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Acidities of Platinum(II) μ-Hydroxo Complexes Bearing Diphosphine Ligands

U. Anandhi and Paul R. Sharp*

125 Chemistry, University of Missouri, Columbia, Missouri 65211

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The pK_a values in DMSO of the monoprotic complexes $[(L_2Pt)_2(\mu\text{-OH})(\mu\text{-NMePh})]^{2+}$ (**4**) (L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCMe_2PPh_2$ (dppip)) are 11.9 ± 0.1 (L_2 = dppe) and 13.5 ± 0.2 (L_2 = dppip) as determined by ^{31}P NMR equilibrium titration with bases of known pK_a. Complexes **4** were prepared by treatment of $[L_2Pt(\mu\text{-OH})]_2^{2+}$ (**1**) with *N*-methylaniline. The oxo complexes $[(L_2Pt)_2(\mu\text{-O})(\mu\text{-NMePh})]^+$, formed in the equilibrium titration reactions, were independently synthesized in THF by deprotonation of $[(L_2Pt)_2(\mu\text{-OH})(\mu\text{-NMePh})]^{2+}$ with $NaN(SiMe_3)_2$ and characterized as $NaBF_4$ adducts. Similar experiments with diprotic $[L_2Pt(\mu\text{-OH})]_2^{2+}$ (L_2 = dppe, $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp)) were complicated by exchange processes and were less conclusive, giving $pK_{a1} < 18$ and $pK_{a2} > 18$ in DMSO.

Introduction

Proton transfer is an important process in many areas of chemistry.[1−5] The tendency of a compound to undergo proton transfer is usually expressed in terms of its Brønsted acidity as indicated by the pK_a value for the compound. The pK_a value of a compound is also an indication of the basicity of its conjugate base. Late transition metal oxo and imido complexes have been noted, in many cases, to display reaction chemistry consistent with strong Brønsted basicity.[6−9] Strong nonaqueous bases are frequently used to deprotonate the conjugate hydroxo and amido complexes, a major synthetic route to late transition metal oxo and imido complexes, and reactions of oxo and imido complexes with weak acids frequently lead to protonation of the oxo or imido ligand.[10−13] To understand the chemistry of these complexes, a quantitative knowledge of the acidity of late transition metal hydroxo and amido complexes (i.e., pK_a values) is needed. In this paper, we report our efforts to determine the pK_a values of dinuclear platinum(II) bridging hydroxo complexes supported by phosphine ligands. We have chosen the nonprotic, polar solvent DMSO for these measurements for the following reasons: (1) The hydroxo and oxo complexes are readily soluble and stable in DMSO, (2) the strong solvating properties of DMSO reduce concerns about ion pairing effects, and (3) DMSO has been used extensively for pK_a determinations of very weak acids, giving a large selection of comparison acids for our measurements.[3,14,15] Successful pK_a determinations are reported along with the synthesis of new hydroxo and oxo complexes required to optimize the system behavior. Acetonitrile, another common nonaqueous, nonprotic solvent for pK_a measurements (see Discussion), could not be used because of poor stability of the oxo complexes in solution.

Results

Dihydroxo Complexes. We began this investigation with the diprotic dihydroxo complexes $[L_2Pt(\mu\text{-OH})]_2^{2+}$ (**1**) (L = a phosphine), which are known to be doubly deprotonated in THF by two or more equivalents of $MN(SiMe_3)_2$ (M =

* To whom correspondence should be addressed. E-mail: SharpP@missouri.edu.

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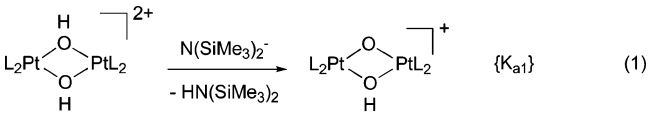
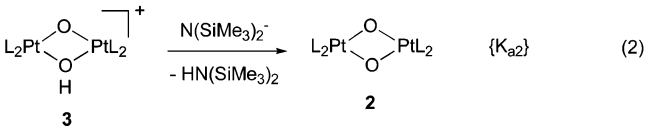
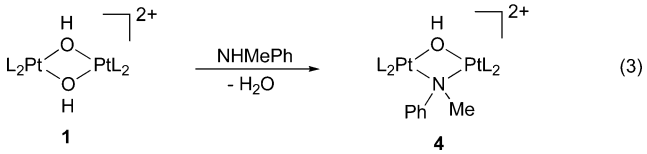
Li, Na, K) to give the dioxo complexes $[L_2Pt(\mu\text{-}O)]_2$ (**2**).[16−18] Presumably, this occurs in two separate steps, giving the hydroxo-oxo complexes $[(L_2Pt)_2(\mu\text{-}OH)(\mu\text{-}O)]^+$ (**3**) in the first deprotonation (eq 1) and the dioxo complexes **2** in the second deprotonation (eq 2). Each of these deprotonations will have an associated pK_a for the acid: pK_{a1} for the dihydroxo complex **1** and pK_{a2} for the oxo hydroxo complex **3**. Most likely, pK_{a2} is significantly greater than pK_{a1}.





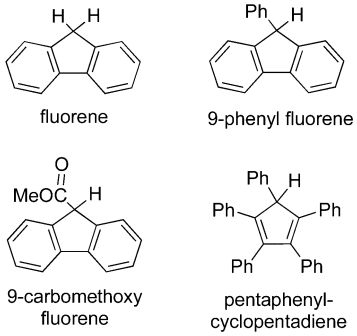
As in THF, double deprotonation of dihydroxo complex **1** (L_2 = dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) by 2 equiv of $MN(SiMe_3)_2$ is also observed in DMSO, indicating that pK_{a1} and pK_{a2} in DMSO are less than pK_a of $HN(SiMe_3)_2$, which is 26.[19] The fluorenyl anion (pK_a = 22 for fluorene),[3] also completely deprotonates **1** (L_2 = dppp) but the weaker base 9-phenyl fluorenyl anion, derived by deprotonation of 9-phenyl fluorene (pK_a = 17.9),[3] gives different results. (See Chart 1 for the structures of the acid form of the bases used in this study.) With excess 9-phenyl fluorenyl, two equal area doublets with satellites appear in the ^{31}P NMR spectrum. This same set of doublets, although considerably broadened, is observed in the reverse reaction of the dioxo complex $[(dppp)Pt(\mu\text{-}O)]_2$ (**2**) with excess 9-phenyl fluorene and in a 1:1 mixture of dioxo complex $[(dppp)Pt(\mu\text{-}O)]_2$ (**2**) and dihydroxo complex **1** (Scheme 1). We therefore assign these signals to the hydroxo-oxo complex $[(L_2Pt)_2(\mu\text{-}OH)(\mu\text{-}O)]^+$ (**3**) (L_2 = dppp). $^{195}Pt-^{31}P$ coupling constants are consistent with this formulation where one doublet, corresponding to the P trans to the strong donor oxo ligand, shows a small $^{195}Pt-^{31}P$ coupling constant of 2488 Hz and the other, trans to the weaker donor hydroxo ligand, shows a larger $^{195}Pt-^{31}P$ coupling constant of 3948 Hz. Unfortunately, attempts to isolate this complex have given only dihydroxo **1**. However, these observations indicate that 9-phenyl fluorenyl is capable of only the first deprotonation of $[L_2Pt(\mu\text{-}OH)]_2^{2+}$ **1** (L_2 = dppp) and that therefore $pK_{a1} < 18$ and $pK_{a2} > 18$. Similar results were obtained with **1** (L_2 = dppe = $Ph_2PCH_2CH_2PPh_2$) and the fluorenyl anion but the DMSO solutions are unstable and produce an unidentified precipitate.

Amido-Hydroxo Complexes. To simplify this system and to eliminate the broadness in the ^{31}P NMR spectra (attributed to proton exchange between the various solution species), we sought the preparation of more sterically hindered monoprotic analogues of the dihydroxo complexes. Steric hindrance would also protect the Pt centers from nucleophilic attack, which we thought might be causing the instability of the complexes in solution. The dihydroxo complexes are known to undergo aminolysis with primary amines giving amido complexes $[L_2Pt(\mu\text{-}NHR)]_2^{2+}$ and $[(L_2Pt)_2(\mu\text{-}OH)(\mu\text{-}NHR)]^{2+}$ where the amido groups can also be deprotonated.[20] Secondary amines should give amido complexes without ionizable hydrogen atoms. Treatment of $[L_2Pt(\mu\text{-}OH)]_2^{2+}$ (L_2 = dppip ($Ph_2PCMe_2PPh_2$), dppe) with *N*-methyl aniline readily yields the amido-hydroxo complexes $[(L_2Pt)_2(\mu\text{-}NMePh)(\mu\text{-}OH)]^{2+}$ (**4**) (eq 3, L_2 = dppip, dppe).



Spectroscopic data are consistent with the expected structure and are similar to the amido-hydroxo complexes derived from primary amines.[20] The ^{31}P NMR spectrum of isolated **4** (L_2 = dppe) in CH_2Cl_2 shows two doublets flanked by ^{195}Pt satellites. The small P−P coupling of 5 Hz is

Chart 1. Acid Form of the Bases Used in This Study (Ionizable Hydrogen Atoms Shown)



Scheme 1

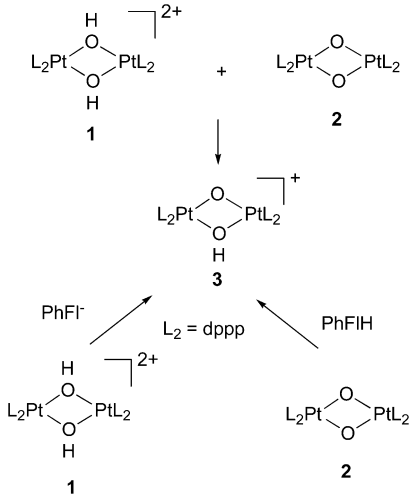


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Table 1. Crystallographic and Data Collection Parameters for **4** (L_2 = Dppe)

formula	$C_{59}H_{57}NOP_4Pt_2B_2F_8{\cdot}2CH_2Cl_2{\cdot}C_7H_8$	a, Å	12.9775(19)
fw	1745.72	b, Å	13.933(2)
space group	$P2_1/m$	c, Å	19.257(3)
V, Å^3	3478.6(9)	β, deg	92.492(2)
d_{calc}, g/cm^3	1.67	λ, Å	0.71070
μ, mm^{-1}	4.33	T, °C	−100
R1[a], wR2[b]	0.0306, 0.1028	Z	2

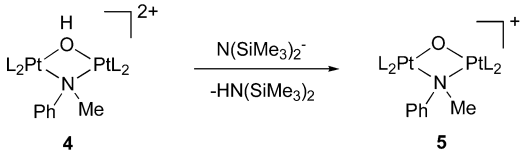
[a] $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [(\Sigma w(F_o^2 - F_c^2)^2)/\Sigma w(F_c^2)^2]^{1/2}$.

consistent with the *cis*-phosphine geometry at the Pt centers. The P−Pt coupling constants for **4** are similar in magnitude to those of related dihydroxo and diamido complexes.[17,18,20] The upfield doublet shows larger P−Pt coupling (3960 Hz) than the downfield doublet (2980 Hz) and is assigned to the P atom trans to the more weakly donating hydroxo group. The downfield doublet is then assigned to the P atom trans to the more strongly donating amido group. Changing the NMR solvent to DMSO markedly alters the appearance of the ^{31}P NMR spectrum of **4** (L_2 = dppe). Instead of two doublets only a singlet is observed. However, two sets of ^{195}Pt satellites are observed, yielding similar J_{Pt-P} values to those in CH_2Cl_2 and indicating that the ^{31}P NMR resonances for the phosphorus trans to the hydroxo group and the phosphorus trans to the amido group are accidentally coincident in DMSO.

The ^{31}P NMR spectrum of **4** (L_2 = dppip) in both DMSO and CH_2Cl_2 shows two doublets for the phosphorus atoms trans to the hydroxo group and the amido group. The small P−P coupling of 61 Hz is consistent with a *cis*-phosphine geometry at the Pt centers. Each doublet displays ^{195}Pt satellites with P−Pt coupling constants, indicative of a trans hydroxo and a trans amido group (3432 and 2518 Hz).

^{1}H NMR spectra of both derivatives of **4** in DMSO-d_6 show a broad triplet for the N-Me protons at 2.93 (L_2 = dppe) or 3.30 ppm (L_2 = dppip) and peaks corresponding to the chelated bidentate phosphine ligand. Decoupling experiments indicate that the triplet pattern is due to coupling of the methyl group to two of the phosphorus nuclei (presumably those trans to the amido group). The peak for the hydroxo group appears at −0.61 (L_2 = dppe) or 2.63 ppm (L_2 = dppip). The structure of **4** (L_2 = dppe) was confirmed by a single-crystal X-ray diffraction study (Table 1). A drawing of the cationic portion is shown in Figure 1. Metrical parameters are presented in Table 2 and closely resemble those of related complexes.[20]

Amido-Oxo Complexes. As anticipated, **4** are readily deprotonated by $NaN(SiMe_3)_2$ in THF or DMSO to give solutions of the amido-oxo complexes $[(L_2Pt)_2(\mu\text{-NMePh})(\mu\text{-O})]^+$ (**5**) (eq 4). Both complexes are isolated from THF and contain 1 equiv of $NaBF_4$ probably through oxo group adduct formation similar to $LiBF_4$ adducts isolated for related oxo complexes.[17,18,20]



4 **5** (4)

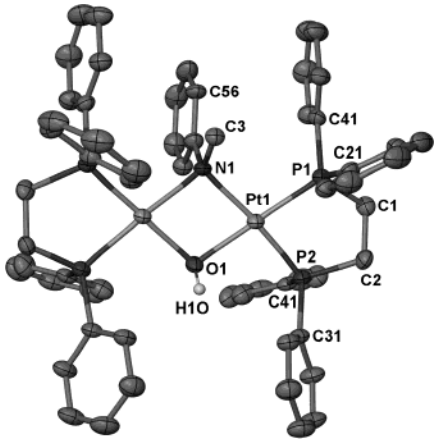


Figure 1. Thermal ellipsoid (50%) plot of the cationic portion of **4** (L = dppe). Labeled and unlabeled atoms are related by a mirror in the O1−N1−C3 plane. Hydrogen atoms (except H1O) have been omitted for clarity.

Table 2. Selected Distances (Å) and Angles (deg) for **4** (L_2 = Dppe)

Pt1−P1	2.2178(11)	Pt1−N1	2.138(3)
Pt1−P2	2.2353(11)	N1−C3	1.479(7)
Pt1−O1	2.100(3)	N1−C51	1.442(8)
P1−Pt1−P2	85.24(4)	O1−Pt1−N1	79.57(15)
O1−Pt1−P1	176.82(13)	Pt1−O1−Pt1	101.17(17)
N1−Pt1−P1	100.58(11)	Pt1−N1−Pt1	98.7(2)
O1−Pt1−P2	95.01(9)	C3−N1−Pt1	113.6(2)
N1−Pt1−P2	170.89(13)	C51−N1−C3	113.6(5)

The ^{31}P NMR spectrum of **5** (L_2 = dppe) in DMSO shows two singlets flanked by ^{195}Pt satellites. The cis coupling between the two phosphorus atoms is evidently too small to be observed. The ^{31}P NMR spectrum of **5** (L_2 = dppip) in DMSO shows a pair of doublets flanked by ^{195}Pt satellites. The cis coupling between the two phosphorus atoms (41 Hz) is 20 Hz less than the starting amido-hydroxo complex **4** (L_2 = dppe). For both derivatives, the phosphorus atom trans to the oxo group is assigned to the downfield resonances with the smaller P−Pt coupling constants (dppip: 2344 Hz, dppe: 2754 Hz) and the phosphorus atom trans to the amido group to the resonances with the larger coupling constants (dppip: 3185 Hz, dppe: 3436 Hz). The ^{1}H NMR spectra of **5** show peaks corresponding to the bidentate phosphine ligands and broad triplet N−Me peaks at 2.77 (L_2 = dppe) and 2.83 ppm (L_2 = dppip).

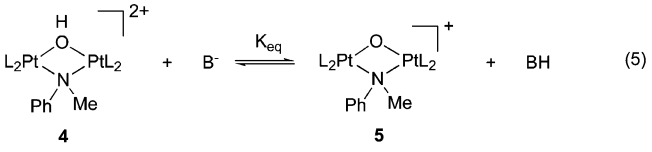
pK_a Determinations. The pK_a values for **4** are obtained by determining K_{eq} for the reaction shown in eq 5 when the pK_a for the acid BH is known (see Chart 1 for the structures of BH). The relevant mathematical relationships appear in eqs 6 and 7. The equilibrium ratios of **4** and **5** are obtained by ^{31}P NMR spectroscopy and from these the equilibrium concentrations of **4**, **5**, BH, and B^- are calculated given the initial concentrations. Practically, the pK_a for the acid BH must be similar (±2) to the pK_a of **4** to give modest K_{eq} values and reasonable concentrations of each species. Assuming that pK_{a1} of the dihydroxo complexes **1** is similar to the pK_a of **4**, our initial experiments suggest a pK_a for **4** of less than 18. This is born out by the complete deprotonation of **4** (L_2 = dppe, dppip) (i.e., K_{eq} is too large to measure) by fluorenyl anion (B^-), giving **5** and fluorene (pK_a = 22.6).[3] Similarly, 9-phenyl fluorenyl anion (pK_a = 17.9 for fluorene)[3] and 2,6-di-*tert*-butylphenoxy anion (pK_a = 16.85 for

Table 3. pK_a of **4** (DMSO, 25 °C)

$[(L_2Pt)_2(\mu\text{-NMePh})(\mu\text{-OH})]^{2+}$ **4**	pK_a[a]
L_2 = dppe	11.9 (0.1)[b]
L_2 = dppip	13.5 (0.2)[c]

[a] Average of 4 measurements, standard deviation in parentheses. [b] BH = 9-carbomethoxy fluorene (pK_a = 10.35). [c] BH = pentaphenylcylcopentadiene (pK_a = 12.5).

2,6-di-*tert*-butylphenol) give **5** and the organic acid with no detectable equilibrium, indicating that the pK_a for **4** is less than ca. 15. A detectable equilibrium mixture is finally obtained with the base 9-carbomethoxy fluorenyl anion (pK_a = 10.35)[3] for **4** (L_2 = dppe). Successive additions of this base allow multiple determinations of K_{eq}. The averaged value is given in Table 3. With time and with increasing concentrations of the base small additional peaks grow into the ^{31}P NMR spectra, indicating reactions other than deprotonation (probably attack of base at the platinum centers) are occurring. However, the extent of these reactions is small and does not significantly affect the determined pK_a values as shown by the good agreement between successive values (see Supporting Information). Poor stability of the solutions is more serious with acetate ion (pK_a = 12.3).[3] Sodium acetate addition to a DMSO solution of **4** (L_2 = dppe) gives **5** but the solution is unstable, yielding (dppe)Pt(OAc)$_2$.

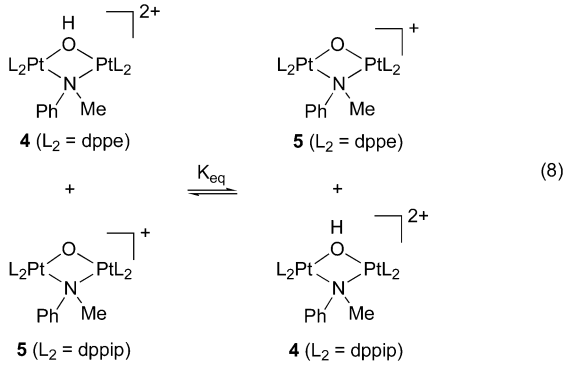


$$K_{eq} = K_a(\mathbf{4})/K_a(BH) \quad (6)$$

$$pK_a(\mathbf{4}) = pK_a(BH) - \log(K_{eq}) \quad (7)$$

In contrast to **4** (L_2 = dppe), 9-carbomethoxy fluorenyl does not deprotonate **4** (L_2 = dppip). This suggests that the dppip derivative has a higher pK_a than the dppe derivative and that bases with higher pK_a values are needed to observe equilibrium. Pentaphenylcyclopentadienyl (pK_a = 12.5)[3] is such a base and equilibrium is observed again, allowing multiple determinations of the pK_a (Supporting Information). As with the dppe derivative, there is good agreement between the successive values and the average is given in Table 3.

As a final check on the measurements, equilibrium mixtures of hydroxo **4** (L_2 = dppip) and oxo **5** (L_2 = dppe) were examined (eq 8). This gives a determination of the relative pK_a values for the two derivatives where $K_{eq} = K_a$(dppe)/K_a(dppip). Again, good agreement from successive measurements was observed with an average ΔpK_a (pK_a(dppe) − pK_a(dppip)) of −1.6 ± 0.1, in excellent agreement with the difference in the measured pK_a values (11.6 − 13.9 = −1.6).



Discussion

The synthesis of $[L_2Pt(\mu\text{-O})]_2$ (**2**) by deprotonation of the dihydroxo complex **1** with LiN(SiMe$_3$)$_2$ and the reaction chemistry of **2** suggested that **2** is highly basic and therefore **1** is a very weak acid.[17] We suspected that pK_{a1} for **1** was probably not more than a few pK_a units below that for HN(SiMe$_3$)$_2$ (pK_a = 26[19]). However, the poor solubility of **1** in the reaction solvent (THF) prevented an assessment of the pK_a values. This problem is eliminated in DMSO, which readily dissolves all of the complexes. Although we were unable to determine pK_{a1} values for **1**, they are probably very similar to the pK_a values for **4**.

Despite the unexpectedly low pK_a values for **4**, the values still indicate a basic μ-oxo complex relative to other μ-hydroxo complexes for which the pK_a has been determined. (Terminal hydroxo complex pK_a values are not comparable as these are generally expected to be higher than μ-hydroxo complexes.[21]) Two Mn complexes (**6** and **7**, Chart 2) that are structurally related to **1** and **4** in that they contain a M(μ-OH)$_2$M core have pK_{a1} values in MeCN of 11.5 and 6.5.[22,23] Comparisons of pK_a values of various organic acids, including cationic acids, in DMSO and MeCN show that pK_a values in MeCN are 6−10 units higher than those in DMSO.[3,24] Assuming that these results apply to the Mn complexes **6** and **7**, their pK_a values in DMSO should be far below those for **4**. Even pK_{a2} (13.4 in MeCN) for **7** should be below the pK_a values for **4**.[23] However, reducing **7** from a Mn(IV),Mn(IV) state to a Mn(III),Mn(IV) state increases pK_{a2} dramatically to 24.5 in MeCN, likely above the pK_a values for **4**. Reduction produces a neutral Mn(μ-OH)(μ-O)Mn complex while all the other Mn complexes are cationic and this likely contributes to the higher pK_{a2} value. Although not as structurally similar to **4**, complexes containing the adamantine-like $\{Mn_4O_6\}^{4+}$ core have pK_a values in MeCN that can range from 1.54 to 12.5[25] and a singly bridged μ-hydroxo Fe−Cu complex (**8**, Chart 2) has a pK_a value in MeCN between 16.7 and 17.6, which in DMSO would be below those of **4**.[26]

pK_a values for several other μ-hydroxo complexes have been measured in water.[25,27−34] Unfortunately, comparison

(21) For an example of a terminal hydroxo complex determination in DMSO see: Gupta, R.; Borovik, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 13234−13242.
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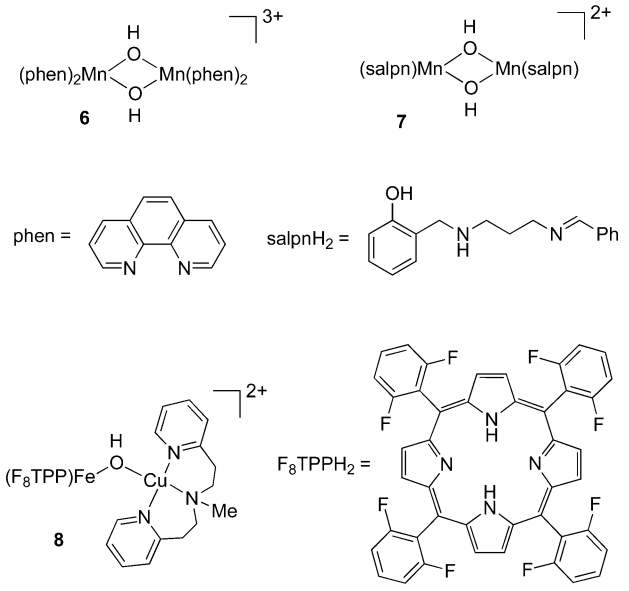
(26) Kopf, M.-A.; Neuhold, Y.-M.; Zuberbuehler, A. D.; Karlin, K. D. *Inorg. Chem.* **1999**, *38*, 3093−3102.
(27) Lebeau, E. L.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 6476−6484.

Chart 2



of these pK_a values with DMSO results are problematic since variations in hydrogen bonding can dramatically shift relative values.[3] For example, pK_a for $PhNH_3^+$ in water and DMSO differ by only one unit whereas acetic acid is a markedly weaker acid in DMSO with a pK_a of 12.3 versus 4.75 in water.[3]

Such dramatic changes in pK_a on transfer to water suggest the possibility that **4** and **1** could be much more acidic in water. Poor aqueous solubility prevents us from examining our platinum hydroxo complexes in water but the aqueous chemistry of the bipyridyl analogue of **1**, $[L_2Pt(\mu\text{-}OH)]_2^{2+}$ (L_2 = bpy), has been studied.[35] This dihydroxo complex is stable in neutral solution but on increasing the pH to 8 the yellow complex converts to a red complex. This red complex was assigned the tri-hydroxo bridged formulation $[(L_2Pt)_2(\mu\text{-}OH)_3]^+$ (L_2 = bpy) primarily on the basis of elemental analysis results. We propose that the complex should be reformulated as the hydroxo-oxo complex $[(L_2Pt)_2(\mu\text{-}OH)(\mu\text{-}O)]^+$ **3** (L_2 = bpy) formed by deprotonation of the dihydroxo complex. The elemental analysis data fit this formulation if a water of solvation is included. Future work in our group will attempt to confirm this proposed formulation.

One of the objectives of this work was to establish the effect of the diphosphine bite angle on the acidity of dinuclear platinum hydroxo and amido complexes.[36] Synthetic work by our group indicates a greater acidity for the diamido complexes $[L_2Pt(\mu\text{-}NHAr)]_2^{2+}$ with the small bite angle diphosphine, L_2 = dppip, over analogous complexes with larger bite angle diphosphines (L_2 = dppp, dppb).[18,20] The dppip derivatives are readily deprotonated by $LiN(SiMe_3)_2$ while the dppp and dppb derivatives are unreactive. However, this difference could result from either kinetic or thermodynamic factors. A kinetic acidity increase would be expected from decreased steric hindrance at the acidic centers. The single carbon bridge of dppip results in a retraction of the phosphorus phenyl groups away from the amido groups, allowing greater access to the acidic protons. The pK_a measurements on **4** do show a thermodynamic acidity difference between the dppip and the dppe complexes. However, it is in the opposite direction to that observed in the diamido complexes, strongly suggesting that the diamido differences are indeed kinetic with a steric origin.

The lower acidity of **4** with L_2 = dppip as compared to the dppe complex is consistent with a bite angle effect. Reducing the P−Pt−P angle of the L_2Pt fragment raises the energy of the occupied frontier orbital that are involved in bonding to the OH group.[37,38] This transfers more electron density to the OH group, decreasing its acidity as is observed. Another possible contributing factor in the lower acidity of the dppip derivative is the presence of the methyl groups on the bridging carbon atom of the dppip ligand. This should increase the electron donation from the phosphorus centers as compared to the dppe derivative. Greater electron donation results in a more electron-rich platinum center and more electron density on the OH group. Unfortunately, separation of these two factors by elimination of the methyl groups from dppip is not possible. Previous work on the dppm hydroxo complexes **1** (L_2 = dppm) has shown that the dppm methylene group of the complex is more readily deprotonated than the hydroxo groups.[17,39]

Finally, it should be noted that platinum oxo complexes, including **5**, are often, but not always,[20] isolated in association with Group 1 salts.[17,39] Interaction of the oxo complexes with these salts could influence the measured pK_a values. X-ray crystallography has revealed that in the solid-state Li ion coordinates to the oxo group of platinum oxo complexes. Similar interactions are likely for other Group 1 ions but are expected to weaken as the Group 1 ion size increases. Ion coordination to the oxo group is most likely also present in THF solution. Pt−P coupling constants in THF have been observed to decrease (~100 Hz) in the dioxo complexes $[L_2Pt(\mu\text{-}O)]_2$ (L = a phosphine) as the associated salt ion is changed from Li to Na.[17] A weaker Na ion interaction with the oxo group results in a more strongly donating oxo ligand, which in turn weakens the Pt−P bond trans to the oxo ligand. However, in more strongly donating solvents coordination of the group 1 ion by solvent molecules is expected to

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become more important and ultimately dominate. This is evident in the decrease (200 Hz) in the Pt−P coupling constant observed when the dioxo complex $[(dppp)Pt(\mu\text{-}O)]_2 \cdot 2LiOTf$ is dissolved in strongly solvating DMSO as compared to THF.[40] Data on **5** indicate a weak to nonexistent interaction with all group 1 ions in DMSO. Pt−P coupling constants trans to the oxo group are nearly invariant for **5** in the presence of Li (2757 Hz), Na (2754 Hz), or K (2745 Hz) ions. Furthermore, the Pt−P coupling constant of **5** in DMSO solution in the presence of K ions remains unchanged on addition of 18-crown-6, a strong binder of K ions.[41] Ion interactions with **5** in DMSO do not appear to be important in the pK_a values for **4** determined here.

Experimental Section

Experiments were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox. DMSO was dried according to the literature procedure.[42] Other solvents were dried by standard techniques and stored under dinitrogen over 4 Å molecular sieves or sodium metal. The precursor complexes **1** $[L_2\text{-}Pt(u\text{-}OH)]^{2+}$ (L_2 = dppe, dppip) were synthesized by known methods.[17,18] *N*-methyl aniline, $MN(SiMe_3)_2$ (M = Na, K), fluorene, 9-phenyl fluorene, 2,6-di-*tert*-butylphenol, and pentaphenylcyclopentadiene were obtained from commercial sources. 9-Carbomethoxy fluorene was prepared according to the reported procedure.[42] Bases were prepared by treating the neutral organic acids with 1 equiv of $KN(SiMe_3)_2$ in ether. The precipitated product was washed thoroughly with hexane or petroleum ether and dried in vacuo. NMR spectra were recorded on a Bruker AMX-250 spectrometer at 25 °C. Shifts are given in ppm with positive values downfield of TMS (^1H), external H_3PO_4 (^{31}P), or $CFCl_3$ (^{19}F). Desert Analytics performed the microanalyses (inert atmosphere). The presence of CH_2Cl_2 or THF of crystallization in the analyzed samples was confirmed by ^1H NMR spectroscopy in DMSO-d_6.

$[(dppe)_2Pt_2(\mu\text{-}NMeC_6H_4)(\mu\text{-}OH)](BF_4)_2$ (4) (L_2 = dppe). To a stirred solution of $[Pt(\mu\text{-}OH)(dppe)]_2(BF_4)_2$ (0.100 g, 0.0717 mmol) in 5 mL of CH_2Cl_2 is added *N*-methyl aniline (0.012 g, 0.11 mmol). The yellow solution is stirred overnight, concentrated under reduced pressure, filtered, and layered with an equal amount of toluene. Pale yellow crystals of the product, suitable for X-ray analysis, form overnight. Yield: 0.080 g (75%). ^{31}P $\{^1H\}$ NMR (DMSO): −34.1 (s, $^1J_{Pt-P}$ = 3740 Hz, $^1J_{Pt-P}$ = 2980 Hz). ^{31}P $\{^1H\}$ NMR (CH_2Cl_2): −37.1 (d, $^1J_{Pt-P}$ = 3960 Hz, $^2J_{P-P}$ = 5 Hz), −32.4 (d, $^1J_{Pt-P}$ = 2888 Hz, $^2J_{P-P}$ = 5 Hz). ^1H NMR (CD_2Cl_2): 7.79−6.58 (m, 45H, Ph), 2.93 (br t, $^4J_{P-H}$ = 5 Hz, N−Me, 3H), 1.77−2.83 (m, 8H, CH_2), −0.61 (s, 1H, OH). Anal. Calcd (Found) for $C_{59}H_{57}B_2F_8NOP_4Pt_2 \cdot 2CH_2Cl_2$: C, 44.29 (44.33); H, 3.72 (3.68); N, 0.848 (1.30).

$[(dppip)Pt_2(\mu\text{-}NMeC_6H_4)(\mu\text{-}OH)](BF_4)_2$ (4) (L_2 = dppip). The procedure is the same as that used for **2** (L_2 = dppip) except the white crystalline product is obtained by layering the reaction mixture with diethyl ether. Yield: 0.075 g (71%). ^{31}P $\{^1H\}$ NMR (DMSO): −27.4 (d, $^1J_{Pt-P}$ = 3432 Hz, $^2J_{P-P}$ = 61 Hz), −24.3 (d, $^1J_{Pt-P}$ = 2518 Hz, $^2J_{P-P}$ = 61 Hz). ^1H NMR (DMSO-d_6): 8.48−6.49 (m, 45H, Ph), 3.30 (t, $^4J_{P-H}$ = 5 Hz, 3H, N−Me), 2.63 (s, 1H, OH), 1.37 (t, $^3J_{P-H}$ = 17.5 Hz, 6H, CMe_2), 0.76 (t, $^3J_{P-H}$ = 17.5 Hz, 6H, CMe_2) Anal. Calcd (Found) for $C_{61}H_{61}B_2F_8NOP_4Pt_2 \cdot 2CH_2Cl_2$: C, 44.99 (44.99); H, 4.12 (3.89); N, 0.83 (0.68).

$[(dppe)_2Pt_2(\mu\text{-}NMePh)(\mu\text{-}O)](BF_4) \cdot NaBF_4$ (5) (L_2 = dppe). $NaN(SiMe_3)_2$ (0.009 g, 0.0491 mmol) in 1 mL of THF is added dropwise to a stirred suspension of $[(dppe)_2Pt_2(\mu\text{-}NMePh)(\mu\text{-}OH)](BF_4)_2$ (**4**) (0.050 g, 0.033 mmol) in 3 mL of THF. During the base addition the colorless suspension slowly becomes yellow and after complete addition a clear yellow solution forms. With continued stirring, the dark yellow crystalline product precipitates. This is filtered off, washed with petroleum ether, and dried in vacuo. Yield: 0.035 g (70%). ^{31}P $\{^1H\}$ NMR (THF): 35.8 (s with satellites, $^1J_{Pt-P}$ = 2768 Hz), 21.2 (s with satellites, $^1J_{Pt-P}$ = 3430 Hz). ^{31}P $\{^1H\}$ NMR (DMSO): 35.8 (s with satellites, $^1J_{Pt-P}$ = 2754 Hz), 21.2 (s with satellites, $^1J_{Pt-P}$ = 3436 Hz). ^1H NMR (CD_2Cl_2): 8.18−6.56 (m, 45H, Ph), 2.77 (br t, $^4J_{P-H}$ = 5 Hz, 3H, N−Me), 2.18 (br, 4H, CH_2), 1.80 (br, 4H, CH_2). ^{19}F $\{^1H\}$ NMR (DMSO): −154.1 (s, BF_4). Anal. Calcd (Found) for $C_{59}H_{56}B_2F_8NNaOP_4Pt_2 \cdot C_4H_8O$: C, 47.96 (47.93); H, 4.08 (3.89); N, 0.89 (1.16).

$[(dppip)_2Pt_2(\mu\text{-}NMeC_6H_4)(\mu\text{-}O)](BF_4) \cdot NaBF_4$ (5) (L_2 = dppip). The procedure is the same as that used for **5** (L_2 = dppe). Yield: 0.040 g (78%). ^{31}P $\{^1H\}$ NMR (DMSO): −14.7 (d, $^1J_{Pt-P}$ = 2344 Hz, $^2J_{P-P}$ = 40.5 Hz), −21.9 (d, $^1J_{Pt-P}$ = 3185 Hz, $^2J_{P-P}$ = 40.5 Hz). ^1H NMR (DMSO-d_6): 8.64−6.97 (m, 45H, Ph), 2.83 (br t, $^4J_{P-H}$ = 5 Hz, 3H, N−Me), 1.36 (t, $^3J_{P-H}$ = 15.0 Hz, 12H, CMe_2), 1.03 (t, $^3J_{P-H}$ = 15.0 Hz, 12H, CMe_2). ^{19}F $\{^1H\}$ NMR (DMSO): −148.1 (s, BF_4). Anal. Calcd (Found) for $C_{61}H_{60}B_2F_8NNaOP_4Pt_2 \cdot 0.5C_4H_8O$: C, 48.20 (48.18); H, 4.11 (3.93); N, 0.89 (1.24).

General Procedure for the pK_a Determinations. Solid hydroxo complex **4** (40−50 mg) was placed in a 5 mL vial and ca. 1.5 mL of DMSO was added to dissolve the solid. A portion of solid base was then added with stirring. After the base had dissolved, an NMR aliquot was removed and the ^{31}P NMR spectrum recorded. The aliquot was returned to the vial and another sample of the base added. An NMR aliquot was removed and the ^{31}P NMR spectrum recorded. This procedure was repeated until the ^{31}P NMR spectrum indicated almost complete conversion of **4** to **5**. The mmol of hydroxo complex **4** and oxo complex **5** present in the solution are calculated from the integrated intensity ratios. The amount of base consumed is determined by subtracting the amount of oxo complex formed from the total amount of base added. (See Tables S1 and S2 in the Supporting Information.)

Procedure for 4/5 (L_2 = dppe and dppip) Equilibrium Measurements. The procedure was similar to that described for the pK_a determinations except that oxo complex **5** (L = dppip) was added in place of the base to a solution of hydroxo complex **4** (dppe). The ratio of all species is given by NMR integration and is used to directly calculate the equilibrium constant. (See Table S3.)

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Supporting Information Available: X-ray crystallographic data for **4** (L_2 = dppe) in the form of CIF files and example ^{31}P NMR spectra and data for the equilibrium measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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