affinity is demonstrated for compounds **2** and **3**, no conclusions can be drawn regarding the role of iodine or the C-4 stereochemistry in the sequence specificity of calicheamicin $\gamma_1{}^I$. The simple footprinting techniques used to determine these interactions and the power of synthesis to produce a variety of oligosaccharides and glycopeptides should facilitate further studies in this new and important area of molecular recognition.[12]

(12) A number of partial oligosaccharide fragments of calicheamicin $\gamma_1{}^I$ were studied using the footprinting techniques described in this paper, and in each case no specific binding was observed.

Reversible Formation of (μ-H)Ru₄(CO)₁₀(μ-PPh₂)[μ₄-η¹(P),η¹(P),η¹(P),η¹,η²-{C₆H₄}PPh] from the Electron-Rich Cluster Ru₄(CO)₁₃(μ-PPh₂)₂: The First Example of a Molecule with a Five-Coordinate Bis(aryl)phosphido Bridge
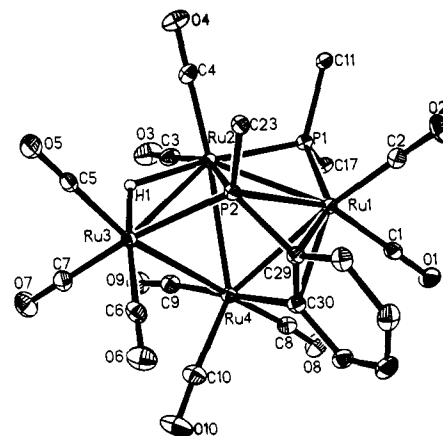
John F. Corrigan, Simon Doherty, Nicholas J. Taylor, and Arthur J. Carty*

Guelph–Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo Ontario, Canada N2L 3G1

Bridging five-coordinate phosphines and phosphido ligands have long been implicated as intermediates in organometallic processes, including ligand exchange.[1] Yet to date only one example of a μ_2- or μ_3-PR₃ ligand has been reported.[2] By analogy, five-coordinate μ_3-phosphido (μ_3-PR₂) groups should be accessible from their μ_2-counterparts. While exploring the chemistry of the electron-rich cluster Ru₄(CO)₁₃(μ_2-PPh₂)₂ (**1**),[3,4] we discovered a remarkably facile transformation via overall two-electron loss to the novel molecule (μ-H)Ru₄(CO)₁₀(μ-PPh₂)[μ₄-η¹(P),η¹(P),η¹(P),η¹,η²-{C₆H₄}PPh] (**2**). Cluster **2** contains an example of a five-coordinate phosphido bridge bound simultaneously to three metal atoms. We also describe a unique, reversible phosphido orthometalation and η^2-arene coordination process.

Heating an *n*-heptane suspension of **1** at reflux for 5–6 h results in a remarkably smooth conversion to a single brown product **2**[5] in near-quantitative yield (90%) (Scheme I). The $^{31}P\{^1H\}$ NMR spectrum[6] of **2** at 298 K consists of two singlet resonances, one at low field ($\delta = 214.31$ ppm) the other at high field ($\delta = 59.57$ ppm) relative to those of the parent cluster **1** ($\delta = 119$ ppm). The high-field resonance in **1** reflects a considerable elongation of the

(1) (a) Crowte, R. J.; Evans, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1332. (b) Bradford, A. M.; Douglas, G.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 409 and references therein. (c) Chi, Y.; Hsu, H. F.; Liu, L. K.; Peng, S. M.; Lee, G. H. *Organometallics* **1992**, *11*, 1763.

(2) Balch, A. L.; Davis, B. J.; Olmsted, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 8592.

(3) Hogarth, G.; Phillips, J. A.; van Gastel, F.; Taylor, N. J.; Marder, T. B.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1570.

(4) Hogarth, G.; Hadj-Bagheri, N.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1352.

(5) Data for **2**: ^1H NMR (CDCl₃, 298 K, δ) 8.12 (d, 1 H, $^3J_{PH} = 7.9$ Hz, H ortho), 7.67 (m, 6 H, H ortho), 7.25 (m, 12 H, phenyl), −14.06 (broad t, 1 H, M*H*M); ^1H NMR (CD₂Cl₂, 196 K, δ) 6.9–8.2 (m, phenyl), −11.13 (t, $^2J_{PH} = 23.0$ Hz, M*H*M), −20.05 (d, $^2J_{PH} = 16.4$ Hz, M*H*M). Anal. Calcd for C₃₄H₂₀O₁₀P₂Ru₄: C, 38.72; H, 1.91. Found: C, 38.72; H, 1.90.

(6) Data for **2**: $^{31}P\{^1H\}$ NMR (CD₂Cl₂, 298 K, δ) 214.31 (s, br, μ-PPh₂), 59.57 (s, br, P(C₆H₄)Ph); (193 K, δ) isomer A 211.83 (s, μ-PPh₂), 38.34 (s, μ-PPhC₆H₄), isomer B 199.26 (d, $^2J_{PP} = 26.5$ Hz, μ-PPh₂), 91.64 (d, $^2J_{PP} = 26.5$ Hz, μ-PPhC₆H₄).

Figure 1. Perspective view of the molecular structure of (μ-H)Ru₄(CO)₁₀(μ-PPh₂)[μ₄-η¹(P),η¹(P),η¹(P),η¹,η²-{C₆H₄}PPh] (**2**) showing the atomic numbering. For clarity, only the ipso carbon atoms of the noninteracting phenyl rings are shown. Selected bond lengths and angles: Ru(1)–Ru(2) = 2.829 (1) Å, Ru(1)–Ru(4) = 2.905 (1) Å, Ru(3)–Ru(4) = 2.885 (1) Å, Ru(2)–Ru(4) = 2.916 (1) Å, Ru(2)–Ru(3) = 2.908 (1) Å; Ru(1)–P(2)–Ru(3) = 121.6 (1)°, Ru(1)–P(2)–Ru(2) = 68.3 (1)°, Ru(2)–P(2)–Ru(3) = 74.6 (1)°, Ru(1)–P(2)–C(29) = 61.4 (1)°, Ru(3)–P(2)–C(20) = 111.9 (1)°.

Scheme I[a]

        1   **2**
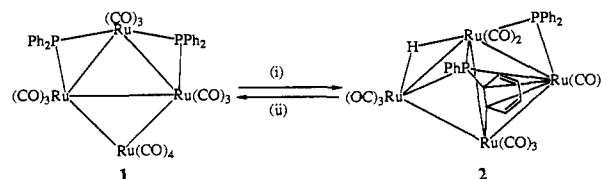
[a] Reagents: (i) 97 °C, *n*-heptane; (ii) CO, 60 °C, *n*-hexane.

Ru–Ru vectors bridged by the phosphido ligands,[3] a fact consistent with the unusual electronic structure of this flat 64-electron butterfly cluster.[7] Thus, the lower field ^{31}P shift of **2** was confidently attributed to the formation of an electron-precise structure containing a μ-PPh₂ group bridging a normal metal–metal bond.[4] Conversely, the remaining ^{31}P resonance suggested a severe structural rearrangement at this phosphorus atom. These spectroscopic features coupled with the observation that the conversion of **1** to **2** is reversible (vide infra) prompted a single-crystal X-ray study. The molecular structure (Figure 1)[8] identifies **2** as (μ-H)Ru₄(CO)₁₀(μ-PPh₂)[μ₄-η¹(P),η¹(P),η¹(P),η¹,η²-{C₆H₄}PPh]. With a 62-electron count the butterfly structure of **2** is compatible with the polyhedral skeletal electron count. The net loss of two electrons from **1** yields a framework with metal–metal bond lengths [2.828 (1)–2.910 (1) Å] and a dihedral angle [117.9°] more consistent with other butterfly structures.[9] The reduction in the phosphido-bridged Ru–Ru bond length [Ru(1)–Ru(2) = 2.828 (1) Å] accounts for the low-field ^{31}P shift of the μ-PPh₂ bridge P(1) [$\delta = 214.31$].[10]

The most unusual features of **2** are the triply bridging nature of the phosphido ligand P(2) [Ru(1)–P(2) = 2.567 (1), Ru-

(7) Mealli, C.; Proserpio, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5484.

(8) Deep brown crystals of (H)Ru₄(CO)₁₀[P{C₆H₄}Ph] **2** from (C₂H₅)₂O at 298 K are triclinic, space group $P\bar{1}$, with $a = 10.287$ (1) Å, $b = 11.122$ (1) Å, $c = 15.934$ (1) Å, $\alpha = 89.67$ (1)°, $\beta = 81.66$ (1)°, and $\gamma = 81.11$ (1)° at 150 K, $V = 1781.3$ (4) Å³, $d_{calcd} = 1.966$ g cm⁻³, and $Z = 2$. Data were collected via ω scans on an LT2-equipped Nicolet-Siemens R3m/V diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation in the 2θ range 4.0–55°. A total of 8238 reflections were collected, of which 7350 were observed [$F > 6.0\sigma(F)$]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to yield $R = 0.0202$ and $R_w = 0.0261$.

(9) (a) Sappa, E.; Tiripicchio, A.; Toogood, G. E.; Carty, A. J. *Prog. Inorg. Chem.* **1987**, *35*, 407. (b) Rossi, S.; Pursiainen, J.; Pakkanen, T. A. *Organometallics* **1991**, *10*, 1390.

(10) Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quinn, L. D., Eds.; VCH Publishers, Inc.: New York, 1987; Chapter 16, p 605.

(2)–P(2) = 2.478 (1), and Ru(3)–P(2) = 2.316 (1) Å] and the overall five-coordinate stereochemistry at phosphorus. Apart from the three metal atoms, the two remaining coordination sites at P(2) are occupied by two phenyl rings, one of which has undergone metalation [Ru(4)–C(30) = 2.151 (3) Å] and formation of an η^2-arene interaction to Ru(1) [Ru(1)–C(30) = 2.327 (3) and Ru(1)–C(29) = 2.335 (3) Å]. The stereochemical change at P(2) is best described as a transformation from tetrahedral to square-pyramidal geometry. The Ru–P bond lengths associated with this novel coordination mode are slightly longer than those found for normal μ_2-phosphido-bridged clusters.[3,10]

While the μ_3-phosphido metal bonding in 2 is unprecedented for a bis(aryl)phosphido group, there are a few examples of compounds in the literature where *weaker* secondary interactions to μ_2-PR$_2$ ligands have been demonstrated. Two clusters, (H)-Ru$_3$(CO)$_9$(μ-PPh$_2$)[11] and an iron analogue HFe$_3$(CO)$_9$[μ-P-(C$_6$H$_4$OMe)(CH$_2$C$_6$H$_5$)],[12] may have weak M···P contacts with a third metal site; HRu$_3$Rh(μ-CO)(CO)$_6$(PPh$_3$)$_2$[μ-P(C$_6$H$_4$)Ph][13] has a long Rh···P (phosphido) contact, and Fe$_3$(CO)$_{10}$(μ-RP=CH$_2$)[14] contains a coordinatively stabilized phosphaalkene. Finally, insertion of alkynes into metal–phosphinidene (μ_3- or μ_4-RP) bonds affords μ-RP{C(R)C(R')} ligands related to that in 2.[15]

The ^{13}C NMR shifts of the η^1,η^2-bound phenyl ring [δ = 98.52 d ($^2J_{PC}$ = 36.8 Hz) C(29), δ = 143.7 dd ($^2J_{PC}$ = 40.0, 4.9 Hz) C(30)][16] are typical of C$_\beta$ and C$_\alpha$ shifts for σ–π-bound alkenyl ligands. In solution, 2 undergoes a dynamic exchange process which can be frozen out at 193 K. The two isomers (ratio 45:55)[6] differ in the location of the hydride along the Ru(2)–Ru(3) or Ru(3)–Ru(4) edges.[5]

Heating a C$_6$H$_{14}$ solution of 2 at 60 °C under a CO purge reforms 1 in high yield (Scheme I). Although the involvement of bridging ligands via C–H or C–P activation during reactions performed under forcing conditions is well documented,[17] very few examples of facile reversibility of these reaction types are known.[18] The reversibility of the present ortho-metalation and η^2-arene transformation, under mild conditions, is notable. The demonstration of a triply bridging mode for a phosphido group in 2 provides additional evidence to support the involvement of five-coordinate μ-PR$_2$ ligands in ligand-exchange processes and skeletal rearrangements in phosphido bridge containing clusters.

(11) (a) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Can. J. Chem.* **1982**, *60*, 87. (b) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 392.

(12) Knoll, K.; Huttner, G.; Zsolnai, L.; Orama, O.; Wasiucionek, M. *J. Organomet. Chem.* **1986**, *310*, 225.

(13) Jungbluth, H.; Suss-Fink, G.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1990**, *9*, 1670.

(14) Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 739.

(15) Knoll, K.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743 and references therein.

(16) ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K, δ): 202.5 (d, CO, $^2J_{PC}$ = 8.32 Hz), 202.2 (d, CO, $^2J_{PC}$ = 10.4 Hz), 199.8 (d, CO, $^2J_{PC}$ = 17.6 Hz), 197.9 (d, CO, $^2J_{PC}$ = 33.2 Hz), 195.2 (s, CO), 192.2 (s, CO), 191.8 (d, CO, $^2J_{PC}$ = 13.5 Hz), 188.5 (d, CO, $^2J_{PC}$ = 12.4 Hz), 188.2 (t, CO, $^2J_{PC}$ = 10.1 Hz), 153.3 (d, C ipso, $^1J_{PC}$ = 27.1 Hz), 149.58 (d, C ortho, $^2J_{PC}$ = 16.6 Hz), 145.1 (d, C ipso, $^1J_{PC}$ = 33.4 Hz), 143.7 (dd, C ortho, $^2J_{PC}$ = 40.0 Hz, $^2J_{PC}$ = 4.4 Hz), 142.42 (d, C meta, $^3J_{PC}$ = 8.8 Hz), 138.8 (d, C ipso, $^2J_{PC}$ = 27.1 Hz), 133.6 (d, C ortho, $^2J_{PC}$ = 11.4 Hz), 132.80 (d, C ortho, $^2J_{PC}$ = 11.4 Hz), 132.04 (d, C ortho, $^2J_{PC}$ = 11.43 Hz), 130.78 (s, C para), 129.8 (d, C meta, $^2J_{PC}$ = 11.4 Hz), 128.3–128.9 (phenyl region), 124.3 (s, C para), 98.52 (d, C ipso, $^1J_{PC}$ = 36.8 Hz).

(17) (a) Clucas, J. A.; Foster, D. F.; Harding, M. M.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1984**, 949. (b) Bergoumhou, C.; Bonnet, J. J.; Fompeyrine, P.; Lavigne, G.; Lugan, N.; Mansilla, F. *Organometallics* **1986**, *5*, 60. (c) van Gastel, F.; Taylor, N. J.; Carty, A. J. *Inorg. Chem.* **1989**, *28*, 384.

(18) Colbran, S. B.; Irele, P. T.; Johnson, B. F. G.; Lahoz, F. J.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 2023.

Double Partial Cone Conformation for Na8{calix[6]arene sulfonate}·20.5H2O and Its Parent Acid

Jerry L. Atwood,*[1a] David L. Clark,*[1b]
Ravindra K. Juneja,[1a] G. William Orr,[1a]
Kerry D. Robinson,[1a] and Rebecca L. Vincent[1a]

*Department of Chemistry, University of Alabama
Tuscaloosa, Alabama 35487
Isotope and Nuclear Chemistry Division
Los Alamos National Laboratory
Mail Stop G739, Los Alamos, New Mexico 87545*

Received March 25, 1992

The chemistry of calixarenes has recently become a very active area of endeavor.[2-5] Of the numerous stimulating findings to appear thus far in the literature, one of the most intriguing concerns the discovery of certain uranophiles by Shinkai.[6,7] It was reported that calix[5]arene sulfonate, calix[6]arene sulfonate, and the two corresponding derivatives substituted at the base by carboxymethoxy groups, 1 with R' = CH$_2$COOH, exhibited stability constants for the uranyl ion of $K = 10^{18.4-19.2}$. Indeed, in competition experiments these calixarenes showed selectivity factors of 10^{12-17} for uranyl over the Ni^{2+}, Zn^{2+}, and Cu^{2+} ions. This selectivity was attributed to a moderately rigid calix[6]arene structure which was preorganized to match the rather unusual pseudoplanar hexacoordination needs of the UO$_2^{2+}$ ion[6,7] as shown in 2. However, on the basis of this study this premise appears untenable.
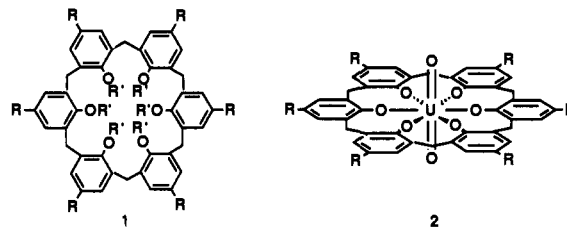
Considering the importance of the abovementioned findings, the structural chemistry of derivatives of calix[6]arene has been slow to develop. In the available selection[8-14] it is difficult to find

(1) (a) University of Alabama. (b) Los Alamos National Laboratory.

(2) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, England, 1989.

(3) *Calixarenes: a Versatile Class of Macrocyclic Compounds*; Bohmer, V., Vicens, J., Eds.; Kluwer: Dordrecht, The Netherlands 1990.

(4) Andreetti, G. D.; Ugozzoli, F.; Ungaro, R.; Pochini, A. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: Oxford, 1991; Vol. 4.

(5) Gutsche, C. D. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: Oxford, 1991; Vol. 4.

(6) Shinkai, S.; Koreishi, H.; Ueda, K.; Arimura, T.; Manabe, O. *J. Am. Chem. Soc.* **1987**, *109*, 6371.

(7) Shinkai, S.; Shiramama, Y.; Satoh, H.; Manaba, O.; Arimura, T.; Fujimoto, K.; Matsuda, T. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1167.

(8) Andreetti, G. D.; Ugozzoli, F.; Cesnati, A.; Ghidini, E.; Pochini, A.; Ungaro, R. *Gazz. Chim. Ital.* **1989**, *119*, 47.

(9) Ungaro, R.; Pochini, A.; Andreetti, G. D.; Domiano, P. *J. Incl. Phenom.* **1985**, *3*, 35.

(10) Andreetti, G. D.; Calestani, G.; Ugozzoli, F.; Arduini, A.; Ghidini, E.; Pochini, A.; Ungaro, R. *J. Incl. Phenom.* **1987**, *5*, 123.