Carbonyl-free Hydride-bridged Mixed Organotransition Metal Complexes: *X*-Ray Crystal Structure of $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2Rh(PPh_3)_2]PF_6$

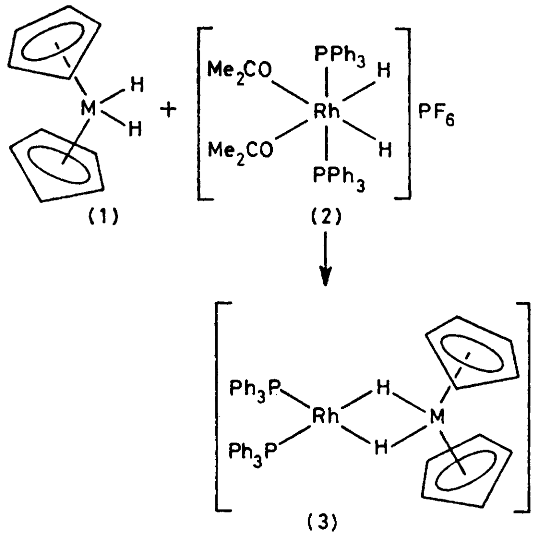
By NATHANIEL W. ALCOCK, OLIVER W. HOWARTH,* PETER MOORE, and GEORGE E. MORRIS

(*Department of Chemistry and Molecular Sciences, University of Warwick, Coventry* CV4 7AL)

Summary The preparation of carbonyl-free mixed organotransition metal complexes $[(\eta^5\text{-}C_5H_5)_2M(\mu\text{-}H)_2Rh(PPh_3)_2]PF_6$, (M = Mo or W) in which $(\eta^5\text{-}C_5H_5)_2MH_2$ exhibits a novel bonding mode is described, and the *X*-ray crystal structure of the title compound, which undergoes H–D exchange at the cyclopentadienyl rings under mild conditions, has been determined.

RECENTLY there has been considerable interest in the structure and chemistry of hydride-bridged mixed organotransition metal complexes,[1] but few complexes not containing carbon monoxide ligands have been characterised.[2] Previously, Kaesz has shown that $(\eta^5\text{-}C_5H_5)_2MH_2$ (**1**; M = W, Mo) acts as a two-electron donor to some metal carbonyl species, the hydrides being considered as non-bridging on the basis of M–H coupling constants.[3] We now report the preparation of carbonyl-free hydride-bridged mixed metal complexes derived from (**1**).

Reaction of (**1**) with (**2**)[4] in acetone or CH_2Cl_2 at room temperature immediately gives deep brown (M = Mo) or



green (M = W) solutions from which the compounds (**3**) may be isolated in high yield (70—80%). The single crystal *X*-ray structure of (**3**; M = W) has been determined (Figure).† The final Fourier difference map revealed a number of residual peaks close to Rh and W. Two of these were in reasonable positions for hydrides and were included in the final refinements, but their positions are likely to be subject to fairly large errors. The structure shows P(1), P(2), Rh, and W to be coplanar (maximum deviation 0·02 Å from best plane) with Rh–W 2·721(8) Å. The Rh–P(1)–P(2) geometry is similar to that recently described for the hydride-bridged dimer $[\mathrm{Rh}(\mathrm{P}\{\mathrm{OPr}^i\}_3)_2(\mu\text{-H})]_2$.[5] The $(\eta^5\text{-C}_5\mathrm{H}_5)_2\mathrm{W}$ unit has eclipsed rings with a bending angle of 136°. The two parts of the molecule are, however, rotated about the Rh–W axis, the plane defined by the ring normals through W making an angle of 17° with the perpendicular to the $\mathrm{P}_2\mathrm{RhW}$ plane and the WH_2 plane making a similar angle with the $\mathrm{P}_2\mathrm{RhW}$ plane itself.

The ^{1}H n.m.r. spectra of (**3**) in $\mathrm{CD}_2\mathrm{Cl}_2$ at room temperature consist of a complex phenyl region (30 *H*), an $(\eta^5\text{-C}_5\mathrm{H}_5)$ singlet (10 H) and a doublet of triplets at high field [M = Mo, δ −16·69, 2 H, *J*(Rh–H) 29, *J*(P–H) 6·5 Hz; M = W, δ −18·11, 2 H, *J*(Rh–H) 29, *J*(W–H) 107 Hz, *J*(P–H) 10 Hz]. The metal-H coupling constants are comparable to those of the terminal hydrides in (**1**) and (**2**) [(**1**; M = W), *J*(W–H) 74 Hz; (**2**), *J*(Rh–H) 26 Hz]. As the samples are cooled to −70 °C, the central lines of the high field triplets collapse while the separation of the outer lines and the M–H couplings are maintained. The *X*-ray structure and ^{1}H n.m.r. data are consistent with two bridging hydride ligands in positions which satisfy both square planar co-ordination at Rh and the usual $(\eta^5\text{-C}_5\mathrm{H}_5)_2\mathrm{MX}_2$ geometry at W, and are undergoing rapid intramolecular exchange in solution at room temperature.

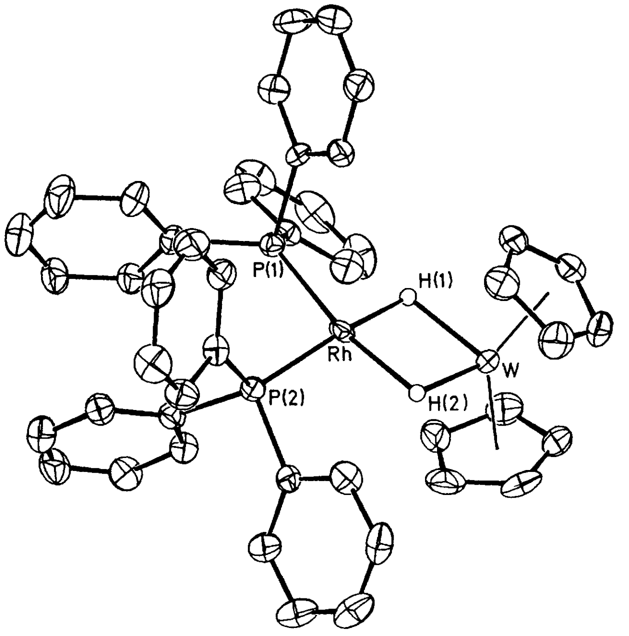


FIGURE. The *X*-ray crystal structure of $[(\eta^5\text{-C}_5\mathrm{H}_5)_2\mathrm{W}(\mu\text{-H})_2\mathrm{Rh}(\mathrm{PPh})_3)_2]^+$ (ORTEP drawing). All C–H hydrogens have been omitted for clarity. *Crystal data:* $[(\eta^5\text{-C}_5\mathrm{H}_5)_2\mathrm{W}(\mu\text{-H})_2\mathrm{Rh}(\mathrm{PPh}_3)_2]\mathrm{PF}_6$, monoclinic, *a* = 12·511(1), *b* = 9·273(1), *c* = 36·036(6) Å, β = 98·98(1)°, $P2_1/c$, *Z* = 4, four circle diffractometry, 6051 independent reflections with $I > 3\sigma$ at −120 °C. Anisotropic temperature factors for non-H atoms. Final *R* = 0·039. Selected distances and angles are Rh–P(1), 2·238(2); Rh–P(2), 2·219(10); W–C (average) 2·299 Å, P(1)–Rh–P(2), 97·13(7); W–Rh–P(1), 132·05(5); W–Rh–P(2), 130·79(5)°.

The low temperature hydride ^{1}H n.m.r. spectra should be part of an AA′MXX′ system[6] and are consistent with *J*(P–H, *cis*) and *J*(P–H, *trans*) of opposite sign together with a suitable value of *J*(P–P).[7]‡ The relatively small value of [*J*(P–H, *cis*) + *J*(P–H, *trans*)] suggests that the hydride ligands may be out of the $\mathrm{P}_2\mathrm{RhW}$ plane in solution as well as in the crystal structure.

The large metal–H coupling constants to both metals in compounds (**3**) confirm the evidence of the structure determination for bridging hydrides. Thus, the bonding does not resemble that in compounds such as $[(\eta^5\text{-C}_5\mathrm{H}_5)_2\mathrm{WH}_2\cdot\mathrm{W}'(\mathrm{CO})_5]$, in which $J(\mathrm{W\text{–}H}) \gg J(\mathrm{W'\text{–}H})$, where the hydrides are thought to be non-bridging.[3] The best comparison is therefore with the bonding in the singly hydride-bridged complex $[(\eta^5\text{-C}_5\mathrm{H}_5)_2(\mathrm{CO})\mathrm{Nb}(\mu\text{-H})\mathrm{Fe}(\mathrm{CO})_4]$.[8]

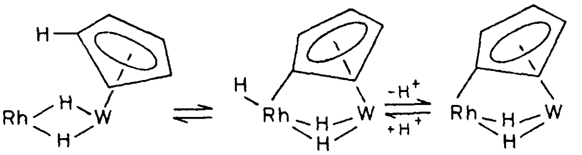
In solution, compounds (**3**) are readily decomposed by oxygen, but in the solid state they are moderately stable. In acetone, (**3**; M = W) is immediately cleaved by excess of pyridine (py) to give $[(\mathrm{py})_2\mathrm{Rh}(\mathrm{PPh})_3)_2]\mathrm{PF}_6$ and (**1**), and by dilute aqueous HCl to give $[\mathrm{Rh}(\mathrm{PPh}_3)_2\mathrm{Cl}]_2$ and $[(\eta^5\text{-C}_5\mathrm{H}_5)_2\mathrm{WH}_3]\mathrm{PF}_6$ (**4**). ^{1}H N.m.r. spectra of (**3**; M = W) in $(\mathrm{CD}_3)_2\mathrm{CO\text{–}D_2O}$ show that H/D exchange of bridging

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ A unique set of coupling constants cannot be derived from the spectra. However, for example, calculated spectra (line width 2 Hz) with *J*(P–H,*cis*) ± 20 Hz, *J*(P–H,*trans*) ∓ 40 Hz and 70 Hz < *J*(P–P) < 90 Hz are deceptively simple doublets with a splitting of 20 Hz as observed for (**3**; M = W) at low temperature.

hydrides occurs readily at room temperature and of $(\eta^5\text{-}C_5H_5)$ hydrogens on heating. Thus, on refluxing (**3**; $M = W$) in acetone–D_2O (10:1) for 5 h, the ^1H n.m.r. spectrum of (**4**), recovered by treatment of (**3**) with excess of pyridine then aqueous HCl and NH_4PF_6, showed 85% D-incorporation on the rings (mull i.r., Nujol, 3100m cm^{-1}, ν_{C-H}; 2330vs cm^{-1}, ν_{C-D}; $\nu_{C-H}/\nu_{C-D} = 1{\cdot}33$). Ring H/D exchange presumably occurs *via* reversible Rh insertion into a C–H bond of an $(\eta^5\text{-}C_5H_5)$ ring, since preliminary ^1H n.m.r. and i.r. results indicate that the Ir analogue of this postulated intermediate can be isolated; also deprotonation equilibria have been demonstrated for cationic Rh hydride complexes.[4]



We thank Johnson Matthey Ltd. for a generous loan of precious metals and the S.R.C. for financial support (G. E. M.).

(*Received, 13th September* 1979; *Com.* 981.)

[1] R. Bau, R. G. Teller, S. W. Kirtley, and T. F. Koetzle, *Accounts Chem. Res.*, 1979, **12**, 176.

[2] J. P. C. M. van Dongen, C. Masters, and J. P. Visser, *J. Organometallic Chem.*, 1975, **94**, C29.

[3] B. Deubzer and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1968, **90**, 3276.

[4] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1976, **98**, 2134.

[5] R. K. Brown, J. M. Williams, M. F. Fredrich, V. W. Day, A. J. Sivak, and E. L. Muetterties, *Proc. Nat. Acad. Sci. U.S.A.*, 1979, **76**, 2099.

[6] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[7] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.

[8] K. S. Wong, W. R. Scheidt, and J. A. Labinger, *Inorg. Chem.*, 1979, **18**, 136.