Bridge *vs.* Terminal Protonation of Isostructural Mo–Pt and W–Pt Heterobimetallic Compounds

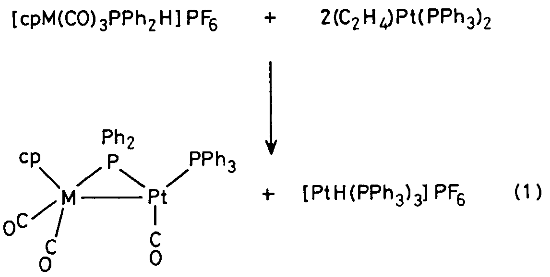
John Powell,* Jeffery F. Sawyer, and Stuart J. Smith

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Protonation of the complexes $cp(OC)_2\overline{M(\mu\text{-}PPh_2)Pt}(CO)(PPh_3)$ (cp = cyclopentadienyl) exhibits an M-dependent site selectivity, with protonation occurring at the metal–metal bond for M = Mo to give $[cp(OC)_2Mo(\mu\text{-}PPh_2)(\mu\text{-}H)\text{-}Pt(CO)PPh_3]^+$ whilst for M = W protonation occurs directly at the tungsten to give a terminal hydrido cation $[cp\text{-}(OC)_2H\overline{W(\mu\text{-}PPh_2)Pt}(CO)PPh_3]^+$.

Interest in the catalytic potential of metal clusters has helped focus attention on bridging hydrido species[1—3] many of which may be formed *via* the direct protonation of a metal–metal bond.[4] The recently developed isolobal theory, which provides a guide for heterometallic cluster synthesis,[5] and the protonation of such clusters,[4] together with protonation/deprotonation phenomena of mononuclear[6] and multinuclear[7,8] species are areas of active research. Of particular interest with respect to protonation of heterometallic clusters are those factors which may influence the preferred protonation site. This may be illustrated by a consideration of metal–metal bonded heterobimetallic complexes where, excluding direct ligand protonation, three potential protonation sites may be considered, namely, either of the two metal centres, or the metal–metal bond. Herein we report the first observation of a difference in site preference for the protonation of isostructural heterobimetallic complexes as illustrated by the reaction of the Mo–Pt and W–Pt bimetallic complexes (**1**) with HBF_4.

Complexes (**1**) are readily obtained from the reaction of $[cpM(CO)_3PPh_2H]PF_6$[9] (cp = cyclopentadienyl) with $(C_2H_4)Pt(PPh_3)_2$ according to equation (1). The molecular structure of (**1b**) as determined by single crystal *X*-ray diffraction, is shown in Figure 1.† Spectroscopic data for (**1a,b**) confirm that the molecules are isostructural and retain the structure shown in Figure 1 in solution.‡ Whilst molecules of (**1**) are not very basic they may be protonated by strong acids such as HBF_4 (CD_2Cl_2 solutions). The high field ^1H n.m.r. spectra reveal surprising differences (Mo *vs.* W) in the structures of the resultant hydrido cations. Protonation of (**1a**; M = Mo) occurs at the Mo–Pt bond to give the μ-hydrido cation (**2**) readily characterised by i.r. and n.m.r. spectroscopy.§ The ^1H n.m.r. parameters of the μ-hydrido ligand



(1)

(**1**)

a; M = Mo
b; M = W

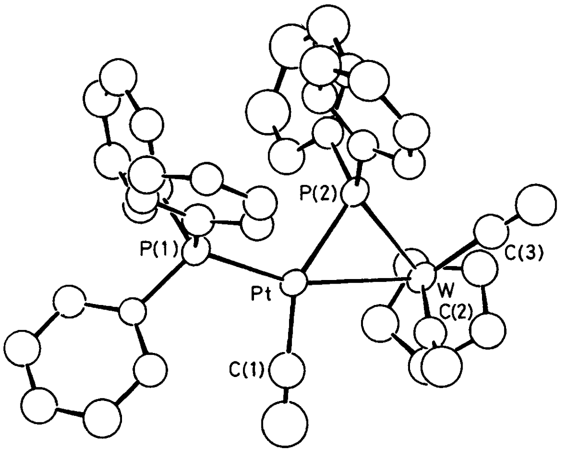


Figure 1. Molecular structure of (**1b**) as determined by single crystal *X*-ray diffraction. Selected bond lengths (Å); Pt–W 2.810(1), Pt–P(1) 2.312(3), Pt–P(2) 2.287(3), Pt–C(1) 1.848(13), W–P(1) 2.377(3), W–C(2) 1.896(11), W–C(3) 1.906(13). Selected bond angles (°): P(1)–Pt–P(2) 105.5, P(2)–Pt–W 54.5, W–Pt–C(1) 93.1, C(1)–Pt–P(1) 107.0, Pt–P(2)–W 74.0, Pt–W–P(2) 51.5, Pt–W–C(2) 78.1, Pt–W–C(3) 125.0.

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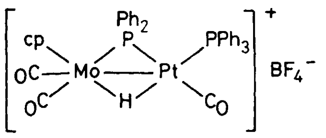
† *Crystal data* for (**1b**): $C_{38}H_{30}P_2PtO_3W$, M_r 975.6, triclinic, space group $P\bar{1}$, $a = 11.573(3)$, $b = 14.264(3)$, $c = 21.681(4)$ Å, $\alpha = 85.96(2)$, $\beta = 82.80(2)$, $\gamma = 70.65(2)°$, $U = 3349$ Å^3, $D_c = 1.94$ g cm^{-3} for $Z = 4$. (Two independent molecules related by a pseudo B centre.) Mo-$K_{\bar{\alpha}}$ Radiation ($\lambda = 0.71069$ Å), (Mo-$K_{\bar{\alpha}}$) = 78.5 cm^{-1}. Lattice parameters were derived from setting angles of 25 reflections ($4.8 < \theta < 15.1°$) on an Enraf–Nonius CAD4 diffractometer. Data collection [θ—2θ scans, h, ±, $\pm l$ quadrants, $2\theta < 50°$, scan range ($0.75 + 0.35 \tan\theta$)°, max. scan time: 65 s] gave 12 565 reflections. Lorentz, polarization, absorption and corrections for slight (5.3%) crystal decomposition were applied. The heavy atoms were located by direct methods and the remaining atoms in Fourier maps. Least-squares refinement has converged (max. shift/error = 0.11) to $R = 0.0487$ ($R_w = 0.0652$) for 7812 observed [$I > 3\sigma(I)$] reflections (Pt, W, and P anisotropic). Weights: $w = 4F^2/\sigma(F)^2$ where $\sigma(F)^2 = [\sigma(I)^2 + (0.065F^2)^2]$.

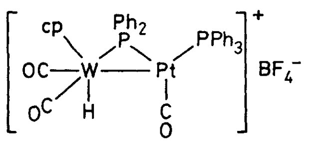
Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ *E.g.* Data for (**1a**): i.r. ν(CO) (CH_2Cl_2) 2018, 1911, and 1834 cm^{-1}; ^{31}P n.m.r. (relative to 85% H_3PO_4): δ(PPh_2) 177 p.p.m.; $J(^{195}Pt^{31}P)$ 2742; $J(PPh_2PPh_3)$ 11.4 Hz; δ(PPh_3) 30 p.p.m.; $J(^{195}Pt^{31}P)$ 3332 Hz. Data for (**1b**): i.r. ν(CO) (CH_2Cl_2) 2019, 1904, and 1824 cm^{-1}; ^{31}P n.m.r.: δ(PPh_2) 140 p.p.m.; $J(^{183}W^{31}P)$ 317; $J(^{195}Pt^{31}P)$ 2528; $J(^{31}P^{31}P)$ 18.9 Hz; δ(PPh_3) 21 p.p.m.; $J(^{183}W^{31}P)$ 0; $J(^{195}Pt^{31}P)$ 3271 Hz.

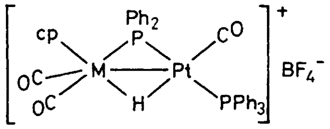
§ *Spectroscopic data* for (**2**) [(**3**) in square brackets]. ^1H N.m.r. and ^{31}P n.m.r. (p.p.m. relative to 85% H_3PO_4) δ (CD_2Cl_2), J in Hz. I.r. ν(CO) (CH_2Cl_2) cm^{-1}. δ(H) − 8.87 [−5.04], $J(PPh_3H)$ 65 [7.5], $J(PPh_2H)$ 29 [45], $J(^{195}PtH)$ 520 [85], $J(^{183}WH)$ – [42]; δ(PPh_2) 169 [119], J(PP) 7.2 [11.6], $J(^{195}PtP)$ 2202 [2272], $J(^{183}WP)$ – [202]; δ(PPh_3) 20 [26], $J(^{195}PtP)$ 3635 [3500]; ν(CO) (Pt) 2102 [2083]; ν(CO) (M) 1991, 1928 [2010, 1961].



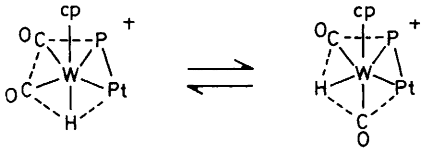
(2)



(3)

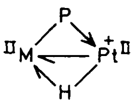


(4)
a; M = Mo
b; M = W

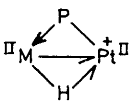


(2)

confirm[10,11] the structure of (**2**) as shown. On standing (**2**) isomerizes slowly (*ca.* 24 h at 25 °C) to the μ-hydrido cation (**4a**). In marked contrast to protonation of (**1a**), the isostructural tungsten–platinum dimer (**1b**) reacts with HBF_4 to give the hydrido cation (**3**) formulated as a terminal hydrido species (*i.e.*, protonation occurs directly at W rather than at the W–Pt bond). Support for this structure comes from the high field ^1H n.m.r. spectrum.§ Of particular significance are the very small spin–spin couplings of the hydride with ^{195}Pt (85 Hz) and with the ^{31}P of the platinum bonded PPh_3 (7.4 Hz). [*N.b.* The *cis* configuration of μ-PPh_2 and PPh_3 at Pt in (**3**) is confirmed by ^{31}P n.m.r.§ $J(^{195}Pt^1H)$ values are typically in the range 450—950 and 700—1400 Hz respectively for bridging and terminal platinum(II)-hydrido complexes, and $J(^{31}P$*trans*-H) coupling to a μ-hydride is generally in the range 60—110 Hz].[9,10] In contrast the $J(^{183}WH)$ (42 Hz) and $J(PPh_2H)$ (45 Hz; confirmed by proton coupled ^{31}P n.m.r.) values for (**3**) are of a similar magnitude to those of *cis* and *trans* $cpW(CO)_2(PPh_3)H$.[12] On cooling solutions of (**3**) to −90 °C, with the aim of assessing the possibility of conformational isomerism at W [*cf.* $cpW(CO)_2(PPh_3)H$], the values of $J(^{195}PtH)$ and $J(PPh_3H)$ were observed to decrease steadily to values of 45 and 2.9 Hz respectively. In contrast the $J(^{183}WH)$ and $J(PPh_2H)$ values remain essentially constant whilst δ(H) changes from −5.04 to −4.92 on cooling. This observation suggests a rapid equilibration (even at −90 °C) between two conformational isomers of (**3**) with relative ratios changing with temperature. One possibility, based on isomerism in a pseudo pentagonal pyramidal structure, is illustrated in equation (2). A second possibility could involve a rapid equilibration of (**3**) with a small amount of a μ-hydrido species structurally analogous to (**2**) with (**3**) being the dominant low temperature form. On prolonged standing, (**3**) isomerizes (*ca.* 2 weeks at 25 °C) to give the bridged hydrido complex (**4b**). Complexes (**2**), (**3**), and (**4**) react 'instantly' with PPh_3 to give the isolable μ-hydrido complexes $[cp(OC)_2M(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(Ph_3)_2]BF_4$ (M = Mo, W). On exposure to base (**2**), (**3**), and (**4**) revert to the neutral dimers (**1**).



(A)



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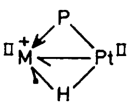

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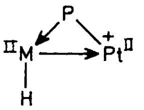

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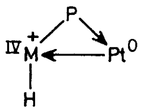

(E)

The preferred protonation at W in (**1b**), *vis à vis* protonation at the Mo–Pt bond in the isostructural (**1a**), can probably be related to (i) the greater bond strength of third row (W) *vs.* second row (Mo) M–H bonds;[11] (ii) the greater ease of oxidation at W *vs.* Mo; and (iii) the relative ease of reduction at platinum. This can be illustrated by a comparison of some possible bonding representations for metal–metal bond protonation, [*e.g.* (A)—(C)] with the representations (D) and (E) for protonation at a metal centre. Features (i)—(iii) would favour the terminal hydrido cation representation (E). The lower ν(CO) (Pt) and higher ν(CO)'s (W) of (**3**) *vs.* corresponding data for (**2**)§ are consistent with this view. [*N.b.* in (**1a,b**) and (**4a,b**) ν(CO) (Pt) are essentially the same (Mo *vs.* W) whilst ν(CO)'s (M) are lower for M = W *vs.* Mo].

Clearly factors (i)—(iii) leading to terminal *vs.* bridge protonation may be only found in a limited range of heterometallic clusters. However, a recognition of the potential for direct metal protonation in preference to the very frequently observed metal–metal bond protonation under certain circumstances has already been of significance in understanding and rationalising H-migration reactions in cationic heterometallic clusters.[13]

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