance between the two atoms in projection is 2·3 Å while the shortest distance possible between the iridium atoms is 5·6 Å, which excludes a dimeric structure.

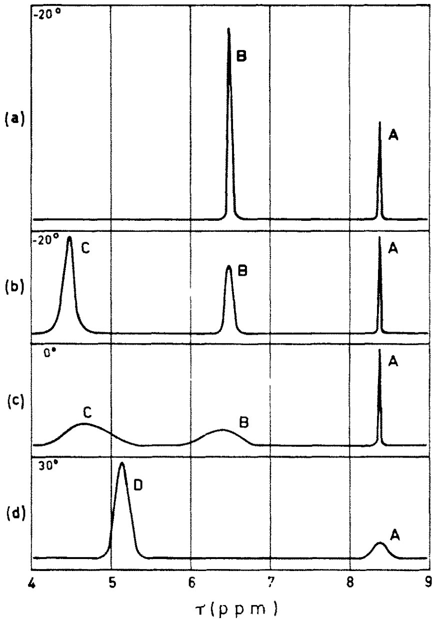
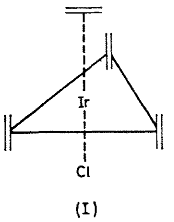


FIGURE. *N.m.r. spectra (diagrammatic) of solutions of* $IrCl(C_2H_4)_4$ *in chloroform at different temperatures.*

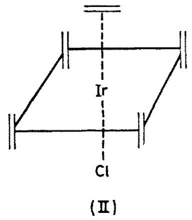
Far i.r. absorption frequencies (cm^{-1}) of rhodium(I) *and iridium*(I) *ethylene complexes*

Compound	ν(M–Cl)	Other bands
$[RhCl(C_2H_4)_2]_2$	274(s), 260(sh), 248(s)	502(w), 407(sh), 398(s), 308(w)
$[IrCl(C_2H_4)_2]_2$	292(sh), 289(m), 260(m)	537(w), 448(s), 308(vw)
$IrCl(C_2H_4)_4$	280(s)‡	505(m), 397(m), 372(w)

‡ This band has a broad shoulder centred at 308 cm^{-1}.



(I)



(II)

White $IrCl(C_2H_4)_4$ was isolated from a suspension of $[IrCl(C_8H_{14})_2]_2$ (see ref. 7) in heptane after treatment with ethylene.† Under nitrogen it is stable below *ca.* −50°, and under ethylene below *ca.* 30°. At higher temperatures it decomposes to $[IrCl(C_2H_4)_2]_2$ losing two molecules of ethylene. An interpretation of the far i.r. data (Table),

---

† An improved preparation method of $[IrCl(C_8H_{14})_2]_2$ will be published elsewhere.

analogous to the interpretation of data for chlorine-bridged rhodium(I) complexes,[8] suggests that $[IrCl(C_2H_4)_2]_2$ has a planar structure. *X*-Ray powder diagrams show that it is not isomorphous with the corresponding rhodium–ethylene complex $[RhCl(C_2H_4)_2]_2$, which has been assigned a bent structure.[8,9] Strictly speaking, the structure difference in both compounds prevents us from solving the problem concerning the metal–alkene bond strength in rhodium(I) and iridium(I) complexes.[10] Nevertheless, we conclude from the i.r. data given in the Table and those of new iridium(I) complexes, which will be published in the near future, that in corresponding complexes the iridium(I)–alkene bond is stronger than the rhodium(I)–alkene bond.

We thank Mr. A. L. Onderdelinden and Mr. E. C. Royers for their assistance.

(*Received, December* 19th, 1969; *Com.* 1914.)

---

[1] F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, 1958, **29**, 1427; R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, 1962, **58**, 1893.

[2] H. W. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, 1953, **21**, 279.

[3] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

[4] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084.

[5] J. Downs and R. E. Johnson, *J. Chem. Phys.*, 1954, **22**, 143.

[6] D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3133.

[7] B. L. Shaw and E. Singleton, *J. Chem. Soc.* (*A*), 1967, 1683.

[8] D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1969, 588.

[9] K. Klanderman and L. F. Dahl, quoted by W. E. Oberhansli and L. F. Dahl, *J. Organometallic Chem.*, 1965, **3**, 43.

[10] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1969, **6**, 1647.