Metal-assisted CO Labilization and Intramolecular Hydride Transfer Reactions in Heterobimetallic μ-Phosphido–Hydrido Carbonyl Complexes

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The oxidative addition of the P–H bond of $(OC)_5M(PPh_2H)$ (M = Cr, Mo, W) to zerovalent platinum complexes initially forms heterobimetallic μ-phosphido terminal hydrido complexes which readily rearrange *via* bridging carbonyl and platinum-terminal carbonyl intermediates to give the μ-phosphido-μ-hydrido complexes $(OC)_4M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(PR_3)_2$.

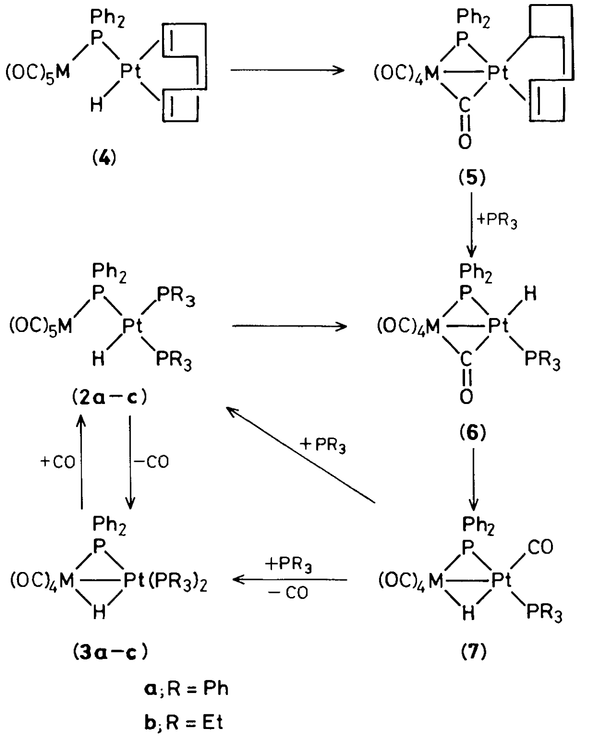
Recent reports provide several examples of CO labilization during the synthesis of heterobimetallic μ-phosphido complexes.[1,2] We here describe reactions of diphenylphosphine–group 6 metal carbonyls $(OC)_5M(PPh_2H)$ (**1**),[3] with zerovalent complexes of platinum which provide an insight into the CO labilization mechanism(s). The complexes synthesised and the reactions studied are outlined in Scheme 1.

$$(OC)_5M(PPh_2H)$$
(**1**)

Reaction of (**1**) with $Pt(C_2H_4)(PPh_3)_2$ or $Pt(PPh_3)_4$ in CH_2Cl_2 (25 °C) gives the μ-phosphido-μ-hydrido complexes (**3a**) as the final product. The triethylphosphine analogues (**3b**) (R = Et) are obtained from the reaction of $M(CO)_5PPh_2Li$ with *trans*-$PtHCl(PEt_3)_2$. The molecular structure of (**3b**) (M = Cr; R = Et), as determined by *X*-ray diffraction methods is shown in Figure 1.†

By monitoring reactions using ^1H and ^{31}P n.m.r. and i.r. spectroscopy the reaction sequences shown in Scheme 1 have been established.‡ For the reaction of (**1**) with $Pt(C_2H_4)(PPh_3)_2$, the major intermediate is the *cis*-μ-phosphido-platinum hydride (**2a**), which is readily characterized spectroscopically. The rate of formation of the terminal hydride (**2a**) decreases in the order Cr > Mo > W which is the order of decreasing acidity of the P–H bond of (**1**).[4] The rate of formation of (**3a**) from (**2a**) also decreases in the order Cr > Mo ≫ W. [Reaction (**2a**) → (**3a**) (25 °C) is >90% complete in 8 min for Cr, 15 min for Mo, and 150 min for W.] The reaction (**2a,b**) → (**3a,b**) is readily reversed within 5 min at room temperature by bubbling CO (1 atm) through the solution. In contrast the corresponding reaction of the diphos, $Ph_2PCH_2CH_2PPh_2$, substituted bridged hydrides (**3c**) [obtained from reaction of (**3a**) with diphos] with CO occurs very slowly [*e.g.* for M = W, no (**2c**) is formed after bubbling CO through the solution for 2 h]. By adding one molar equivalent of diphos to a solution of (**2a**) the diphos *cis*-hydride (**2c**) is formed *in situ* as the major species. On standing (**2c**) is converted into (**3c**) very slowly (*ca.* 20% reaction in 4 days at room temperature for M = W).

Possible mechanisms for the formation of (**3**) from (**2**) are illustrated in Scheme 2. The remarkable ease of substitution of



Scheme 1. Heterobimetallic complexes obtained from the reaction of $(OC)_5MPPh_2Y$ (M = Cr, Mo, W; Y = H, Li) and various platinum complexes (see text).

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† *Crystal data* for (**3b**) (M = Cr; R = Et): $C_{28}H_{41}CrP_3PtO_4$, M = 781.6, monoclinic, space group Cc, a = 16.719(9), b = 11.468(3), c = 18.275(6) Å, β = 113.68(3)°, U = 3209 Å^3, and D_c = 1.62 g cm^{-3} for Z = 4. Mo-$K_{\bar{\alpha}}$ radiation (λ = 0.71069 Å), μ(Mo-$K_{\bar{\alpha}}$) = 49.1 cm^{-1}. The structure was solved by Patterson methods and least-squares refinement and has converged (max. shift/error = 0.09) to R = 0.0346 (R_w = 0.0401) for 3801 observed [$I > 3\sigma(I)$] reflections. Weights were given by $w = 1/\sigma(F)^2$ where $\sigma(F)^2 = [\sigma(I)^2 + (0.05F^2)^2]^{\frac{1}{2}}$.

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.

‡ Complexes (**2**)—(**7**) have been fully characterized by i.r. [ν(CO) region], ^{31}P, ^{13}C, and ^1H n.m.r. spectroscopy (particularly the hydridic region),[6] by elemental analyses for (**3**), (**4**), (**5**), and (**7**) [(**2**) → (**3**) and rapid (**6**) → (**7**) rearrangements prevent isolation of (**2**) and (**6**)], and by *X*-ray diffraction studies (Figure 1). *E.g.* Data for (**2a**) (M = W): i.r. ν(CO) (CH_2Cl_2) 2057w and 1902vs (br.) cm^{-1}; ^1H n.m.r. δ −5.2 [Pt–H, 1:4:1, t of ddd, J(P–*trans*-H) 167, J(P–*cis*-H) 18, J(P–phosphido) 22, $J(^{195}Pt\text{–}H)$ 850 Hz]; $^{31}P\{^1H\}$ n.m.r. δ (relative to H_3PO_4) −8.5 [μ-phosphido, 1:4:1, t of dd, $J(^{31}P\text{–}^{31}P)$ 260, 14.6, $J(^{195}Pt\text{–}^{31}P)$ 1530 Hz, $J(^{183}W\text{–}^{31}P)$ not resolved], 24.3 [P–*trans*-H, 1:4:1, t of dd, $J(^{31}P\text{–}^{31}P)$ 14.6, 15.3, $J(^{195}Pt\text{–}^{31}P)$ 2330 Hz], 18.5 p.p.m. [P–*cis*-H, 1:4:1, t of dd, $J(^{31}P\text{–}^{31}P)$ 15.3, 260, $J(^{195}Pt\text{–}^{31}P)$ 2330 Hz]. Data for (**3a**) (M = W): i.r. ν(CO) (CH_2Cl_2) 2002s, 1899m, 1881vs, 1864s cm^{-1}; ^1H n.m.r. δ −7.9 [μ-H, 1:4:1, t of ddd, J(P–*trans*-H) 111, J(P–*cis*-H) 14, J(P–phosphido) 30, $J(^{195}Pt\text{–}H)$ 668, $J(^{183}W\text{–}H)$ 30 Hz]; $^{31}P\{^1H\}$ n.m.r. δ 100 [μ-phosphido, 1:4:1, t of dd, $J(^{31}P\text{–}^{31}P)$ 191, 21, $J(^{195}Pt\text{–}^{31}P)$ 1420, $J(^{183}W\text{–}^{31}P)$ 198 Hz], 14 [P–*trans*-H, 1:4:1, t of dd, $J(^{31}P\text{–}^{31}P)$ 21, 8, $J(^{195}Pt\text{–}^{31}P)$ 3500 Hz], 13 p.p.m. [P–*cis*-H, 1:4:1, t of dd, $J(^{31}P\text{–}^{31}P)$ 191, 8, $J(^{195}Pt\text{–}^{31}P)$ 2250 Hz]. Satisfactory elemental analyses were obtained.

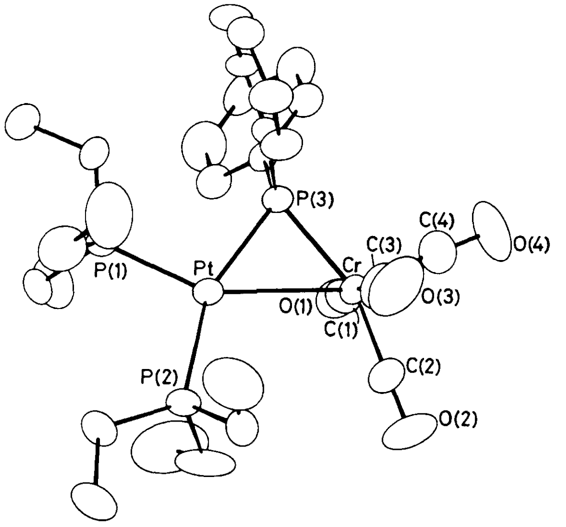
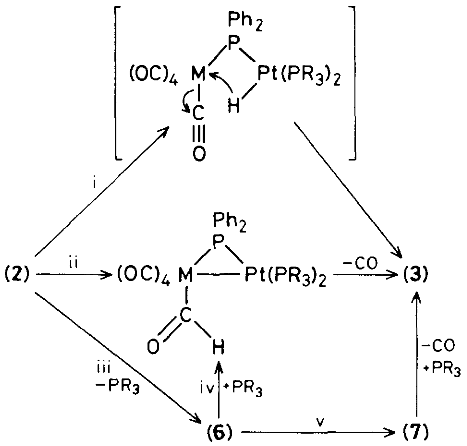


Figure 1. Molecular structure of (**3b**) (M = Cr; R = Et) as determined by single crystal *X*-ray diffraction.† Selected bond lengths (Å): Pt–Cr 2.905(2), Pt–P(1) 2.287(2), Pt–P(2) 2.322(2), Pt–P(3) 2.321(2), Cr–P(3) 2.320(3), Cr–C(1) 1.877(12), Cr–C(2) 1.819(10), Cr–C(3) 1.864(10), Cr–C(4) 1.815(12). Selected bond angles (°): P(1)–Pt–P(2) 101.5, P(1)–Pt–P(3) 102.0, P(3)–Pt–Cr 51.2, Cr–Pt–P(1) 153.2, P(3)–Cr–Pt 51.2, Pt–Cr–C(1) 92.8, Pt–Cr–C(2) 109.3, Pt–Cr–C(3) 94.1, Pt–Cr–C(4) 157.0. The position of the bridging hydride ligand is assumed to be approximately *trans* to P(1) and C(4).



Scheme 2. Possible reaction pathways for the formation of (**3**) from (**2**).

CO into, or from, the group 6 metal centre, and the relative rate of the (**2**) → (**3**) reaction as a function of the group 6 metal (Cr > Mo ≫ W) are not typical of the known CO substitution reactions of group 6 metal carbonyls (relatively slow; Mo > Cr > W).[5] Consequently a simple substitution (Scheme 2, route i) seems unlikely. Furthermore, the fact that CO substitution at M is very sensitive to the nature of the phosphine ligand on the platinum metal [relative rates for (**2**) → (**3**) and (**3**) → (**2**): $PPh_3 \simeq PEt_3 \ggg$ diphos] argues for an 'adjacent platinum-assisted mechanism involving PR_3 dissociation'. (Hydride ligands are known to be good *trans*-labilizers of tertiary phosphine ligands.[6]) Based on this last observation a mechanism involving formation of a formyl intermediate *via* direct hydride ligand attack on a co-ordinated CO [Scheme 2, route ii, no PR_3 dissociation] can be excluded. The involvement of a μ-CO intermediate (**6**) (Scheme 2, route iii) is consistent with the effect of the phosphines on the rate (*i.e.* displacement of diphos is more difficult than loss of PR_3 ligands) and could account for the relative rates of Cr > Mo > W since it is well known that μ-CO groups are more accessible to first row transition metals.[7] Support for a μ-CO intermediate is obtained from the reaction of (**1**) with $Pt(C_2H_4)_3$ in the presence of cyclo-octa-1,5-diene in hexane to give the terminal hydride (**4**) (Scheme 1). In CH_2Cl_2 (**4**) rearranges quantitatively into the bridged carbonyl cyclo-octenyl heterobimetallic (**5**). Addition of one molar equivalent of PR_3 to (**5**) gives the μ-hydrido platinum carbonyl (**7**) *via* the shortlived intermediate species (**6**). [(**7**) can also be obtained by the reaction of (**1**) with $Pt(C_2H_4)_2PR_3$.] Addition of one molar equivalent of PR_3 to (**7**) results in the rapid loss of CO from platinum and the formation of the bridged hydride (**3**) together with the formation of some (**2**).

The relative rate data for (**2**) $\rightleftarrows$ (**3**) rearrangements and the reactions of (**4**) (summarised in Scheme 1) are consistent with a 'platinum-assisted' CO labilization mechanism for the (**2**) → (**3**) rearrangement that involves PR_3 dissociation and the formation of a bridging carbonyl intermediate (**6**). Rearrangement of (**6**) to the μ-hydrido platinum carbonyl (**7**) which readily reacts with PR_3 to give the final μ-hydrido product has also been established. Furthermore when (**1**) (M = Cr) is treated with a large excess of $Pt(C_2H_4)(PPh_3)_2$ two, low-concentration, short-lived hydridic intermediates [in addition to (**2a**) and (**3a**)] are observed in the ^1H n.m.r. spectrum. These species have the same spectral characteristics as (**6**) and (**7**) which are also observed to be products from the reaction of (**5**) with one mole of PPh_3. These results strongly support route iii → v, Scheme 2, as the mechanism of CO labilization, though as yet a mechanism involving a formyl intermediate formed *via* reductive coupling of μ-CO and H (*i.e.* route iii → iv, Scheme 2) cannot be totally excluded.

Molecules of the type described here provide an insight into both co-operative metal-assisted CO substitution and hydride transfer mechanisms in heterobimetallic systems.

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