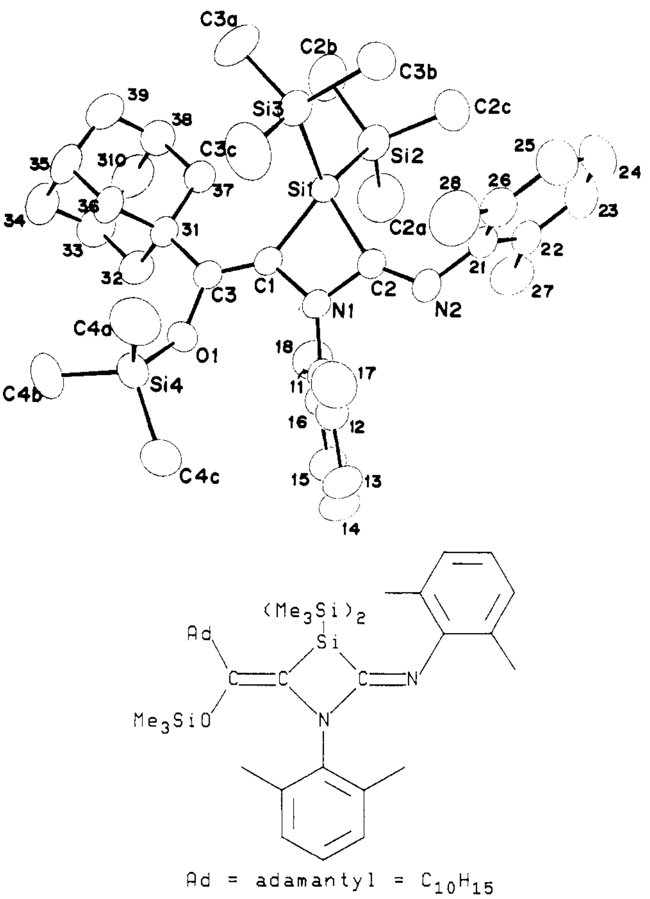


Figure 1. ORTEP view of the 1-sila-3-azacyclobutane **4a** showing the crystallographic numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): C1–C3 = 1.327 (6), C1–N1 = 1.454 (5), N1–C2 = 1.407 (5), C2–N2 = 1.265 (5), C3–O1 = 1.404 (4), Si4–O1 = 1.653 (3), N1–C11 = 1.434 (5); C3–C31 = 1.523 (5); C1–Si1–Si2 = 123.8 (1), C1–Si1–Si3 = 114.5 (1), C2–Si1–Si2 = 115.2 (1), C2–Si1–Si3 = 112.6 (1), C1–N1–C11 = 129.4 (3), C2–N1–C11 = 122.5 (3), Si1–C1–C3 = 140.5 (3), N1–C1–C3 = 127.5 (3), Si1–C2–N2 = 146.1 (3), N1–C2–N2 = 122.8 (3), C1–C3–O1 = 119.8 (3), C1–C3–C31 = 125.6 (3), O1–C3–C31 = 114.3 (3); C1–Si1–C2 = 72.4 (2), C1–N1–C2 = 105.2 (3), Si1–C1–N1 = 91.3 (2), and Si1–C2–N1 = 91.0 (2).

eclipsed arrangement, with Si–Si–C and C–Si–C angles in the range 106.9–112.7 (3)°.

We are continuing these studies by investigating the scope, generality, and the mechanisms involved in these unusual reactions.

Acknowledgment. We are grateful to the Natural Science and Engineering Research Council of Canada for financial support of this research and to Dr. Y. K. Kong for preliminary experiments.

Supplementary Material Available: Final crystallographic details for the structure refinement of 1-sila-3-azacyclobutane **4a** consisting of final positional and thermal parameters, complete bond lengths and bond angles, and least-squares mean planes (9 pages); a listing of final structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

---

(3) Properties of **4a**: air-sensitive, light brown solid; mp 208 °C. MS Calcd for $C_{38}H_{60}N_2OSi_4$: 672.3782. Found: 672.3762. Large well-formed block-shaped crystals of **4a** as a benzene solvate slowly reacted in air and hence were cut to size and rapidly transferred to Lindemann capillaries in a glovebag under dry argon. Crystal data: $C_{38}H_{60}N_2OSi_4 \cdot C_6H_6$; fw = 750.4; monoclinic; space group $P2_1/n$; $a = 9.917$ (3) Å, $b = 23.811$ (4) Å, $c = 19.431$ (7) Å; $\beta = 97.94$ (2)°; $U = 4544$ Å^3; $D_{\mathrm{calcd}} = 1.10$ g cm^{-3} for $Z = 4$; $T = 298$K. Unit cell dimensions based on 25 reflections ($8.8 < \theta < 13.9°$) centered on an Enraf-Nonius CAD4 diffractometer (graphite-monochromatized Mo K$\bar{\alpha}$ radiation) and a fairly large crystal of overall dimensions 0.35 × 0.40 × 0.47 mm. Intensity data collection [ω–2θ scans over $(0.60 + 0.35 \tan\theta)°$, maximum scan time 55 s] gave 8905 data (including standards) in the octants $h,k,\pm l$ with $2\theta \leqslant 50°$. A further 2500 symmetry-related data with $2\theta \leqslant 32°$ and an incomplete shell of data with $50 < 2\theta < 55°$ completed the data collection. The crystal was recentered several times during data collection. Lorentz, polarization, and slight (+5%) corrections for intensity fluctuations of standard reflections were applied. Rejection of 1698 systematically absent or zero F_o data and the averaging of 1884 symmetry equivalent reflections ($R_{\mathrm{merge}}(F) = 0.026$) gave a final data set of 7563 reflections. Structure solution used direct methods followed by standard refinements. All H atoms except those in the benzene solvent were included in calculated positions. Blocked least-squares refinements minimizing $\sum_w \Delta F^2$ (all non-H atoms except solvent anisotropic) converged (maximum $\Delta/\sigma = 0.09$) to $R = 0.0586$ ($wR = 0.0640$) for 4610 reflections with $F > 6\sigma(F)$ $\{w = [\sigma^2(F) + 0.001\,414F^2]^{-1}$ and maximum $\Delta P = 0.40$ e Å$^{-3}\}$. Scattering factors stored in programs were from ref 4. Programs: Enraf-Nonius SDP package on PDP 11/23 and SHELX on Gould 9705 computers.[5]

(4) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England (Present distributor D. Reidel, Dordrecht), 1974; Vol. IV.

(5) Frenz, B. A. *Enraf-Nonius Structure Determination Package*; Texas A&M University: College Station, TX, 1981. Sheldrick, G. M. *SHELX-76*, Cambridge University: Cambridge, England.

(6) Ishikawa, M.; Matsuzawa, S.; Hirotsu, K.; Kamitori, S.; Higuchi, T. *Organometallics* **1984**, *3*, 1930.

Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 7. A Novel Bonding Mode That Stabilizes Metal Triangles[1]

Evan P. Kyba,*,† Michael C. Kerby,‡ Ram P. Kashyap, John A. Mountzouris, and Raymond E. Davis*

Department of Chemistry, The University of Texas
Austin, Texas 78712

Received March 31, 1988

Summary: Two heterotetrametalla tetrahedral clusters, containing the Mo_2Co_2 (**3**) and $MoCo_3$ (**4**) cores, have been synthesized. A key part of the supporting ligand framework in each of these clusters is an *o*-phenylenebis(μ-*tert*-butylphosphido) moiety, which exhibits a novel bonding mode in stabilizing a metal triangle. Cluster **3** undergoes a thermal rearrangement to an isomer at temperatures >75 °C, in which, inter alia, the bis(μ-*tert*-butylphosphido) ligand migrates on the metal triangle. The activation parameters for this process are reported, as are the crystal structures of **3** and **7**.

We have been concerned for some time in the stabilization of metal–metal bonds by utilizing what we have termed linked bis(μ-phosphido and -sulfido) supporting ligands.[2] In particular, we have used the *o*-phenylene link between μ-phosphido groups (as in **1**) because it rigidly enforces a cisoid relationship between the ligating sites. There is now a relatively convenient synthetic route to *o*-phenylenebis(*sec*-phosphines), which are immediate precursors of **1** (Scheme I).[3] This type of ligand has stabilized unusual iron clusters,[4] an interesting triply

---

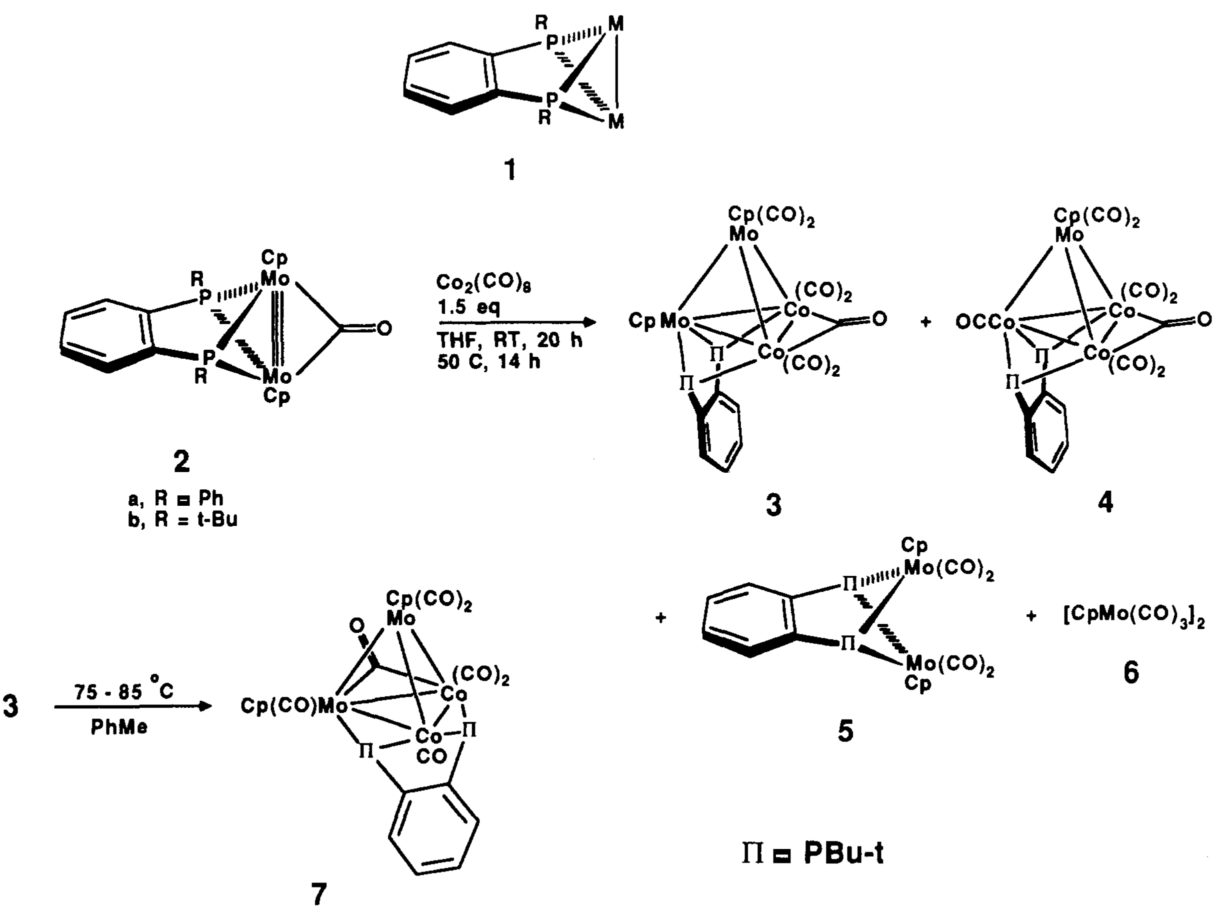
† Current address: Conner Research Center, Alcon Laboratories, Inc., 6201 South Freeway, Fort Worth, TX 76134.

‡ Current address: Exxon Corporate Research, Rte 22 East, Annandale, NJ 08801.

(1) For the preceding paper in this series, see: Kyba, E. P.; Kerby, M. C.; Kashyap, R. P.; Hassett, K. L.; Davis, R. E. *J. Organomet. Chem.* **1988**, *346*, C19.

0276-7333/89/2308-0852$01.50/0

Scheme I



bridged molybenum–molybenum triple bond,[5] and has fostered some unusual nucleophilic selectivities in a hexacarbonyldiiron moiety.[6] In almost all the cases reported so far, the linked bis(phosphido) ligand has had the bonding arrangement shown in **1**; i.e., it has stabilized a dinuclear transition-metal complex. This report describes a new bonding arrangement which stabilizes a trimetal triangle within a heteronuclear tetrahedral transition-metal cluster. In addition, we describe the synthesis, under kinetic control, of a Mo_2Co_2 cluster, which can be thermally isomerized to a much more stable one by apparent ligand migrations on the periphery of the cluster.

In the course of investigating the reactivity of the Mo≡Mo moiety in complexes **2**, with a view to the synthesis of polynuclear clusters, **2b** was treated with octacarbonyldicobalt (mole ratio of $Co_2(CO)_8$/**2b** = 1.5) in THF at ambient temperature (Scheme I). Following chromatography on alumina under anaerobic conditions and recrystallization, four complexes were isolated: **3** (50%), **4** (3%), **5** (7%), **6** (2%).[7] When the mole ratio of cobalt carbonyl to **2b** was increased to 2.4 and the temperature

---

(2) McKennis, J. S.; Kyba, E. P. *Organometallics* **1983**, *2*, 1249.

(3) Kyba, E. P.; Liu, S.-T.; Harris, R. L. *Organometallics* **1983**, *2*, 1877.

(4) Kyba, E. P.; Hassett, K. L.; Sheikh, B.; McKennis, J. S.; King, R. B.; Davis, R. E. *Organometallics* **1985**, *4*, 944.

(5) Kyba, E. P.; Mather, J. D.; Hassett, K. L.; McKennis, J. S.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 5371.

(6) Kyba, E. P.; Davis, R. E.; Clubb, C. N.; Liu, S.-T.; Palacios, H. O. A.; McKennis, J. S. *Organometallics* **1986**, *5*, 869.

(7) Complex **6** is commercially available, and **4** and **5** were fully characterized, including by X-ray crystallography: $^{31}P\{^1H\}$ NMR ($CDCl_3$): **4**, δ 378 (v br s) ppm; **5**, δ −19 (s) ppm. Full spectroscopic and structural details will be described in a full paper.

(8) Control experiments established that although **3** is transformed into **4** upon heating with $Co_2(CO)_8$, it does so too slowly to account for the amount of **4** produced starting from **2b**.

(9) **3**: mp >295 °C; ^1H NMR ($CDCl_3$) δ 8.14 (m, 2 H), 7.22 (m, 2 H), 5.41 (s, 5 H), 4.80 (s, 5 H), 1.58 (v br s, 18 H); ^{13}C NMR (C_7H_8, partial, −90 °C) 248.1 (br s), 246.6 (s), 205.5 (br s), 204.0 (br s), 94.6 (s), 87.4 (s), 44.0 (d, J = 12.6 Hz) 35.2 (s), 31.3 (d, J = 10.8 Hz), 26.9 (s); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 284 (br s); IR (CH_2Cl_2) ν_{CO} 2018 (s), 1985 (s), 1952 (s, br), 1882 (m, br), 1835 (m, br), 1735 (w, br); MS (CI) *m/e* 832 (M^+ − 2 CO, 4%), 804 (M^+ − 3 CO, 100%); UV (CH_2Cl_2) λ_{max} = 242 nm (ϵ = 18 300 cm^{-1} M^{-1}). Anal. Calcd for $C_{31}H_{32}O_7P_2Co_2Mo_2$: C, 41.92; H, 3.63. Found: C, 41.73; H, 3.66. **Crystal structure of 3**: crystals of **3** were grown by slow evaporation from toluene. Data crystals dimensions were 0.15 × 0.083 × 0.23 mm. Data were collected at 163 K on a Nicolet P2$_1$ diffractometer, with a graphite monochromator and using Mo Kα radiation (λ = 0.710 73 Å). The crystal system is monoclinic, and the space group is $P2_1/c$ (No. 14). Lattice parameters were obtained from least-squares refinement of 45 reflections with $11.6° < 2\theta < 21.4°$: a = 11.006 (8), b = 16.474 (8), c = 18.596 (4) Å; β = 105.57 (2)°, d_{calcd} = 1.82 g·cm^{-3} for Z = 4; $F(000)$ = 1768. Intensities were collected for 6380 unique reflections using the ω scan technique, 2θ range 4.0–50.0°, and 1° ω scan at 2–5° min^{-1}. Four reflections (1,1,0; 0,0,2; 0,2,−1; 1,1,−1) were remeasured after every 96 reflections to monitor instrument and crystal stability; maximum decay correction <1.6%. Data were corrected for Lp effects and for absorption (μ = 18.8 cm^{-1}; absorption coefficient range 1.126–1.236). Intensity, I, is given by $(I_{peak} - I_{background}) \times$ (scan rate). Reflections having $F_o < 4.0\sigma(F_o)$ were omitted (2838 reflections). The structure was solved by Patterson and heavy-atom methods and refined by full-matrix least-squares procedures. Both cp rings were treated as ideal rigid groups. Anisotropic thermal parameters were used for non-H atoms except for the carbons in the cp ring C15–C19. Positional and isotropic thermal parameters for non-cp H atoms were independently refined. Number of parameters refined was 334. $\sum w(|F_o| - |F_c|)^2$ minimized, where w = $1/(\sigma(F_o))^2$ and $\sigma(F_o) = 0.5kI^{-1/2}[(\sigma(I))^2 + (0.02I)^2]^{1/2}$. $\sigma(I)$ estimated from counting statistics; $\sigma(I) = [(I_{peak} + I_{background})^{1/2} \times$ (scan rate)]; 0.02 is a factor to downweight intense reflections and to account for instrument instability; k is the correction due to Lp effects and decay. Final R = 0.080, wR = 0.068, and goodness of fit = 1.78 for 3542 reflections. Maximum $|\Delta/\sigma|$ < 0.02 in the final refinement cycle; minimum and maximum peaks in the final ΔF map were −2.1 and 1.9 e·Å^{-3}, respectively. Scattering factors for the non-H atoms are from: Cromer, D. T.; Mann, J. R. *Acta Crystallogr.* **1968**, *A24*, 321–324, with anomalous dispersion corrections from: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898; scattering factors for the H atoms are from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Phys. Chem.* **1965**, *42*, 3175–3187; linear absorption coefficients are from the *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974. Computer programs are from ref 11 of: Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607–1613.

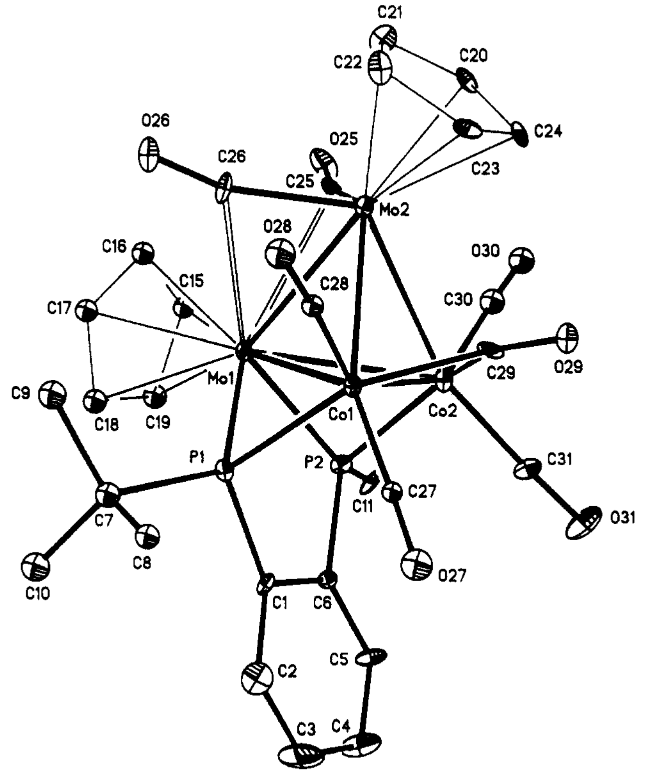


Figure 1. Structure diagram of 3. The *tert*-butyl group on P2 is shown only as its ipso carbon, C11. Selected bond distances (Å): Co1–Mo1, 2.900 (3); Co2–Mo1, 2.886 (3); Co1–Co2, 2.495 (3); Co2–Mo2, 2.791 (3); Co1–Mo2, 2.785 (3); Mo1–Mo2, 2.866 (2); P1–Mo1, 2.337 (5); P1–Co1, 2.225 (4); P2–Mo1, 2.324 (4); P2–Co2, 2.239 (4); Mo2–C25 1.95 (2); Mo2–C26, 1.99 (2); Mo1···C25, 2.782 (15); Mo1···C26, 2.750 (20). Selected bond angles (deg): Co1–Co2–Mo1, 64.74 (6); Co1–Mo1–Co2, 51.10 (7); Co1–Mo2–Co2, 53.17 (7); Co1–Mo2–Mo1, 61.73 (7); Co2–Co1–Mo1, 64.16 (8); Co2–Co1–Mo1, 64.16 (8); Co2–Mo2–Mo1, 61.32 (6); Co2–Co1–Mo2, 63.54 (8); Co2–Mo1–Mo2, 58.05 (6); Co1–Mo1–Mo2, 57.75 (7); Co1–Co2–Mo2, 63.28 (8); Mo1–Co1–Mo2, 60.52 (6); Mo1–Co2–Mo2, 60.63 (6); Co1–P1–Mo1, 78.90 (15); Co2–P2–Mo1, 78.44 (14); O25–C25–Mo2, 166.6 (12); O26–C26–Mo2, 163.5 (13).

raised to 50 °C, the yield of 3 decreased to 8% and that of 4 increased to 24%.[8]

Figure 1 presents the results of an X-ray crystallographic structure determination of 3.[9] The metal atom core is a slightly distorted tetrahedron, the result of bonding two metals from the first transition series and two from the second. Nonetheless, the five of the six metal–metal bond lengths are in the narrow range, 2.785 (3)–2.900 (3) Å, and the last one (Co–Co) is 2.495 (3) Å. One face of the tetrahedron is coordinated by two μ-phosphido groups, in which the molybdenum center is chelated and each of the two cobalt centers is singly bound to the phosphido groups. To our knowledge, this bonding mode of two μ-phosphido groups is unique; we have now structurally characterized six other similar examples.[10] Further detailed discussion of the structure 3 and comparison to related complexes are reserved for a full publication.

In order to probe for any fluxional processes, 3 was heated in toluene solution at 87 °C using ^{31}P NMR as the observation tool, and although no fluxionality was noted, a new species was formed. When 3 was heated at 87 °C for 10 h, followed by anaerobic chromatography on alumina with toluene as eluent and recrystallization from the same solvent, an isomer (7) was isolated in 63% yield.[11] The kinetics of the isomerization were followed by ^{1}H NMR to give the following activation parameters: ΔG^* (25 °C) = 28.9 ± 2.2 kcal mol^{-1}; ΔH^* = 29.8 ± 1.0 kcal mol^{-1}; ΔS^* = 3 ± 4 eu.[12] It was clear at the outset that the phosphorus bonding was different from the starting material, because two signals were observed in the ^{31}P{H} NMR spectrum at δ 357 (v br s) and 345 (br s) ppm. Because other spectroscopic data did not help to elucidate the structure of the isomer, it was determined by X-ray crystallography, the results of which are presented in Figure 2. The tetrahedral tetrametallic core has been maintained in the isomerization, but now it is a cobalt center that is chelated, with one phosphorus center bonded to molybdenum and the other to cobalt, hence different phosphorus sites. The other ligands have also rearranged substantially around the metallic tetrahedron. The basal molybdenum now bears a terminal carbonyl and a bridging carbonyl ligand. The semibridging carbonyls are now

---

(10) Two examples of Ru$_3$ clusters stabilized by *two* bis(μ-phosphido) groups have been found: Kyba, E. P.; Soucek, M. D.; Sheikh, B.; Davis, R. E., unpublished work. Other examples of bonding similar to 3 include 4, 7, and a Co$_4$ species, all of which will be described in a full paper.

(11) **7**: mp >295 °C; ^{1}H NMR (CDCl$_3$) δ 7.95 (m, 1 H), 7.69 (m, 1 H), 7.33 (m, 1 H), 7.22 (m, 1 H), 5.28 (s, 5 H), 5.24 (s, 5 H), 1.52 (d, $J_{\text{P-P}}$ = 7 Hz, 9 H), 1.48 (d, J = 7 Hz, 9 H); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 353 (br m), 342 (br s), at −78 °C (CD$_2$Cl$_2$) 355 (br d, J = 35 Hz), 345 (br d, J = 45 Hz); IR (C$_7$H$_8$) 2004 (m), 1964 (s), 1930 (m, br), 1853 (mw, br), 1821 (mw, br), 1790 (w, sh), 1690 (mw, br); MS (CI) m/e 888 (M$^+$, 4%), 860 (M$^+$ − CO, 5%), 832 (M$^+$ − 2CO, 14%), 804 (M$^+$ − 3CO, 100%), 776 (M$^+$ − 4CO, 84%), 748 (M$^+$ − 5CO, 36%), 720 (M$^+$ − 6CO, 1%), 692 (M$^+$ − 7CO, 10%); UV (CH$_2$Cl$_2$) $\lambda_{\max}$ = 358 nm (ϵ = 12 500 cm^{-1} M^{-1}). Anal. Calcd for C$_{31}$H$_{32}$O$_7$P$_2$Co$_2$Mo$_2$: C, 41.92; H, 3.63. Found: C, 41.62; H, 3.78. **Crystal structure of 7·1.5C$_7$H$_8$:** Crystals of **7**·1.5C$_7$H$_8$ were grown by slow evaporation from toluene. Data were collected at 163 K on a Nicolet P2$_1$ diffractometer, with a graphite monochromator and using Mo Kα-radiation (λ = 0.710 73 Å). The crystal system is monoclinic, and the space group is $P2_1/c$ (No. 14). Lattice parameters were obtained from least-squares refinement of 45 reflections with 10.0° < 2θ < 23.0°: a = 16.922 (6), b = 10.624 (3), c = 23.666 (8) Å; β = 104.03 (2)°, d_{calcd} = 1.65 g·cm^{-3} for Z = 4; F(000) = 2068. Intensities were collected for 9776 unique reflections using the ω scan technique, 2θ range 4.0–55.0°, and 1° ω scan at 3–6°/min^{-1}. Four reflections (1,3,−1; −1,0,4; 2,1,0; 6,0,−4) were remeasured after every 96 reflections to monitor instrument and crystal stability; maximum decay correction <1.0%. Data were corrected for Lp effects and for absorption (μ = 14.9 cm^{-1}). Intensity, I, is given by ($I_{\text{peak}} - I_{\text{background}}$) × (scan rate). Reflections having $F_o < 4.0\sigma(F_o)$ were omitted. The structure was solved by Patterson and heavy-atom methods and refined by full-matrix least-squares procedures. Anisotropic thermal parameters were used for non-H atoms. Both cp rings were treated as ideal rigid groups with C anisotropic and H isotropic thermal parameters separately refined for each atom. Positional and isotropic thermal parameters for non-cp H atoms were independently refined. The crystal contains two independent toluene solvent molecules. One solvent (CS1–CS7) is at general positions; its C$_6$ ring was refined as an idealized rigid group and all C and H thermal parameters were independently refined. The other solvent (CSS1–CSS5) is disordered about an inversion center; its C positional and thermal parameters were independently refined and its H atoms were not included; in spite of its quite high thermal parameters, the quite reasonable geometry of the disordered model and the behavior of agreement factors is taken as evidence for its presence. Number of parameters refined was 534. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/(\sigma(F_o))^2$ and $\sigma(F_o) = 0.5kI^{-1/2}[(\sigma(I))^2 + (0.02I)^2]^{1/2}$. $\sigma(I)$ estimated from counting statistics; $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})^{1/2} \times (\text{scan rate})]$; 0.02 is a factor to downweight intense reflections and to account for instrument instability; k is the correction due to Lp effects and decay. Final R = 0.071, wR = 0.050, and goodness of fit = 1.50 for 5065 reflections. Maximum $|\Delta/\sigma|$ < 0.27 in the final refinement cycle; minimum and maximum peaks in the final ΔF map were −1.0 and 1.7 e·Å^{-3}, respectively. Scattering factors, absorption coefficients, and computer programs were as described in ref 9.

(12) ^{1}H NMR samples of **3** (ca. 0.03 M in C$_7$D$_8$) were prepared under argon in a drybox. The isomerization process, **3** → **7**, was followed by the disappearance of the two singlets for the Cp protons for cluster **3** (5.41 and 4.80 ppm) and the appearance of the corresponding singlets for the Cp protons for cluster **7** (5.28 and 5.24 ppm) at 360.1 MHz. The temperatures used in the kinetic experiments ranged from 87 to 98 °C. At temperatures greater than 100 °C, **3** decomposed to other uncharacterized products. The isomerization was followed for at least 2 half-lives of **3**. The relatively high degree of error in the ΔH^* and ΔS^* measurements is due to the uncertainty of the NT 360 temperature controller unit (±1 °C).

Organometallics 1989, *8*, 855–857

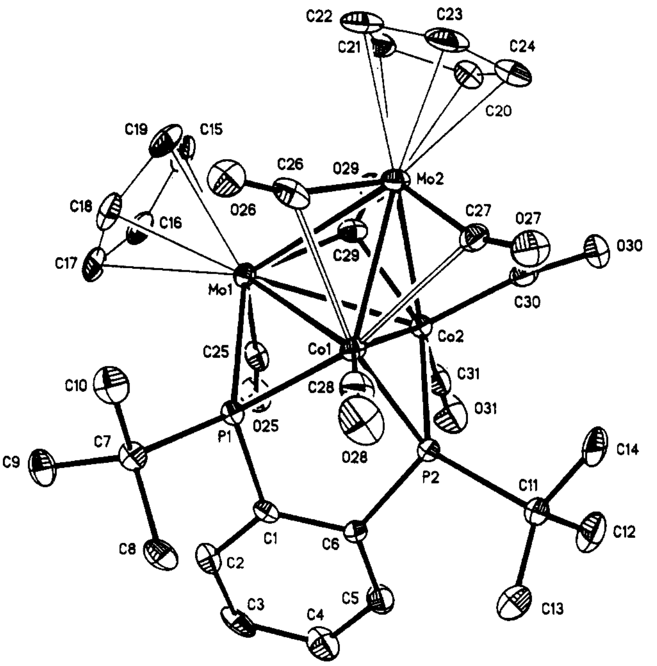


Figure 2. Structure diagram of 7. To facilitate comparison with Figure 1, the molecule shown is an inversion relative of the one whose coordinates appear in the supplementary tables. Selected bond distances (Å): Co1–Mo1, 2.871 (2); Co2–Mo1, 2.802 (2); Co1–Co2, 2.535 (2); Co2–Mo2, 2.776 (2); Co1–Mo2, 2.579 (2); Mo1–Mo2, 3.0570 (13); P1–Co1, 2.145 (3); P1–Mo1, 2.426 (3); P2–Co1, 2.137 (3); P2–Co2, 2.214 (3); Mo2–C26 1.927 (510); Mo2–C27, 1.976 (511); Co1⋯C26, 2.432 (11); Co1⋯C27, 2.454 (410). Selected bond angles (deg): Co1–Co2–Mo1, 64.87 (5); Co1–Mo1–Co2, 53.07 (4); Co1–Mo2–Co2, 56.35 (5); Co1–Mo2–Mo1, 60.54 (4); Co2–Co1–Mo1, 62.07 (5); Co2–Mo2–Mo1, 57.17 (4); Co2–Co1–Mo2, 65.75 (5); Co2–Mo1–Mo2, 56.37 (4); Co1–Mo1–Mo2, 51.47 (4); Co1–Co2–Mo2, 57.90 (5); Mo1–Co1–Mo2, 67.99 (5); Mo1–Co2–Mo2, 66.46 (4); Co1–P1–Mo1, 77.55 (9); Co2–P2–Co1, 71.25 (10); O26–C26–Mo2, 163.7 (9); O27–C27–Mo2, 162.5 (9).

associated with the chelated cobalt instead of the molybdenum center. As a result of this deep-seated rearrangement, the metallic tetrahedron is much less symmetrical in terms of bond lengths of the metallic tetrahedron (see metal–metal bond lengths in the figure captions).

It is reasonable that the bis(μ-phosphido) ligand system in 7 leads to a more stable complex, since the better σ-donor ligands now chelate the more electronegative cobalt carbonyl site. Our attempts to establish an equilibrium between 3 and 7 starting from 7 led to no detectable amounts of the former. Since this attempted equilibration was carried out 13 °C higher and for 14 h longer than when 3 was converted into 7, it can be estimated that 7 is at least 3.4 kcal/mol more stable than 3. Since carbonyl ligands are quite mobile on cluster frameworks,[13] presumably it is the barrier to migration of the bis(μ-phosphido) ligand which confers the kinetic stability upon cluster 3. This property gives us a clue to the mechanism of formation 3, since no 7 is formed in the process. Apparently, 3 is assembled via a pathway which does not allow access to the more stable isomer. We are continuing to investigate this aspect.

Preliminary work on the chemistry of cluster 3 indicates that it is reactive toward electrophilic reagents such as Brønsted acids and nitrosonium ion (to give a novel μ^2,η^4-NO cluster complex[14]) and that the bis(μ-phosphido) ligand enforces cluster integrity in such reactions.

Acknowledgment. Financial support from the Robert A. Welch Foundation (Grant No. F573 to E.P.K. and Grant No. F233 to R.E.D.), Alcon Laboratories (E.P.K.), and the National Science Foundation (E.P.K., Grant CHE84-19282) is gratefully acknowledged.

Supplementary Material Available: Tables of fractional coordinates and isotropic or equivalent thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and torsional angles (non-hydrogens) for 3 and 7 (25 pages); listings of observed and calculated structure factor amplitudes for 3 and 7 (75 pages). Ordering information is given on any current masthead page.

---

[13] Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 7.

[14] Kyba, E. P.; Kerby, M. C.; Kashyap, R. P.; Davis, R. E., manuscript in preparation.

First Example of a Neutral Homoleptic Uranium Alkyl. Synthesis, Properties, and Structure of $U[CH(SiMe_3)_2]_3$

William G. Van Der Sluys, Carol J. Burns, and Alfred P. Sattelberger*

Inorganic and Structural Chemistry Group (INC-4)
Isotope and Nuclear Chemistry Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Received December 5, 1988

Summary: The reaction of $U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)_3$ with 3 equiv of $LiCH(SiMe_3)_2$ in hexane at ambient temperature provides royal blue $U[CH(SiMe_3)_2]_3$ (**1**) in ca. 40% isolated yield. In the solid state, **1** is pyramidal with crystallographically imposed C_3 symmetry, a U(1)–C(4) (i.e., U–C_α) bond length of 2.48 (2) Å, and a C(4)–U(1)–C(4′) bond angle of 107.7 (4)°. The molecular structure also features a γ-agostic interaction with three symmetry-related silyl methyl groups [U(1)–C(7) = 3.09 (2) Å]. **1** is thermally stable as a solid at room temperature but decomposes with loss of $H_2C(SiMe_3)_2$ at ca. 60 °C. Solutions of **1** in hexane or THF slowly decompose over the course of several hours. Reaction of $UCl_3(THF)_x$ with 3 equiv of $LiCH(SiMe_3)_2$ in THF does not produce $U[CH(SiMe_3)_2]_3$ but rather a green ionic complex of formula $[Li(THF)_3][UCl\{CH(SiMe_3)_2\}_3]$.

The synthesis of isolable binary σ-alkyl complexes of uranium has been a goal of organometallic chemists for almost half a century. Prior to World War II, Gilman and co-workers attempted the preparation of simple uranium(IV) organometallics such as UMe_4. They concluded that homoleptic uranium alkyls, if they existed at all, were highly unstable and that their isolation offered little chance of success.[1] Subsequent attempts to prepare UR_4 complexes were likewise unsuccessful,[2-4] and the course of the complicated reactions between UCl_4 and alkyllithium reagents in alkane and ether solvents has been contro-

---

[1] (a) Gilman, H. *Adv. Organomet. Chem.* **1968**, *7*, 33. (b) Gilman, H.; Jones, R. G.; Bindschadler, E.; Blume, D.; Karmas, G.; Martin, G. A., Jr.; Nobis, J. F.; Thirtle, J. R.; Yale, H. L.; Yoeman, F. A. *J. Am. Chem. Soc.* **1956**, *78*, 2790.

[2] Yagupski, G.; Mowat, W.; Shortland, A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1970**, 1369.

[3] Cotton, S. A.; Hart, F. A., unpublished results cited by: Cotton, S. A. In *Organometallic Chemistry Library 3*; Seyferth, D., Ed.; Elsevier: Amsterdam, 1977; p 197.

[4] Marks, T. J.; Seyam, A. M. *J. Organomet. Chem.* **1974**, *67*, 61.

0276-7333/89/2308-0855$01.50/0