Unusual Hydrogen Transfer Pathways in a Re–Pt Heterobimetallic System
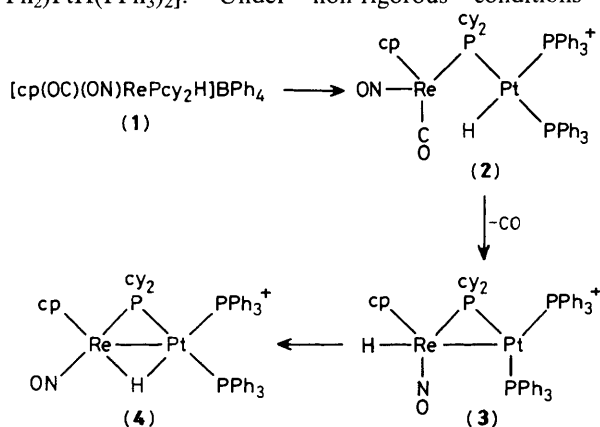
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The cation cis-[cp(OC)(ON)Re(μ-Pcy₂)PtH(PPh₃)₂]⁺ {obtained from the oxidative addition of [cp(OC)(ON)RePcy₂H]⁺ to Pt(C₂H₄)(PPh₃)₂; cp = cyclopentadienyl, cy = cyclohexyl} undergoes a base-catalysed proton transfer accompanied by CO loss to give a terminal rhenium–hydrido cation [cp(ON)HRe(μ-Pcy₂)Pt(PPh₃)₂]⁺ as the kinetically formed product, which, in the presence of halide ions (other than F⁻) isomerizes to the thermodynamically preferred product [cp(ON)Re(μ-Pcy₂)(μ-H)Pt(PPh₃)₂]⁺.

Studies of hydrogen atom transfer processes have played a basic and ubiquitous role in the development of organometallic chemistry. Given the current interest in heterometallic cluster chemistry[1,2] an analysis of the mechanistic aspects of H-transfer within such compounds is particularly topical.[3,4] We here report on the novel aspects of H-transfer and CO labilization in a heterobimetallic Re–Pt system.

The secondary phosphine rhenium complex [cp(OC)-(ON)RePcy₂H]BPh₄, (1), {cp = η⁵-C₅H₅; cy = cyclohexyl; prepared by a method analogous to that for [cp(OC)(ON)-RePPh₃]BF₄⁵}, reacts with Pt(C₂H₄)(PPh₃)₂ in CD₂Cl₂ to give the cationic μ-phosphido terminal platinum hydride (2). The structure of (2) is fully characterized by its spectroscopic data† which are very similar to those of cis-[(OC)₅W(μ-PPh₂)PtH(PPh₃)₂].[3] Under 'non-rigorous' conditions (2)

Figure 1. Molecular structure of [cp(ON)Re(μ-PPh₂)(μ-H)Pt(PPh₃)₂]⁺BF₄⁻ [μ-diphenylphosphido analogue of (4)] as determined by single crystal X-ray diffraction. Selected bond lengths (Å): Pt–Re 2.8673(4), Pt–P(1) 2.269(2), Pt–P(2) 2.255(2). Pt–P(3) 2.361(2). Re–P(2) 2.340(2), Pt–H(1) 2.21(6), Re–H(1) 1.57(6).

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† *Spectroscopic data* ¹H n.m.r. and ³¹P n.m.r. (p.p.m. relative to 85% H₃PO₄) δ (CD₂Cl₂), *J* in Hz. I.r. ν (CH₂Cl₂) cm⁻¹.

(2): hydrido region: δ(H) −6.91 [Pt–*H*, 1:4:1, t of ddd, *J*(*P*trans-H) 163, *J*(P*cis*-H) 17, *J*(Pphosphido) 19, *J*(¹⁹⁵PtH) 807]; ³¹P{¹H}: δ −10.8 [μ-phosphido, 1:4:1, t of dd, *J*(³¹P³¹P) 16, 288, *J*(¹⁹⁵Pt³¹P) 2190], 26.1 [*P*trans-H, 1:4:1 t of dd, *J*(³¹P³¹P) 16, 19, *J*(¹⁹⁵Pt³¹P) 2210], 15.9 [P*cis*-H, 1:4:1, t of dd, *J*(³¹P³¹P) 19, 288, *J*(¹⁹⁵Pt³¹P) 2350]; ν(CO) 1991, ν(NO) 1738.

(3): hydrido region: δ −7.72 [Re–*H*, 1:4:1, t of dd, *J*(³¹P¹H) 34, 7, *ca.* 0, *J*(¹⁹⁵PtH) 40]; ³¹P{¹H} δ 200.2 [μ-phosphido, 1:4:1, t of dd, *J*(³¹P³¹P) 8, 224, *J*(¹⁹⁵Pt³¹P) 2131], 23.7 [*P*trans-μ-phosphido, 1:4:1, t of dd, *J*(³¹P³¹P) 6, 224, *J*(¹⁹⁵Pt³¹P) 2842]; 23.8 [P*cis*-phosphido, 1:4:1, t of dd, *J*(³¹P³¹P) 6, 8, *J*(¹⁹⁵Pt³¹P) 3591]; ν(NO) 1705.

(5): hydrido region: δ −17.5 [Pt–*H*, 1.4:1, t of dd, *J*(³¹P¹H) 11, 14, *J*(¹⁹⁵PtH) 1308]; ν(CO) 1988, ν(NO) 1717.

(7): hydrido region: δ −5.00 [μ-H, 1:4:1, t of dd, *J*(³¹P¹H) 4, 29, *J*(¹⁹⁵PtH) 506]; ³¹P{¹H} δ 185.6 [μ-phosphido, 1:4:1, t of d, *J*(³¹P³¹P) 161, *J*(¹⁹⁵Pt³¹P) 1453], 13.2 [*P*trans-μ-phosphido, 1:4:1, t of d, *J*(³¹P³¹P) 161, *J*(¹⁹⁵Pt³¹P) 2445]; ν(CO) 2073, ν(NO) 1711.

(8): hydrido region: δ −7.57 [Re–H, 1:4:1, t of dd, *J*(³¹P¹H) 10, 34, *J*(¹⁹⁵PtH) 50]; ³¹P{¹H} δ 207.1 [μ-phosphido, 1:4:1, t of d, *J*(³¹P³¹P) 187, *J*(¹⁹⁵Pt³¹P) 1841], 21.4 [*P*trans-μ-phosphido, 1:4:1, t of d, *J*(³¹P³¹P) 187, *J*(¹⁹⁵Pt³¹P) 2778]; ν(CO) 2060, ν(NO) 1709.

(9): hydrido region: δ −7.15 [Re–H, 1:4:1, t of d, *J*(³¹P¹H) 33, *ca.* 0, *J*(¹⁹⁵PtH) 38]; ³¹P{¹H} δ 193.7 [μ-phosphido, *J*(³¹P³¹P) 12, *J*(¹⁹⁵PtP) 2362], 22.1 [P*cis*-μ-phosphido, *J*(³¹P³¹P) 12, *J*(¹⁹⁵Pt³¹P) 3386]; ν(CO) 2059, ν(NO) 1725.

Scheme 1. (See text for reaction conditions.)

Scheme 2

Scheme 3
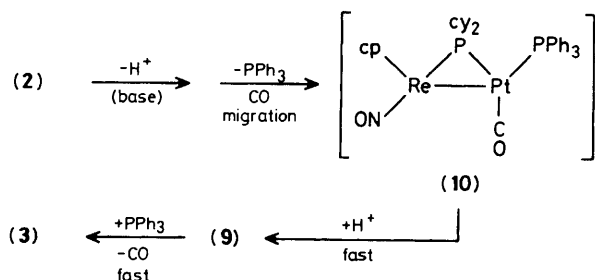
slowly transforms, with CO loss, to give the μ-phosphido *terminal* rhenium hydrido cation (3).† Particularly diagnostic of a terminal Re–H structure is the high field ¹H n.m.r. spectrum. The hydridic resonance of (3) exhibits small $J(^{195}\text{PtH})(40\text{ Hz})$ and $J(^{31}\text{PH})$ values (34, 7, and ca. 0 Hz) similar to those observed for the terminal (hydridic) cation $[\text{cp(OC)}_2\text{HW}(\mu\text{-PPh}_2)\text{Pt(CO)(PPh}_3)]^+$.[6] On standing (3) slowly isomerizes to the μ-phosphido-μ-hydrido species (4). The structure of (4) 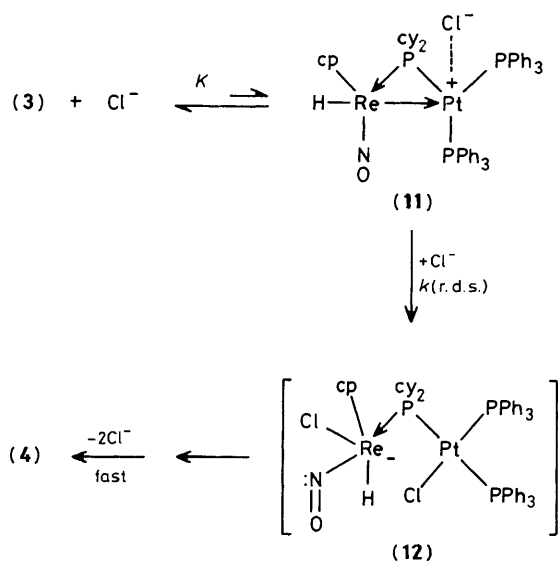as its BF_4^- salt, but with a μ-PPh₂ in place of μ-Pcy₂, has been confirmed by single crystal X-ray diffraction,‡ Figure 1.

Reaction of (2) with an excess of $[\text{Ph}_4\text{As}]\text{Cl}$ gives the neutral, stable hydride (5) in high yield.† Reaction of (5) with AgBF_4 or NaBPh_4 in CD_2Cl_2 (25 °C) results in the sequence of reactions outlined in Scheme 1. The initially formed μ-carbonyl species (6) [identified by i.r. $\nu(\mu\text{-CO})$ 1818; $\nu(\text{NO})$ 1740 cm⁻¹], rapidly rearranges to the μ-hydrido cation (7) (similar rearrangements have been observed in structurally analogous tungsten–platinum μ-phosphido systems[3]). The μ-hydrido cation (7) co-exists with a small amount of its terminal Re–H isomer (8) [ratio (7):(8) = ca. 4:1]. Over a period of of days (7) and (8) rearrange to the terminal Re–H cation (9). The structure and stereochemistry of (7), (8), and (9) are readily characterized by their i.r. and ¹H and ³¹P n.m.r. data.† The terminal Re–H cations (8) and (9) exhibit resonance patterns very similar to those of (3) and $[\text{cp(OC)}_2\text{HW}(\mu\text{-PPh}_2)\text{Pt(CO)PPh}_3]^+$.[6] The reaction sequences shown in Scheme 1 are not however the route by which (2) transforms into (3). The initially formed (7) and (8) (Scheme 1) react rapidly with PPh₃ to give a mixture of (4) and (3) in the ratio ca. 4:1 respectively, whilst under suitable

conditions (2) converts into (3) exclusively (see below). However the final thermodynamically preferred product (9) of Scheme 1, reacts instantly with PPh₃ to give (3) only. This suggests that (9) may be the precursor to the formation of (3) the production of which from (2) is clearly kinetically controlled.

Using carefully dried and degassed solvents (2) [formed from (1) and $(\text{C}_2\text{H}_4)\text{Pt(PPh}_3)_2]$ does *not* rearrange to (3). The (2) → (3) rearrangement is catalysed by the addition of non- or weakly-co-ordinating bases with relative rates for this reaction being base = F⁻ > pyridine > proton sponge. {The effectiveness of F⁻ as a deprotonating agent with regard to the cationic hydride $[\text{Mo(OC)}_2(\text{dpe})_2\text{H}]^+$ (dpe = $\text{Ph}_2\text{PCH}_2\text{-CH}_2\text{PPh}_2$) has been recently commented on.}[7] A plausible mechanism for the (2) → (3) rearrangement involves a base assisted proton transfer as outlined in Scheme 2. Deprotonation of (2) followed by CO transfer gives the short-lived intermediate (10) [analogous to the formation of the isolable species $\text{cp(OC)}_2\text{W}(\mu\text{-PPh}_2)\text{Pt(CO)(PPh}_3)^6$]. Re-protonation of (10) at Re to give the thermodynamically preferred (9) followed by fast PPh₃ substitution of CO would give (3).

Under similar carefully controlled conditions $(\text{CD}_2\text{Cl}_2,$ 25 °C) the terminal Re–H cation (3) is kinetically inert with respect to isomerization to the μ-hydrido cation (4) for several days. However the (3) → (4) rearrangement is promoted by the addition of halide ions (added as $[\text{Ph}_3\text{PNPPh}_3]^+\text{X}^-$) and can be essentially complete within 5 min. The relative rate for (3) → (4) is Cl⁻ > Br⁻ > I⁻ ≫ F⁻ (no effect). The ineffectiveness of F⁻ indicates that the rearrangement is not a simple base assisted proton transfer [cf. (2) → (3), Scheme 2 and ref. 7]. A more detailed analysis of the (3)/chloride system has shown the (3) → (4) reaction to be first order in (3) and *second order* in added chloride. No long-lived intermediates are observed by i.r. or n.m.r. spectroscopy and the reaction is not inhibited by a ten-fold excess of added PPh₃. [*N.b.* In contrast to (2), (4) does not react with an excess of Cl⁻ to give a neutral species structurally similar to (5).] These observations point toward a mechanism involving chloride co-ordination, but without PPh₃ displacement, for the (3) → (4) catalysed rearrangement. Since the addition of an excess of F⁻ has no effect on the Cl⁻ catalysed isomerization, a mechanism

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‡ *Crystal data:* $\text{C}_{53}\text{H}_{45}\text{BF}_4\text{NOP}_3\text{PtRe}$, M_r 1272.9, triclinic, space group $P\bar{1}$, $a = 12.563(2)$, $b = 12.896(1)$, $c = 15.024(2)$ Å, $\alpha = 94.14(1)$, $\beta = 96.93(2)$, $\gamma = 92.01(1)°$, $U = 2407$ Å³, $D_c = 1.76$ g cm⁻³ for $Z = 2$. Mo-$K_{\bar{\alpha}}$ Radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-}K_{\bar{\alpha}}) = 56.28$ cm⁻¹. Lattice parameters were derived from the setting angles of 25 reflections ($7.9 < \theta < 15.7°$) on an Enraf–Nonius CAD4 diffractometer. Data collection [ω—2θ scans; h, ±k, ±l quadrants with 2θ < 40°, h, ±k, ±l with $h \leqslant 7$ for $40 < 2\theta < 50°$; scan ranges: (0.85 + 0.35 tan θ)°, max. scan time: 80 s] gave 6380 reflections. The structure was solved by the use of the Patterson function for the heavy atoms, least-squares and Fourier calculations for the light atoms including the position of the bridging hydrogen. Least-squares refinements have converged (max. shift/error = 0.06) to $R_1 = 0.0310$ ($R_w = 0.0325$) for 4366 observed [$I > 3\sigma(I)$] reflections (phenyl ring carbon and hydrogen atoms with isotropic thermal parameters). Weights: $[\sigma^2(F) + 0.00033F^2]^{-1}$.

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

involving initial Cl^- co-ordination followed by a second Cl^- or F^- (base) promoted H^+ transfer step, [similar to (2) → (3), Scheme 2] can be excluded. A mechanism consistent with these unusual observations, *and a basis for further studies*, is given in Scheme 3. A weak ion pairing of Cl^- at Pt is postulated to give (11) in low concentration. In the rate determining step attack by a second Cl^- at Re generates a short lived Re^{III} 'bent nitrosyl' accompanied by loss of the Re–Pt bond to give the proposed platinum(II) chloride intermediate (12). Subsequent rapid substitution at Pt–Cl by Re–H followed by loss of Cl^- from Re gives the required product. For low concentrations of (11) and (12) Scheme 3 predicts a rate law of the type $-d[(3)]/dt = kK[(3)][Cl^-]^2$.

The above results serve to illustrate that hydrogen transfer and CO labilization reactions in heterometallic systems, which at first sight may be perceived to be a simple substitution process [*e.g.* 'substitution' of Re–CO by H–Pt effects (2) → (4)] may in fact involve far more complex reaction pathways.[3]

References

1 F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89.
2 W. L. Gladfelter and G. L. Geoffroy, *Adv. Organomet. Chem.*, 1980, **18**, 207.
3 J. Powell, M. R. Gregg, and J. F. Sawyer, *J. Chem. Soc., Chem. Commun.*, 1984, 1149.
4 M. Green, R. M. Mills, G. N. Pain, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 1321 and references therein.
5 W. Tam, G-Y. Lin, W-K. Wong, W. A. Kiel, V. K. Wong, and J. A. Gladysz, *J. Am. Chem. Soc.*, 1982, **104**, 141.
6 J. Powell, J. F. Sawyer, and S. J. Smith, preceding communication.
7 J. M. Hanckel and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1983, **105**, 6979.