Journal of Organometallic Chemistry, 94 (1975) C29—C32
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

BI-HETEROMETALLIC HYDRIDO TRANSFER BETWEEN IRIDIUM AND PLATINUM

JACK P.C.M. VAN DONGEN, CHRISTOPHER MASTERS* and JACOBUS P. VISSER
Koninklijke Shell-Laboratorium, Amsterdam (Shell Research B.V.) (The Netherlands)
(Received June 2nd, 1975)

Summary

Hydrido transfer from IrH_5L_2 to $Pt_2Cl_4L_2$ or $Pd_2Cl_4L_2$ (where L = PPr_3) occurs readily at room temperature, and in the case of the platinum dimer is shown to proceed via a hydrido-bridged platinum—iridium complex.

We recently showed that methyl transfer, either between two platinum centres or from a platinum centre to palladium, is a facile process [1]. We now report that under similar mild conditions hydrido transfer from iridium to either platinum or palladium occurs.

Thus, addition of the chloro-bridged dimer $Pt_2Cl_4(PPr_3)_2$ to $IrH_5(PPr_3)_2$ in toluene at 20 °C results in the immediate evolution of molecular hydrogen and the formation of one or more new hydrido species. The ^1H NMR spectrum of the mixture shows that at least one of the hydrido ligands is present on platinum, since one of the hydrido signals shows platinum coupling ($J(^{195}Pt—H)$ 583 Hz). Further, the signal due to the original iridium pentahydride disappears with the appearance of two new iridium-hydrido signals. These NMR data do not show whether two new complexes are formed (i.e. an iridium dihydrido species together with a platinum hydrido complex), or whether there is a single complex containing both iridium and platinum. Conclusive evidence for the latter is provided by: (i) the ^{31}P-decoupled ^1H NMR spectrum of the mixture, which shows that all three hydrido signals are mutually coupled; (ii) the ^{31}P NMR spectrum with all but the hydrido couplings removed, which clearly shows that the phosphorus nucleus of the tertiary phosphine ligand coordinated to the platinum is coupled to two hydrido ligands and to two other equivalent phosphorus nuclei.

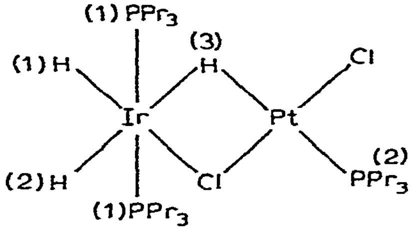
From the combined NMR data (see Table 1) we assign structure I to this mixed metal hydrido complex. Although bi-homo-transition metal complexes containing bridging hydrido ligands are known [2-6], complex I represents one

---

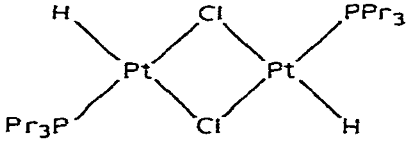
*To whom correspondence should be addressed.

TABLE 1

^{1}H (90 MHz) AND ^{31}P (40.5 MHz) NMR DATA MEASURED IN OCTADEUTEROTOLUENE AT ca. 25 °C (δ in ppm, J in Hz)



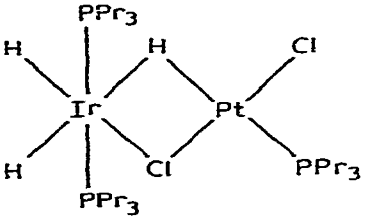
δ(H(1)) −25.2	J(H(1)—H(3)) ≃ 1	$J(^{195}$Pt—H(3)) = 583(586)^{a}
δ(H(2)) −13.9	J(H(1)—H(2)) 7(7)^{a}	δ(P(1)) + 2.2^{b}
δ(H(3)) −11.6	J(H(2)—H(3)) 6(5)^{a}	δ(P(2)) + 45^{b}
$J(^{31}$P(1)—H(1)) 15.8	$J(^{31}$P(2)—H(3)) 122	J(H(3)—^{31}P(2)) 123^{c}
$J(^{31}$P(1)—H(2)) 13.0	$J(^{31}$P(2)—H(2)) 35.5	J(H(2)—^{31}P(2)) 36^{c}
$J(^{31}$P(1)—H(3)) 8	$J(^{31}$P(1)—^{31}P(2)) 3.6^{c}	$J(^{195}$Pt—^{31}P(2)) 3297^{c}



δ(H) −18.1
$J(^{31}$P—H) 20.6
$J(^{195}$Pt—H) 1369

---

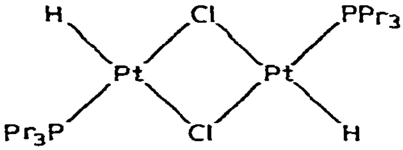
[a] Values in parentheses obtained from ^{31}P-decoupled ^{1}H NMR spectrum (100 MHz). [b] Shifts relative to external 85% H_3PO_4. "+" indicating upfield relative to H_3PO_4. [c] From ^{31}P NMR spectrum.



(I)

of the few [6] examples of such a species containing two different transition metals.

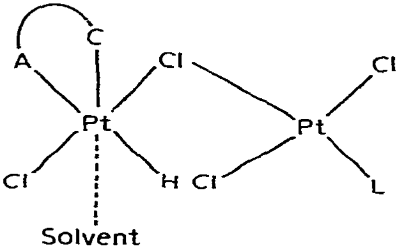
On standing (ca. ½ h) in toluene at room temperature, I disproportionates to give a platinum-hydrido species, to which we tentatively assign structure II, together with an uncharacterised iridium hydrido complex. Analogous reactions



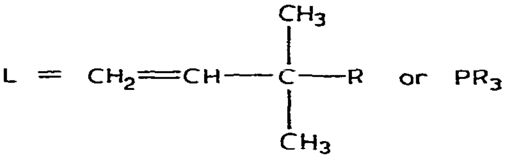
(II)

were observed with the palladium dimer, $Pd_2Cl_4(PPr_3)_2$ but the resulting palladium complexes are much less stable than their platinum analogues and decompose within several minutes at room temperature.

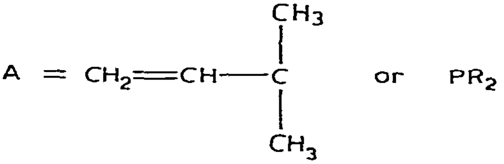
These results have significance for the recently reported [7,8] platinum-catalysed hydrogen/deuterium exchange at a saturated carbon atom. We have shown [7,8] that in the H/D exchange reaction at least two platinum centres are involved, and have further suggested the intermediacy of complexes of type III, implying that C—H insertion and H/D exchange occur at the same platinum atom.



(III)



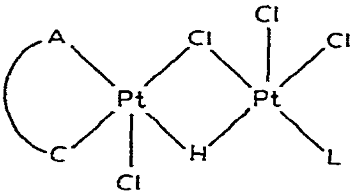
$$L = CH_2{=\!=}CH{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}R \quad \text{or} \quad PR_3$$



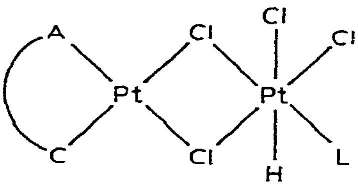
$$A = CH_2{=\!=}CH{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} \quad \text{or} \quad PR_2$$

(where R = Pr or Bu)

The results reported above show that inter-metal hydrido transfer is a facile process, and suggest that reaction intermediates of the types IV and V may play a role in the H/D exchange. This would imply that the function of the second platinum centre is to provide an alternative site for the exchange of the H for D.



(IV)



(V)

References

1 J.P. Visser, W.W. Jager and C. Masters, Rec. Trav. Chim. Pays Bas, 94 (1975) 70.
2 R.A. Schunn in E. Muetterties (Ed.). Transition metal hydrides, Marcel Dekker, New York, 1971.
3 J. Knight and M.J. Mays, J. Chem. Soc. A, (1970) 711.
4 B.F.G. Johnson, J. Lewis and I.G. Williams, J. Chem. Soc. A, (1970) 901.
5 M.R. Churchill and S. Wei-Yang Ni, J. Amer. Chem. Soc., 95 (1973) 2150.
6 C. White, A.J. Oliver and P.M. Maitlis, J. Chem. Soc. Dalton, (1973) 1901.
7 P.A. Kramer and C. Masters, J. Chem. Soc. Dalton, in press.
8 A.A. Kiffen, C. Masters and L. Raynand, J. Chem. Soc. Dalton, in press.