Control of ligand–metal interaction at the lower rim of *p*-*tert*-butylcalix[5]arene

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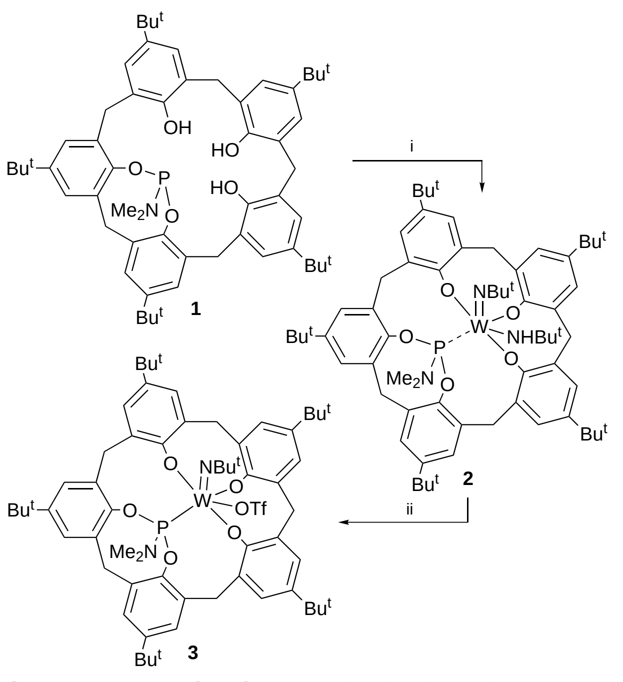
The lower rim of *p*-*tert*-butylcalix[5]arene is able to accommodate both a ligand and metal in close proximity allowing subtle electronic changes to dramatically affect ligand–metal interaction.

The ability to constrain the mobility of a ligand relative to a metal can have far-reaching applications from catalysis to molecular devices. This is particularly true when such systems can stabilize relatively weak ligand–metal interactions. Herein we report the synthesis of such a system based on a calix[5]arene and demonstrate the control of ligand–metal bonding *via* small electronic changes at the metal.

Treatment of *p*-*tert*-butylcalix[5]arene[1] with tris(dimethylamino)phosphine[2] inserts a Me_2NP moiety into the calixarene.† The ^1H NMR spectrum of **1** is consistent with the symmetry of the proposed structure: three singlets in the *tert*-butyl region in a 2 : 1 : 2 ratio and six doublets in the methylene region owing to the fact that the two hydrogens on each methylene carbon are non-equivalent. Also, the ^{31}P NMR signal at δ 131 is in the region for a three-coordinate phosphorus with two phenolic groups and a dialkylamino group.[3] If the cavity of the calix[5]arene is large enough, the three remaining hydroxyls should be able to bind a metal. In fact, insertion of tungsten proceeds smoothly by the reaction of **1** with $(Bu^tN)_2W(NHBu^t)_2$[4] *via* elimination of 2 moles of *tert*-butylamine (Scheme 1).‡ As expected, the ^1H NMR spectrum of **2** is similar to **1** in the *tert*-butyl and methylene regions. In addition, two new Bu^t singlets are present due to the tungsten-bound *tert*-butyl-amido and -imido ligands. The ^{31}P NMR signal at δ 116 is only 15 ppm upfield of **1**. More importantly, this signal shows a small coupling to W of 43 Hz, significantly smaller than usual $^1J_{PW}$ values.[5] This suggests a weak (through-space?) P–W interaction. Amido and imido ligands are known to be excellent π donors to high-oxidation-state metals.[6] If one of these ligands could be replaced with another that puts less electron density at the metal, this might increase the P–W interaction. This is exactly what occurs when triflate replaces *tert*-butylamido *via* the reaction of **2** with an excess of trifluoromethanesulfonic acid in refluxing toluene to give **3**.§ The $^1J_{PW}$ value in **3** of 352 Hz is in the usual range of P–W bonds which is indicative of a significantly stronger P–W interaction.

The X-ray crystal structures¶ of **2** and **3** substantiate the above spectral interpretations and provide detail on the structural changes associated with increasing the P–W interaction. The structures of **2** and **3** are illustrated in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in the captions. In **2**, the calix[5]arene backbone adopts a somewhat flattened conformation. The phosphorus has a distorted pyramidal geometry, while the tungsten adopts a distorted square-pyramidal geometry. The phosphorus lone pair is oriented towards the vacant sixth coordination site at the tungsten with a P···W distance of 3.15 Å, well outside the longest bond lengths reported for P–W bonds;[7] however, it is close enough to exhibit a small through-space PW coupling in the NMR spectrum. After



Scheme 1 *Reagents and conditions:* i, $+(Bu^tN)_2W(NHBu^t)_2$, $-2\ H_2NBu^t$; ii, excess HOTf, reflux, $-H_2NBu^t$

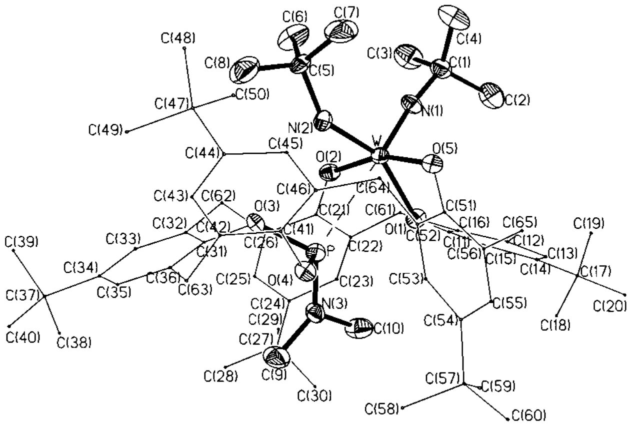


Fig. 1 Molecular structure and atom numbering scheme for **2**. Selected distances (Å) and angles (°): W–P 3.148(3), W–N(1) 1.714(8), W–N(2) 1.924(8), W–O(1) 1.961(7), W–O(2) 1.976(6), W–O(5) 1.972(7), P–N(3) 1.631(9), P–O(3) 1.645(7), P–O(4) 1.644(7), N(1)–C(1) 1.448(14), N(2)–C(5) 1.503(13), N(3)–C(9) 1.454(14), N(3)–C(10) 1.447(14); N(1)–W–P 178.0(3), N(2)–W–P 75.9(3), O(1)–W–P 76.0(2), O(5)–W–P 84.8(2), O(2)–W–P 79.5(2), N(1)–W–N(2) 102.7(4), N(1)–W–O(1) 105.3(4), N(2)–W–O(1) 151.8(3), N(1)–W–O(5) 96.7(3), N(2)–W–O(5) 95.4(3), O(1)–W–O(5) 83.9(3), N(1)–W–O(2) 99.2(3), N(2)–W–O(2) 90.4(3), O(1)–W–O(2) 82.7(3), O(5)–W–O(2) 161.4(3), W–P–O(3) 93.1(2), W–P–O(4) 129.4(3), W–P–N(3) 123.8(3), N(3)–P–O(4) 98.9(4), N(3)–P–O(3) 109.9(4), O(4)–P–O(3) 96.8(4), C(1)–N(1)–W 169.6(8), C(5)–N(2)–W 140.3(7), C(10)–N(3)–C(9), 112.6(9), C(10)–N(3)–P 120.1(7), C(9)–N(3)–P 127.0(7), C(11)–O(1)–W 139.6(6), C(21)–O(2)–W 136.2(6), C(51)–O(5)–W 125.8(6).

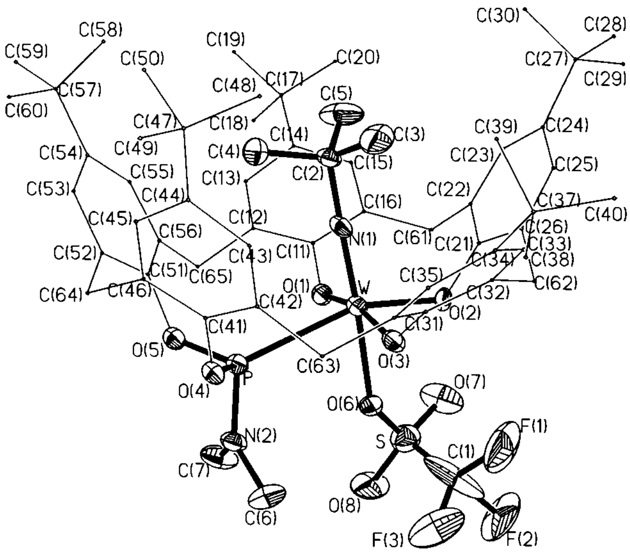


Fig. 2 Molecular structure and atom numbering scheme for **3**. Label for C(36) [carbon attached to C(31) and C(35)] omitted for clarity. Selected distances (Å) and angles (°): W–N(1) 1.725(7), W–O(2) 1.907(5), W–O(1) 1.936(6), W–O(3) 1.943(5), W–O(6) 2.188(6), W–P 2.743(2), P–O(5) 1.598(6), P–O(4) 1.616(6), P–N(2) 1.633(7), N(1)–C(2) 1.464(11), N(2)–C(6) 1.456(11), N(2)–C(7) 1.471(12); N(1)–W—O(2) 102.3(3), N(1)–W–O(1) 96.1(3), O(2)–W–O(1) 90.8(2), N(1)–W–O(3) 97.1(3), O(2)–W–O(3) 89.5(2), O(1)–W–O(3) 166.4(2), N(1)–W–O(6) 177.0(3), O(2)–W–O(6) 80.5(2), O(1)–W–O(6) 82.8(2), O(3)–W–O(6) 83.9(2), N(1)–W–P 99.5(2), O(2)–W–P 158.2(2), O(1)–W–P 86.9(2), O(3)–W–P 87.7(2), O(6)–W–P 77.7(2), O(5)–P–O(4) 106.6(3), O(5)–P–N(2) 97.6(3), O(4)–P–N(2) 99.9(3), O(5)–P–W 118.2(2), O(4)–P–W 118.0(2), N(2)–P–W 113.3(3), C(2)–N(1)–W 178.9(5), C(6)–N(2)–C(7) 113.6(8), C(6)–N(2)–P 121.6(7), C(7)–N(2)–P 121.8(6), C(11)–O(1)–W 133.2(5), C(21)–O(2)–W 123.4(5), C(31)–O(3)–W 134.0(5), S–O(6)–W 138.9(4).

ligand exchange, the calix[5]arene backbone in **3** adopts the cone conformation with the phosphorus bound to the tungsten at the 'lower' rim. The P–W distance is 2.74 Å which is long but still within reported ranges for P–W bonds. The triflate lies outside the cavity of the calixarene, while the imido is within the cavity. As expected, the W–O(6) (triflate) distance is longer than the other W–O distances, indicative of a more weakly bound group.

The structures of **2** and **3** also account for certain anomalies in their ^{1}H NMR spectra. The dimethylamino group resonance in **2** at δ 1.53 is about 1.5 ppm upfield of its usual position, and the (imido) *tert*-butyl group resonance in **3** at $\delta - 1.03$ is about 2 ppm upfield of its usual position. Figs. 1 and 2 show that the protons of these groups lie above and inside the aromatic rings of the calix[5]arene resulting in upfield ring current shifts for these signals.

We have demonstrated that a calix[5]arene is large enough to bind both a ligand and metal at the lower rim. Moreover, the macrocycle appears to orient the ligand and metal toward one another. This constraint supports both a weak and strong ligand–metal interaction, depending on the electron density at the metal. It may also be useful to view the tri-deprotonated form of **1** as a tetradentate ligand with three hard (oxygen) binding sites and one soft (phosphorus) binding site. Work is currently under way to determine how general this chemistry is by incorporating other metals and ligands.

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Footnotes and References

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† In an inert atmosphere, a stirred solution of *p-tert*-butylcalix[5]arene (0.765 g, 0.943 mmol) in toluene (30 ml) was treated dropwise with tris(dimethylamino)phosphine (0.154 g, 0.944 mmol). The mixture was stirred for 1 d. The volatiles were then pumped off and the resulting solid washed with hexane (3 × 2 ml) and pumped dry to yield **1** as a white, air- and moisture-stable solid (0.72 g, 86%). Analytically pure samples can be obtained by recrystallization from toluene to give **1**·C_6H_5Me. Mp 148–150 °C. Anal. Calc. for $C_{57}H_{74}NO_5P{\cdot}C_7H_8$: C, 78.73; H, 8.47. Found: C, 78.80; H, 8.39%. ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 18 H, Bu^t), 1.21 (s, 9 H, Bu^t), 1.29 (s, 18 H, Bu^t), 2.35 (s, 3 H, CH_3 of toluene), 2.96 (d, 6 H, NCH_3, $^3J_{PH}$ 10.2 Hz), 3.39 (d, 2 H, CH_2, $^2J_{HH}$ 14.9 Hz), 3.46 (d, 1 H, CH_2, $^2J_{HH}$ 13.6 Hz), 3.51 (d, 2 H, CH_2, $^2J_{HH}$ 14.2 Hz), 4.13 (d, 2 H, CH_2, $^2J_{HH}$ 14.1 Hz), 4.48 (d, 2 H, CH_2, $^2J_{HH}$ 14.8 Hz), 4.49 (br d, 1 H, CH_2, $^2J_{HH}$ *ca.* 14 Hz), 7.10–7.36 (m, 15 H, aromatic calix and toluene). ^{31}P NMR ($CDCl_3$): δ 131.

‡ In an inert atmosphere, a stirred solution of $(Bu^tN)_2W(NHBu^t)_2$ (0.396 g, 0.839 mmol) in toluene (20 ml) was treated dropwise with a solution of **1** (0.744 g, 0.841 mmol) in toluene (20 ml). The mixture was stirred for 3 d. The mixture was then filtered to remove a small amount of solid, and the volume of the filtrate was reduced to *ca.* 5 ml. A solid precipitated over a few days. This product was filtered and dried to yield **2**·C_6H_5Me as a yellow, crystalline, air-sensitive solid (0.649 g, 77%). Mp 270 °C (decomp.). Anal. Calc. for $C_{65}H_{90}N_3O_5PW{\cdot}C_7H_8$: C, 66.50; H, 7.60. Found: C, 66.14; H, 7.64%. ^{1}H NMR ($CDCl_3$): δ 1.12 (s, 18 H, Bu^t), 1.18 (s, 9 H, Bu^t), 1.33 (s, 18 H, Bu^t), 1.34 (s, 9 H, Bu^t), 1.36 (s, 9 H, Bu^t), 1.53 (d, 6 H, NCH_3, $^3J_{PH}$ 9.4 Hz), 2.34 (s, 3 H, CH_3 of toluene), 3.29 (d, 2 H, CH_2, $^2J_{HH}$ 13.9 Hz), 3.44 (d, 2 H, CH_2, $^2J_{HH}$ 15.8 Hz), 3.51 (d, 1 H, CH_2, $^2J_{HH}$ 15.5 Hz), 4.38 (d, 2 H, CH_2, $^2J_{HH}$ 13.8 Hz), 4.44 (d, 1 H, CH_2, $^2J_{HH}$ 15.3 Hz), 4.58 (d, 2 H, CH_2, $^2J_{HH}$ 15.7 Hz), 6.99–7.62 (m, 15 H, aromatic calix and toluene). ^{31}P NMR ($CDCl_3$): δ 116 ($^1J_{PW}$ 43 Hz). The toluene of crystallization can be removed by extended pumping.

§ In an inert atmosphere, a stirred solution of **2** (0.960 g, 0.795 mmol) in toluene (40 ml) was treated dropwise with trifluoromethanesulfonic acid (0.361 g, 2.41 mmol). The mixture was refluxed for 3 d. The mixture was then filtered to remove a small amount of solid, and the filtrate was pumped to dryness. The residue was recrystallized from toluene yielding **3**·0.5-C_6H_5Me as a red, air- and moisture-stable solid (0.65 g, 61%). Mp 343–345 (decomp.). Anal. Calc. for $C_{62}H_{80}F_3N_3O_8PSW{\cdot}0.5C_7H_8$: C, 59.10; H, 6.36. Found: C, 58.97; H, 6.63%. ^{1}H NMR ($CDCl_3$): δ −1.03 (s, 9 H, Bu^t), 1.16 (s, 18 H, Bu^t), 1.24 (s, 9 H, Bu^t), 1.30 (s, 18 H, Bu^t), 2.34 (s, 1.5 H, CH_3 of toluene), 3.28 (d, 6 H,NCH_3, $^3J_{PH}$ 9.7 Hz), 3.30 (d, 2 H, CH_2, $^2J_{HH}$ 13.1 Hz), 3.35 (d, 2 H, CH_2, $^2J_{HH}$ 13.7 Hz), 3.51 (d, 1 H, CH_2, $^2J_{HH}$ 13.4 Hz), 4.36 (dd, 1 H, CH_2, $^2J_{HH}$ 13.3, $^5J_{PH}$ 2.4 Hz), 4.52 (d, 2 H, CH_2, $^2J_{HH}$ 13.6 Hz), 4.70 (d, 2 H, CH_2, $^2J_{HH}$ 13.1 Hz), 7.11–7.50 (m, 12.5 H, aromatic calix and toluene). ^{31}P NMR ($CDCl_3$): δ 125 ($^1J_{PW}$ 352 Hz).

¶ *Crystal data*: **2**: $C_{65}H_{90}N_3O_5PW{\cdot}2C_7H_8$, $M = 1392.49$, triclinic, space group $P\bar{1}$, $a = 14.073(2)$, $b = 16.615(1)$, $c = 17.880(1)$ Å, $\alpha = 95.67(1)$, $\beta = 110.23(1)$, $\gamma = 105.49(1)$°, $U = 3694.9(6)$ Å^3, $Z = 2$, $T = 228(2)$ K, $\lambda = 0.71073$ Å, $D_c = 1.252$ g cm^{-3}, $\mu = 1.635$ mm^{-1}, for 7561 observed reflections $[I > 2\sigma(I)]$, $R_1 = 0.0484$, $wR_2 = 0.1245$.

3: $2(C_{62}H_{80}F_3N_2O_8PSW){\cdot}2C_7H_8{\cdot}0.5C_6H_6$, $M = 2793.64$, triclinic, space group $P\bar{1}$, $a = 13.282(3)$, $b = 23.909(3)$, $c = 25.770(3)$ Å, $\alpha = 115.844(7)$, $\beta = 101.995(12)$, $\gamma = 94.853(12)$°, $U = 7060(2)$ Å^3, $Z = 2$, $T = 228(2)$ K, $\lambda = 0.71073$ Å, $D_c = 1.314$ g cm^{-3}, $\mu = 1.748$ mm^{-1}, for 12 959 observed reflections $[I > 2\sigma(I)]$, $R_1 = 0.0460$, $wR_2 = 0.1072$.

Both structures were refined on F^2 (SHELX93, G. M. Sheldrick, 1993, University of Göttingen, Germany). CCDC 182/656.

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