Journal of Organometallic Chemistry, 236 (1982) C7—C10
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS, STRUCTURE, AND REACTIONS OF $IrCl_3(CCl_2)(PPh_3)_2$, A COMPOUND WITH AN IRIDIUM—CARBON DOUBLE BOND ($L_nIr{=}CCl_2$)

G.R. CLARK, W.R. ROPER* and A.H. WRIGHT
Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received June 14th, 1982)

Summary

Purple $IrCl_3(CCl_2)(PPh_3)_2$ results from reaction between $IrHCl_2(PPh_3)_3$ and $Hg(CCl_3)_2$. X-ray crystal structure determination reveals an octahedral complex with *trans*-phosphine ligands and a short Ir—C distance to the CCl_2 ligand of 1.872(7) Å, compatible with an iridium—carbon double bond. Chloride is easily displaced from the dichlorocarbene ligand and the products which have been derived include $IrCl_3(CO)(PPh_3)_2$, $IrCl_3(CS)(PPh_3)_2$, $IrCl_3(CNMe)(PPh_3)_2$, $IrCl_3(CClNMe_2)(PPh_3)_2$, $IrCl_3(\overline{CNHCH_2CH_2NH})(PPh_3)_2$ and $IrCl(\overline{CSCH_2CH_2S})(PPh_3)_2$.

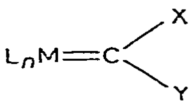
The metal—carbon bond order in transition metal carbene complexes exhibits values ranging from two to one. A situation best regarded as formal double-bonding (Type I) is apparent in those complexes where the carbene substituents are H or R, i.e. groups which cannot effectively conjugate with the carbene carbon, whereas a bond order approaching one (Type II) prevails in those complexes where the substituents are NR_2, OR, SR, etc., i.e. groups which can effectively conjugate with the carbene carbon.

The unusual complexes which have halide substituents on the carbene must belong to Type I. However, good structural information to support this classification is lacking. In the structure determination of $Fe(TPP)(CCl_2)H_2O$, (TPP = tetraphenylporphyrin) [1] accuracy was impaired by disorder between the CCl_2 and H_2O ligands. Disorder between CCl_2 and CO similarly affected the accuracy of the structure determination of $OsCl_2(CCl_2)(CO)(PPh_3)_2$ [2]; We describe here the synthesis of a new CCl_2 complex, $IrCl_3(CCl_2)(PPh_3)_2$, a satisfactory structure determination which reveals a short Ir—C bond, and several reactions of $IrCl_3(CCl_2)(PPh_3)_2$ which are all of a type now emerging as characteristic of dichlorocarbene ligands.

Following the synthesis of $OsCl_2(CCl_2)(CO)(PPh_3)_2$ [2], $IrHCl_2(PPh_3)_3$ [3]

0022-328X/82/0000—0000/$02.75

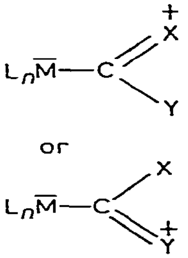
Type I



important for

X,Y = H,R or halide

Type II



important for

X,Y = NR_2 ,OR ,SR,*etc.*

was treated with $Hg(CCl_3)_2$. Successful reaction conditions are as follows: Under nitrogen $IrHCl_2(PPh_3)_3$ (1 g), $Hg(CCl_3)_2$ (1.6 g) and PPh_3 (0.5 g) are heated under reflux for 4 minutes in toluene (150 ml, freshly distilled from Na/benzophenone). During the heating period the solution changes to a deep purple colour. The reaction flask is cooled in an ice-salt bath for 30 minutes and then the contents filtered to remove mercury-containing insoluble material. Removal of the toluene under reduced pressure and crystallisation of the resulting oil from CH_2Cl_2/EtOH gives purple crystals in approx. 60% yield. Anal. Found: C, 49.53; H, 3.67. $C_{37}H_{30}Cl_5IrP_2$ calcd.: C, 49.38; H, 3.36%. IR spectral data for this compound and other compounds to be described are presented in Table 1.

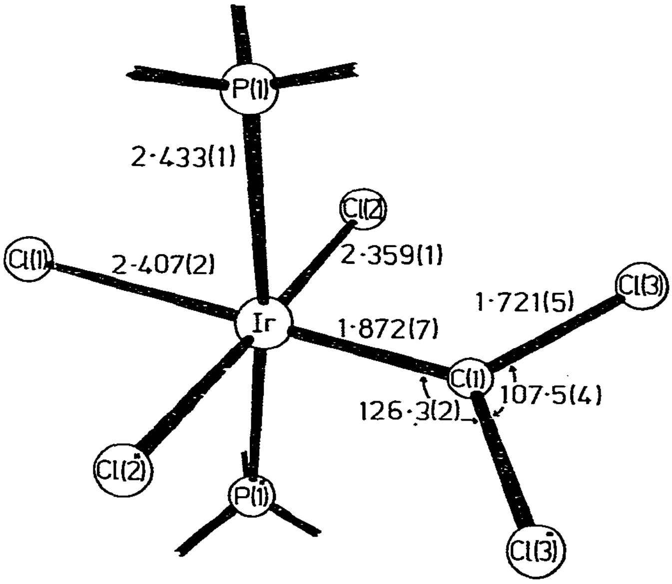


Fig. 1. Molecular structure of $IrCl_3(CCl_2)(PPh_3)_2$ with phenyl groups omitted for clarity. The CCl_2 plane is twisted 24.4° from the Cl(1), Cl(2), Ir, C(1) plane.

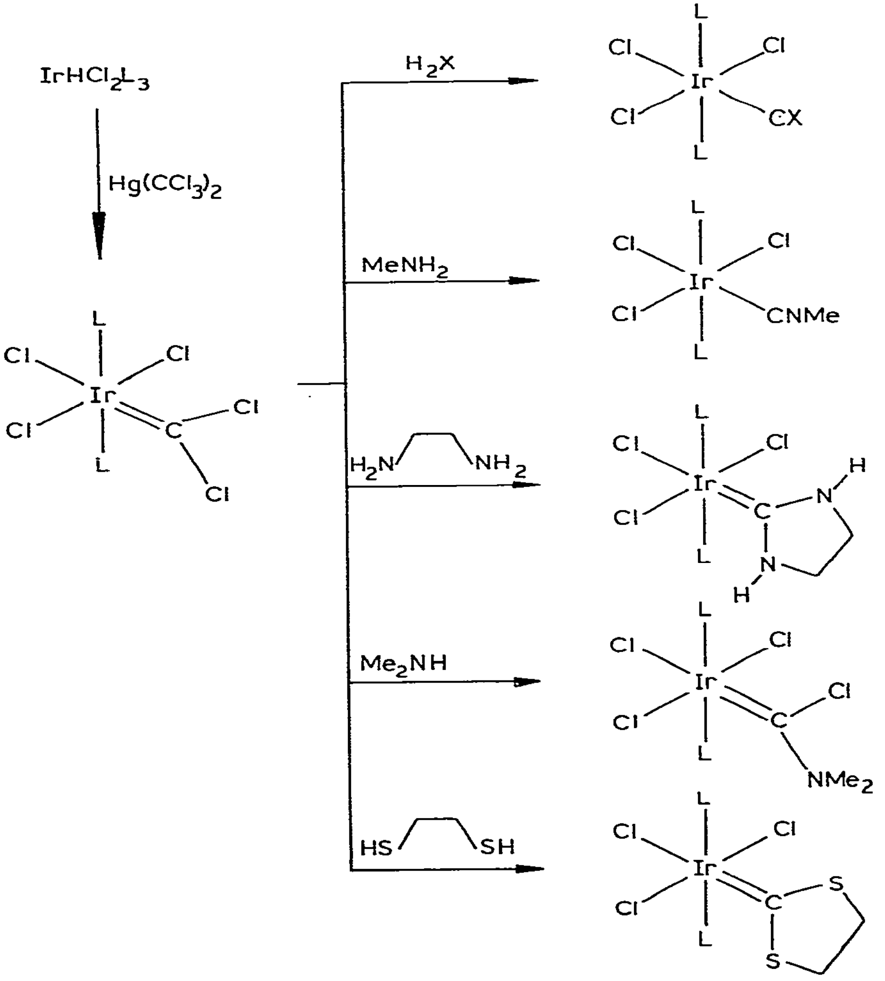
TABLE 1

IR DATA[a] FOR $IrCl_3(CCl_2)(PPh_3)_2$ AND DERIVED COMPLEXES[b]

Compound	IR bands and assignments
$IrCl_3(CCl_2)(PPh_3)_2$	880, 810 ν(C—Cl); 332, 288 ν(Ir—Cl)
$IrCl_3(CO)(PPh_3)_2$ [8]	2080 ν(CO)
$IrCl_3(CS)(PPh_3)_2$ [9]	1375 ν(CS)
$IrCl_3(CNMe)(PPh_3)_2$	2250 ν(CN) 322, 313, 300 ν(Ir—Cl)
$IrCl_3(CNHCH_2CH_2NH)(PPh_3)_2$	1515, 1502, 1330, 1315, 1280 (carbene ligand)
$IrCl_3[CCl(NMe_2)](PPh_3)_2$	1538 ν(CN); 820 ν(C—Cl). 322, 265 ν(Ir—Cl)
$IrCl_3(CSCH_2CH_2S)(PPh_3)_2$	029. 870 (carbene ligand). 322, 275 ν(Ir—Cl)

[a] In cm^{-1} measured as Nujol mulls. [b] All compounds have satisfactory carbon and hydrogen analyses.

The purple-coloured crystals belong in the monoclinic space group $C2/c$, with 4 molecules in a unit cell of dimensions a 20.461(2), b 9.819(3), c 17.813(3) Å, β 102.74(1)°. The structure was solved by conventional methods, and refined by full-matrix least-squares employing anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated



SCHEME 1. Synthesis and reactions of $IrCl_3(CCl_2)L_2$ ($L = PPh_3$; X = O or S).

positions but were not refined. The final residual, *R*, was 0.035 for 3625 observed reflections.

The compound is monomeric, with a crystallographically-imposed 2-fold axis passing through the Ir atom, one Cl atom, and the carbon atom of the dichlorocarbene ligand. The geometry in the coordination sphere is depicted in Fig. 1. The C—Cl distance of 1.721(5) Å can be compared with 1.710(10) Å in 1,1′-dichloroethylene [4] and 1.728(7) Å in vinyl chloride [5] and appears to be of expected length for a C(sp^2)—Cl distance. The multiple bonding must therefore lie between the carbene carbon and iridium and this is reflected in the short Ir—C distance of 1.872(7) Å and the valence bond structure of Type I fairly represents this situation.

Scheme 1 presents a selection of reactions undergone by the new CCl_2 complex and it will be seen that they exactly parallel the reactions recently described for $RuCl_2(CCl_2)(CO)(PPh_3)_2$ [6]. We are examining the possibility of preparing an iridium carbyne complex (analogous to $OsCl(CO)(CR)(PPh_3)_2$ [7]) by reaction with suitable lithium reagents.

We thank the N.Z. Universities Grants Committee for grants towards instrumental facilities and the award of a Postgraduate Fellowship to A.H.W.

References

1 D. Mansuy, M. Lange, J.C. Chottard, J.F. Bartoli, B. Chevrier and R. Weiss, Angew. Chem. Internat. Edn., 17 (1978) 781.
2 G.R. Clark, K. Marsden, W.R. Roper and L.J. Wright, J. Amer. Chem. Soc., 102 (1980) 1206.
3 L. Vaska, J. Amer. Chem. Soc., 83 (1961) 756.
4 R.L. Livingston, C.N.R. Rao, L.M. Kaplan and L. Rocks, J. Amer. Chem. Soc., 80 (1958) 5368.
5 R.C. Ivey and M.I. Davis, J. Chem. Phys., 57 (1972) 1909.
6 W.R. Roper and A.H. Wright, J. Organometal. Chem., 233 (1982) C59.
7 G.R. Clark, K. Marsden, W.R. Roper and L.J. Wright, J. Amer. Chem. Soc., 102 (1980) 6570.
8 L. Vaska, J.W. DiLuzio, J. Amer. Chem. Soc., 84 (1962) 679.
9 M. Kubota and C.J. Curtiss, Inorg. Chem., 13 (1974) 2277.