

Figure 2. ORTEP drawing of the cation in complex **4a**. Selected bond distances and angles: Ir–Ir, 3.428 (1); Ir–Cl, 2.395 (3); Ir–N(1), 2.067 (9); Ir–N(3), 2.096 (9); Ir–C(4), 2.303 (12); Ir–C(7), 2.286 (12); Ir–C(8), 2.264 (13); Ir–C(11), 2.283 (14) Å. N(1)–Ir–Cl, 84.1 (3)⁰; N(3)–Ir–Cl, 162.0 (4)⁰; N(3)–Ir–N(1), 83.3 (4)⁰; Ir–N(3)–Ir, 109.7 (7)⁰; O–N(3)–Ir, 125.2 (3)⁰.

CO gas (1 atm, CH₂Cl₂ solvent) afforded a purple adduct formulated¹⁴ as the carbonyl complex [Ir₂(COD)₂(μ-pz)₂(NO)(CO)]BF₄ (**3**). Bubbling HCl gas through a solution in CH₂Cl₂ of compound **2** led to isolation of a brick-red product **4a** which was characterized by X-ray methods as the tetrafluoroborate salt of a nitrosyl-bridged diiridium(III) cation,¹⁶ the geometry of which is depicted in Figure 2. Treatment of the cation **2** with I₂ yielded (ca. 45%) the diiodo analogue **4b** of **4a**, and the same complex was obtained almost quantitatively via NO⁺ oxidation (NOBF₄) of cation **2** resulted in conversion to the orange dimethylidiriidium(II) complex¹⁷ **6**.

The structure of the cation in complex **2** is striking in that the observed Ir–Ir distance of 3.224 (1) Å is actually marginally longer than that (3.216 Å) in the d⁸–d⁸ dimer **1**, suggesting that the former should be regarded as a d⁸–d⁶ species [i.e., oxidation at only one metal center, to Ir(III)]. By contrast two-center oxidation of **1** and related compounds (which may be accompanied by Ir₂ bond formation) leads to formation of adducts for which a d⁷–d⁷ diiridium(II) formalism is appropriate.^{17–19} Interaction between the adjacent Ir centers in the cation **2** may be opposed by the very strong trans influence associated with nonlinear MNO coordination:³ the Ir(1)–N–O linkage is severely bent (although uncertainty in the bond angle is high due to disorder, see Figure 1), consistent with electron-rich character for Ir(1). There is, however, no evidence for localized mixed-valence (d⁸–d⁶) character in equatorial bond distances which are equal to each Ir center. The bridged cation in compound **4a** is constrained to regularity by twofold crystallographic symmetry along the NO vector with Ir₂ separation of 3.428 (1) Å as expected¹⁹ for two nonbonded Ir(III) centers linked by three bridging ligands.

Acknowledgment. We thank the NSERC, Canada, and Imperial Oil Ltd. for financial support, Johnson-Matthey Inc. for a generous loan of iridium trichloride, the University of Victoria for provision of a graduate fellowship (to D.O.K.F.), Dr. P. Legzdins for discussion, and Dr. G. W. Bushnell for helpful comments regarding structure determination.

Supplementary Material Available: Fractional atomic coordinates and temperature parameters, anisotropic temperature parameters, and tables of bond distances and angles and observed and calculated structure factors for cations **2** and **4a** (27 pages). Ordering information is given on any current masthead page.

(16) Crystal data for compound **4a** (bis(dichloromethane) solvate): *M*_r = 1092.5; orthorhombic; space group *Ibca*; *a* = 15.027 (4) Å, *b* = 13.658 (4) Å, *c* = 32.033 (9) Å; *V* = 6574 Å³; *Z* = 8; *D*_{calc} = 2.21 g cm⁻³; Picker four circle diffractometer Mo Kα (λ = 0.71069 Å) radiation, μ = 83.1 cm⁻¹; 1860 observed reflections refined to a conventional *R* = 0.042 (*R*_w = 0.045).

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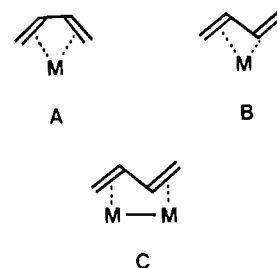
New Mode of Ligation for 1,3-Butadiene to Two Metal Centers. Synthesis and Structure of [(*i*-Pr)₂PCH₂CH₂CH₂P(*i*-Pr)₂Rh]₂(μ-η³-η³-C₄H₆): A Partial Butadiene Sandwich

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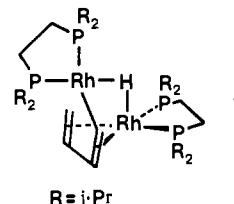
Received July 8, 1985

1,3-Butadiene, the simplest acyclic conjugated diene, normally binds to mononuclear transition-metal centers in the η⁴-*cis* mode³ A, as found in (η⁴-C₄H₆)Fe(CO)₃, for example. More recently,



the less stable η⁴-*trans* form B has been observed⁴ in metallocene derivatives of the formula (η⁴-C₄H₆)M(η⁵-C₅H₅)₂ (M = Zr, Hf). When two or more metal centers are proximate, as in polynuclear metal clusters, the *s-trans* bridging mode C has been characterized,⁵ as found in (μ-η²-η²-C₄H₆)Os₃(CO)₁₀. In this paper, we detail a completely new type of ligating mode for 1,3-butadiene with two metal centers, wherein each metal interacts in a trihapto (η³) fashion with a partially “sandwiched” *cis*-1,3-butadiene fragment.

A previous report⁶ from this laboratory outlined the high yield synthesis of **1** from 1,3-butadiene and the corresponding binuclear



rhodium hydride [(*i*-Pr)₂PCH₂CH₂CH₂P(*i*-Pr)₂Rh]₂(μ-H)₂ (**2a**). This transformation established that certain binuclear rhodium hydrides could deviate from reaction pathways normally associated with mononuclear systems. To examine the effect of chelate ring size on this reaction, we allowed 1,3-butadiene to react with [(*i*-Pr)₂PCH₂CH₂CH₂P(*i*-Pr)₂Rh]₂(μ-H)₂ (**2b**);⁷ this latter binuclear hydride contains the bidentate phosphine 1,3-bis(diisopropylphosphino)propane⁸ (dipp), which generates a six-membered

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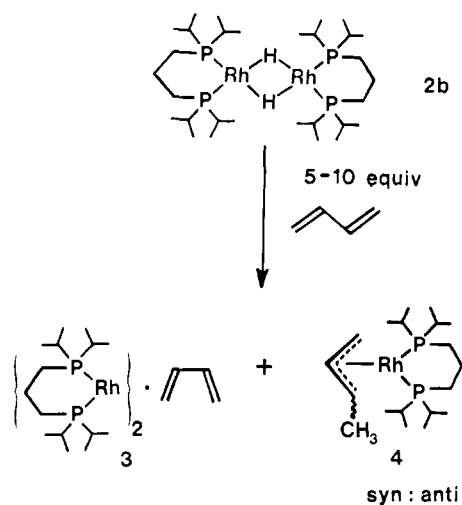
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Scheme I

Table I. Comparison of the Chemical Shifts of 3 and *anti*-4

	 3	 <i>anti</i> -4
¹ H NMR	H _a 0.87 ppm H _b 2.65 ppm H _c 4.78 ppm	H _a 2.12 ppm H _b 3.37 ppm H _c 4.73 ppm H _{c'} 4.45 ppm
¹³ C{ ¹ H} NMR	C ₁ 37.9 ppm C ₂ 60.2 ppm	C ₁ 43.1 ppm C ₂ 101.6 ppm C ₃ 60.4 ppm

bered chelate ring upon coordination. Surprisingly, none of the analogue to **1** was detected; instead two rhodium-containing products were obtained as outlined in Scheme I. A complex of the formula $[[\text{(i-Pr)}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{i-Pr})_2\text{Rh}]_2(\text{C}_4\text{H}_6)]$ (**3**)⁹ is the major isolated product (50–60% as orange crystals) along with a *syn/anti* (1:4) mixture of the 1-methylallyl derivatives (η^3 -1-Me-C₃H₄)Rh(dipp) (**4**),¹⁰ in 20–25% isolated⁹ yield, as the only other phosphorus containing compounds in this reaction. Organic byproducts are a mixture of butenes.¹¹

A single-crystal X-ray analysis¹² of **3** revealed its remarkable structure (Figure 1). The butadiene unit is intact and partially

(9) Typically, **3** is prepared by the addition of 5–10 equiv of 1,3-butadiene to a toluene solution (0.05 M) of **2b**; after it was stirred for 1–2 h at 25 °C, the orange solution is evaporated to dryness and the residue recrystallized from toluene/hexanes at –30 °C. ¹H NMR (C₆D₆, ppm), H_c, 4.78 (m, ³J_{cc'} = 4.45, ³J_{ac} = 10.79, ³J_{bc} = 6.60, ⁴J_{bc} = 1.45 Hz); H_b, 2.65 (m, ²J_{ab} = 3.90 Hz); H_a, 0.87 (m, J_p = 4.0 Hz); ligand resonances, 2.30–1.05 (m). ¹³C{¹H} NMR (C₆D₆, ppm), C₂, 60.2 (d, J_p = 18 Hz); C₁, 37.9 (dd, J_{Rh} = 10, J_p = 35 Hz); ligand resonances, 30.0–18.0 (m). ³¹P{¹H} NMR (C₆D₆, ppm from external P(OMe)₃ set at +141.0), AA'BB'XX' pattern, P_A, 54.4 (²J_{AB} = 40.5, J_{Rh} = 228 Hz); P_B, 36.0 (J_{Rh} = 180 Hz). Mp 178–179 °C dec. Anal. Calcd for C₃₄H₇₄P₄Rh₂: C, 50.24, H, 9.19. Found: C, 49.99, H, 9.32. The filtrate from the recrystallization of **3** contains **4** which can be subsequently isolated by sublimation (70 °C, 10^{–4} mmHg).¹⁰

(10) The identity of **4** was verified by its unambiguous synthesis from [*syn*-1-(methylallyl)-1,5-cyclooctadiene]rhodium^{10b} and dipp. Anal. Calcd for C₁₉H₄₁P₂Rh: C, 52.53, H, 9.53. Found: C, 52.82, H, 9.47. (b) Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134.

(11) A mixture of 1-butene, *cis*-butene, and *trans*-butene in the approximate ratio 4:3:1, respectively, is generated (by GC).

(12) Crystals of **3**, grown from toluene/hexanes at –30 °C, are monoclinic, *a* = 25.583 (3) Å, *b* = 10.883 (1) Å, *c* = 14.602 (2) Å, β = 93.259 (6)°, ρ_c = 1.330 g cm^{–3}, *Z* = 4, space group C2/c. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-square procedures to *R* = 0.033 and *R_w* = 0.035 for 2687 absorption-corrected reflections with *I* ≥ 3σ(*I*) collected at 22 °C on an Enraf-Nonius CAD4-F diffractometer with Mo Kα radiation. The hydrogen atoms of the C₄H₆ moiety were refined and the remaining hydrogen atoms were fixed in calculated positions. The central atom of the chelate ring, C(4), was twofold disordered with occupancy factors of 0.835 and 0.165 for C(4) and C(4b), respectively.

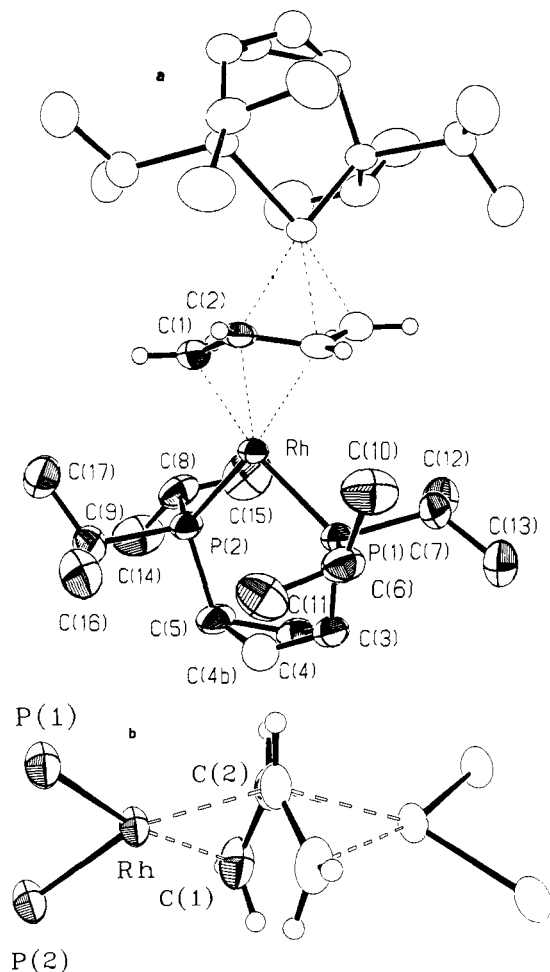


Figure 1. Views of the molecular structure of **3**: (a) the complete structure and numbering scheme; there is a C₂ axis bisecting C(2)–C(2') perpendicular to the page and (b) a sideview with only the phosphorus atoms of the bidentate ligands included; the twisted *cis*-butadiene unit is clearly evident along with the skewed RhP₂ planes. Pertinent bond lengths (Å) and bond angles (deg): Rh–P(1), 2.2492 (11); Rh–P(2), 2.1996 (11); Rh–C(1), 2.139 (5); Rh–C(2), 2.208 (4); Rh–C(2'), 2.297; C(1)–C(2), 1.438 (7); C(2)–C(2'), 1.441 (9); P(1)–Rh–P(2), 96.96 (4); P(1)–Rh–C(1), 166.00 (14); P(1)–Rh–C(2), 128.15 (13); P(1)–Rh–C(2'), 97.66 (11); P(2)–Rh–C(1), 96.98 (14); P(2)–Rh–C(2), 133.68 (12); P(2)–Rh–C(2'), 160.86 (12); C(1)–C(2)–C(2'), 120.4 (3); C(1)–Rh–C(2)', 68.5 (2).

sandwiched¹³ between the two rhodium centers; each rhodium interacts in a η^3 fashion with the opposite faces of the twisted *cis*-1,3-butadiene fragment (torsion angle of 45.0 (8)°). Some pertinent bond lengths and bond angles are given in the figure caption. Of particular interest are the nearly identical carbon-carbon bond lengths of 1.44 Å in the butadiene ligand, which are slightly longer than found¹⁴ in comparable allyl derivatives (1.40 Å). In valence bond terms, a reasonable picture for the bonding of **3** involves a *cis*-C₄H₆²⁺ ligand, with one double bond delocalized over the four-carbon fragment, interacting with two RhP₂⁺ (Rh(I), d⁸) fragments. To our knowledge, this is the first example of this mode of ligation for a diene¹⁵ or in fact for any organic π -system.

(13) The term *sandwich* in this context is usually applied to the cyclic hydrocarbon moieties η^6 -C₆H₆^{13b} and η^5 -C₅H₅^{13c}. Because the butadiene ligand is not η^2 bonded to each metal, it is regarded as being only "partially" sandwiched. (b) Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479. (c) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219 and references therein.

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(15) Interestingly, theoretical calculations on the structure of the related molecule 1,4-dithio-*cis*-2-butene have been reported;¹⁵ however, the particular mode represented by **3** was not reported. (b) Kos, A. J.; Stein, P.; Schleyer, P. N. R. *J. Organomet. Chem.* **1985**, *280*, C1.

Although the solid-state results (Figure 1) indicate a η^3 interaction of the two RhP_2 fragments with the *cis*- C_4H_6 moiety, both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts of **3** are more consistent with typical η^4 *cis*-1,3-butadiene complexes¹⁶ than with η^3 allyl derivatives; in Table I, a comparison of the chemical shifts of **3** vs. the corresponding shifts in the *anti*-1-methylallyl isomer **4** clearly shows dramatic differences in the ^1H NMR (i.e., H_a in **3** vs. H_a in **4**) and the $^{13}\text{C}\{^1\text{H}\}$ NMR (i.e., C_2 in **3** vs. C_2 in **4**).

Further studies will be aimed at the rational syntheses of other complexes that contain this novel structural unit; in addition, we are continuing to probe the mechanism by which **3** is generated in an effort to understand the pronounced influence of the chelate ring size¹⁷ on the course of the reaction of 1,3-butadiene with binuclear rhodium hydrides.

Acknowledgment. Financial support was provided by NSERC and the Alfred P. Sloan Foundation. We also thank Professor James Trotter for the use of the diffractometer and computer programs for structure solution. Johnson-Matthey is also acknowledged for the generous loan of RhCl_3 .

Supplementary Material Available: Tables of final positional and isotropic thermal parameters, calculated hydrogen coordinates and isotropic thermal parameters, final anisotropic thermal parameters, bond lengths, and bond angles (5 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of the $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{-O-TiW}_5\text{O}_{19})_2\}^{4-}$ Anion

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Received June 27, 1985

If polyoxoanion-supported organometallic complexes are to become involved in organometallic reaction chemistry, the balance between metal-carbon and metal-oxygen bond strengths at the organometallic center must be such that metal-oxygen bonds can withstand conditions under which metal-carbon bonds are broken and reformed. Polyoxoanion-supported organoactinides offer such a possibility,² but compounds of this type like $\{[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^1\text{-O-NbW}_5\text{O}_{19})_2]^{5-}$ (**1**)² and $\{[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^1\text{-O-NbW}_5\text{O}_{19})]^{2-}$ (**2**)³ have been disappointing from this point of view on account of the ease with which the organometallic unit dissociates from its polyoxoanion ligand.² Since this lability arises in part from the unidentate polyoxoanion binding mode in **1** and **2**, we sought to prepare analogous compounds containing tridentate polyoxoanion ligands. To this end, we prepared $\text{CITiW}_5\text{O}_{18}^{3-}$ (**3**), a potential tridentate ligand,⁴ from TiCl_4 plus WO_4^{2-} and reacted

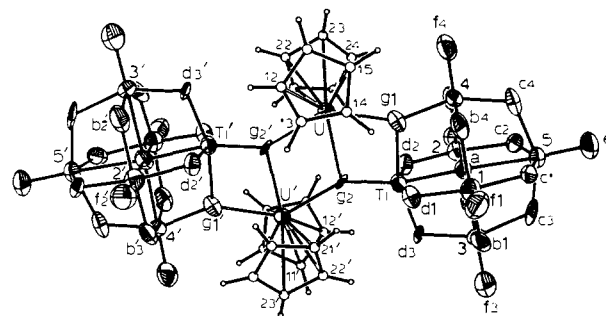


Figure 1. Perspective drawing of the solid-state structure for the $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{-O-TiW}_5\text{O}_{19})_2\}^{4-}$ anion (**4**), as observed in the form of acetonitrile-solvated crystals of its $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salt. Metal and oxygen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Carbon atoms are represented by large open circles and hydrogen atoms by small open circles. Uranium and titanium atoms are labeled with their atomic symbols while tungsten atoms are labeled with numbers. Oxygen atoms are labeled with letters and numbers. Atoms labeled with a prime are related to those labeled without a prime by the crystallographic inversion center at $(1/2, 0, 0)$ in the unit cell.

it with $(\text{C}_5\text{H}_5)_3\text{UCl}$ in an attempt to form $\{[(\eta^5\text{-C}_5\text{H}_5)_3\text{U}(\kappa^3\text{-O-CITiW}_5\text{O}_{18})]^{2-}$. Instead of the expected adduct, however, we isolated a more complex product in 30% yield having the empirical formula $\{[(\text{C}_5\text{H}_5)_2\text{U}(\text{TiW}_5\text{O}_{19})]^{2-}$. In contrast to **1** and **2**, this anion is quite stable and is not readily attacked by electrophilic and weakly nucleophilic reagents such as H_2O , $\text{CH}_3\text{CH}_2\text{OH}$, $(\text{C}_5\text{H}_5)_2\text{CHNO}_2$, and CH_3CN .⁵

X-ray structural analysis⁶ of crystalline $(\text{C}_5\text{H}_5)_2\text{U}(\text{TiW}_5\text{O}_{19})\{(\text{C}_4\text{H}_9)_4\text{N}\}_2$, obtained from CH_3CN solution, revealed the presence of discrete $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ cations, acetonitrile molecules of crystallization, and $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{-O-TiW}_5\text{O}_{19})_2\}^{4-}$ anions, **4**, shown in Figure 1, in which two $\text{TiW}_5\text{O}_{19}^{4-}$ polyoxoanions are bridged by two "bent sandwich" $(\text{C}_5\text{H}_5)_2\text{U}^{2+}$ units. Although the preferred coordination number is usually 10-12 when two or more C_5H_5^- ligands η^5 -bond to a single actinide ion,⁸ the U(IV) centers in **4** are both formally nine-coordinate by being η^5 -bonded to two C_5H_5^- groups and σ -bonded to three polyoxoanion oxygen atoms. Similar coordination geometries have been observed in several organoactinide systems, but these complexes usually employ the sterically bulky $(\text{CH}_3)_5\text{C}_5^-$ ligand.⁸ The manner in which the $(\text{C}_5\text{H}_5)_2\text{U}^{2+}$ units are linked in **4** bears a close resemblance to the linkage of the same units by $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH})(\text{CH}_2)^{2-}$ ligands in $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2[\mu\text{-}\eta^2\text{-}(\text{C}_6\text{H}_5)_2\text{P}(\text{CH})(\text{CH}_2)]_2\}^{2-}$,⁹ where the three oxygen atoms of **4** have been replaced by sterically bulkier carbon atoms, and the linkage of $(\text{C}_5\text{H}_5)_2\text{Ti}$ units by $(\text{C}_6\text{H}_5)_2\text{C}_2\text{O}$ ligands in $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2[\mu\text{-}\eta^2\text{-}(\text{C}_6\text{H}_5)_2\text{C}_2\text{O}]_2\}^{2-}$,¹⁰ where the large U(IV) center of **4** has been replaced by the smaller Ti(IV) center. Presumably, the stability of the observed U(IV) coordination geometry in **4** can be attributed in part to the steric bulk of the $\text{TiW}_5\text{O}_{19}^{4-}$ ligands that effectively block off a substantial portion

(5) According to ^1H NMR spectroscopy, solutions of the title anion in CH_3CN as a $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salt show <10% decomposition after 2-h exposure to 10 equiv of water or $\text{CH}_3\text{CH}_2\text{OH}$ in air. The anion similarly fails to react significantly with 10 equiv of $(\text{CH}_3)_2\text{CHNO}_2$ in CH_3CN under N_2 after 5 days at ambient temperature.

(6) Single crystals of $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{U}]_2(\mu\text{-}\kappa^2\text{-O-TiW}_5\text{O}_{19})_2\}(\text{C}_4\text{H}_9)_4\text{N}^{4-} \cdot 4\text{CH}_3\text{CN}$ are at $20 \pm 1^\circ\text{C}$ triclinic, space group $P1\bar{C}1$ (No. 2), with $a = 12.903(3)$ Å, $b = 15.604(5)$ Å, $c = 19.199(5)$ Å, $\alpha = 115.04(2)^\circ$, $\beta = 88.96(2)^\circ$, $\gamma = 108.33(2)^\circ$, and $Z = 1$ dimeric unit [$d_{\text{calcd}} = 2.224$ g cm^{-3} ; $\mu_a(\text{Mo K}\alpha) = 11.38$ mm $^{-1}$]. A structural model which utilized anisotropic thermal parameters for all anionic U, W, Ti, and O atoms as well as all cationic and solvent N and C atoms and isotropic thermal parameters for all cyclopentadienyl C and H atoms has been refined to convergence⁷ [$R(\text{unweighted, based on } F) = 0.058$ for 6477 independent absorption-corrected reflections having $2\theta_{\text{Mo K}\alpha} < 48.3^\circ$ and $I > 3\sigma(I)$] using counting statistics weighted cascade block diagonal least-squares techniques. Two carbons in the cations were not located.⁷

(7) See paragraph at end of paper regarding supplementary material.

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(4) Cf. $\text{C}_5\text{H}_5\text{TiMo}_5\text{O}_{18}^{3-}$ as a $\kappa^3\text{O}$ ligand in $\{[\kappa^3\text{O-C}_5\text{H}_5\text{TiMo}_5\text{O}_{18}]\text{Mn}(\text{CO})_2\}^{2-}$ and $\{[\kappa^3\text{O-C}_5\text{H}_5\text{TiMo}_5\text{O}_{18}]\text{MoO}_2\text{Cl}\}^{2-}$: Day, V. W.; Fredrich, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R.-S.; Shum, W. *J. Am. Chem. Soc.* **1981**, *103*, 3597.