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Preliminary communication

EFFECT OF THE NATURE OF THE PHOSPHIDO BRIDGE ON THE CO LABILISATION IN HETEROBIMETALLIC μ-PHOSPHIDO COMPLEXES

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Summary

In contrast to their μ-PPh_2 analogues, the compounds $(OC)_5M(\mu\text{-}PRH)Pt(H)(PPh_3)_2$ (M = Cr, Mo, W; R = Ph or cyclohexyl) do not rearrange to form $(OC)_4M(\mu\text{-}PRH)(\mu\text{-}H)Pt(PPh_3)_2$.

There have been several recent reports of CO labilisation during the synthesis of heterobimetallic μ-phosphido complexes [1–5]. For example, the *cis*-μ-phosphido-platinum hydrides **1** were found to rearrange to give the metal–metal bonded μ-phosphido-μ-hydrido complexes **2** within 8–150 min, depending on M [1].

The reaction was thought to proceed via an "adjacent platinum assisted mechanism involving PR_3 dissociation". The pathway is initiated by loss of PR_3 followed by the formation of the μ-CO intermediate **3** and then the terminal CO intermediate **4**. This mechanism is in keeping with the sensitivity of the CO substitution on M to the nature of the phosphine ligand on Pt.

We have now found that this CO labilisation reaction is very sensitive to the nature of the phosphido bridge. Complexes **5** and **6** which have a PRH bridge

TABLE 1

NMR DATA FOR $(OC)_5M(\mu\text{-}PRH)Pt(H)(PPh_3)_2$ [a]

	δ(P(1))	δ(P(2))	δ(P(3))	δ(Pt) [b]	^1J(PtP(1))	^1J(PtP(2))	^1J(PtP(3))
5a	23.3	27.8	−19.5	−5078	2375	2108	1594
5b	19.1	27.8	−45.6	−5079	2377	2124	1505
5c	22.2	27.5	−67.0	−5058	2393	2105	1585
6a	20.9	28.4	−7.3	−5124	2249	2174	1625
6b	21.5	28.8	−30.6	−5113	2251	2164	1517
6c	20.6	28.2	−51.9	−5101	2275	2170	1606

[a] Solvent toluene, 300 K, ^{31}P shifts relative to H_3PO_4, ^{195}Pt shifts in ppm relative to Na_2PtCl_6, positive to high frequency of the reference; *J* in Hz. [b] ddd.

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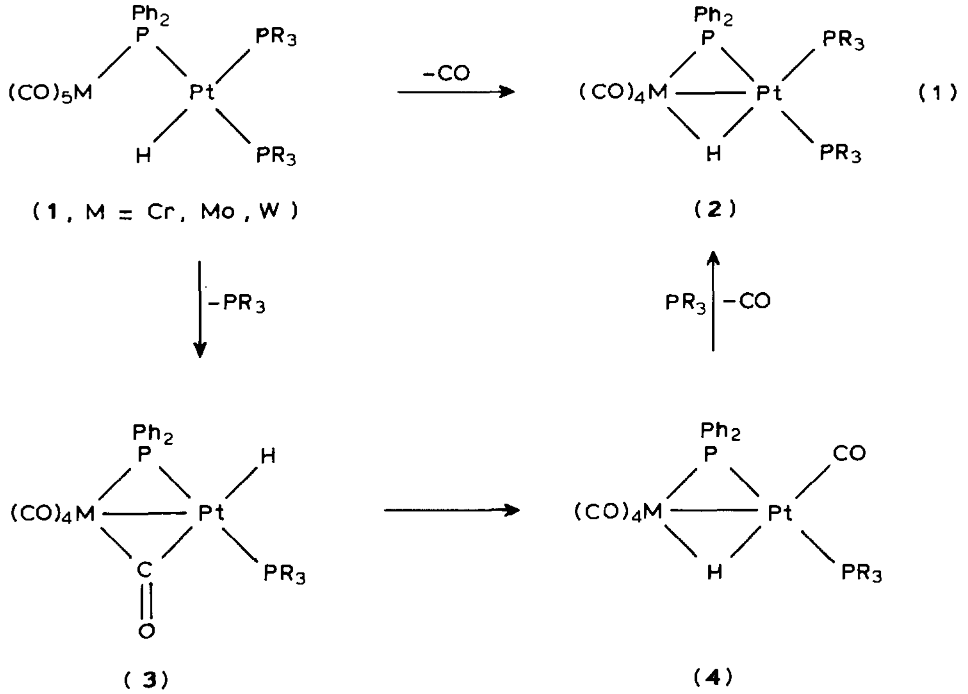
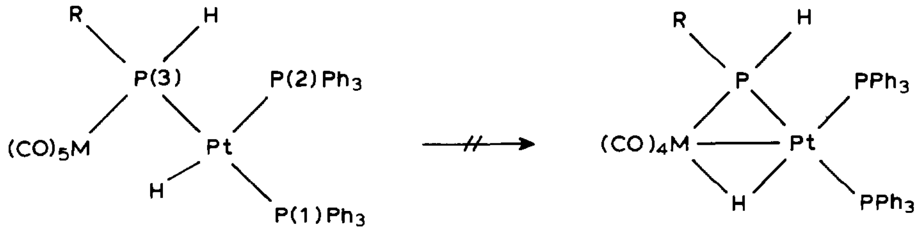


Scheme 1

instead of the PR_2 bridge present in **1** are not converted into the corresponding metal–metal bonded μ-hydrido compounds **7**, and can be crystallized without decomposition. The compounds **5** and **6** were formed by oxidative addition of $M(CO)_5PRH_2$ to $Pt(PPh_3)_2C_2H_4$, i.e. analogously to **1** [1]. The new compounds were characterized by ^{31}P and ^{195}Pt NMR spectroscopy (Table 1).



(**5a** : R = Ph , M = Cr ;
5b : R = Ph , M = Mo ;
5c : R = Ph , M = W ;
6a : R = c-Hx , M = Cr ;
6b : R = c-Hx , M = Mo ;
6c : R = c-Hx , M = W) (c-Hx = cyclohexyl)

(**7**)

References

1 J. Powell, M.R. Gregg and J.F. Sawyer, J. Chem. Soc., Chem. Commun., (1984) 1149.

2 J. Powell, J.F. Sawyer and S.J. Smith, J. Chem. Soc., Chem. Commun., (1985) 1312.

3 J. Powell, J.F. Sawyer and M.V.R. Stainer, J. Chem. Soc., Chem. Commun., (1985) 1314.

4 R.A. Jones, J.G. Lasch, N.C. Norman, A.L. Stuart, T.C. Wright and B.R. Whittlesey, Organometallics, 3 (1984) 114 and ref. cited therein.

5 M.J. Breen, P.M. Shulman, G.L. Geoffrey, A.L. Rheingold and W.C. Fultz, Organometallics, 3 (1984) 782 and ref. cited therein.