nitrene[10] but instead undergo photochemical H atom abstraction to give radical pairs, which eventually collapse to form covalent adducts in high yields upon warming the matrix.

Acknowledgment. We gratefuly acknowledge the assistance of David Chang of The Ohio State University Campus Chemical Instrument Center with GC–MS analyses.

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Formation of a Heterometallic Carbon Dioxide Complex with Concurrent Reduction of CO_2

Eric G. Lundquist, John C. Huffman, and
Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405

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Recently, we have pursued the objective of the synthesis of heterobimetallic polyhydride complexes[1–5] in the hope that these complexes would activate and reduce dipolar substrates such as CO and CO_2. Our strategy in making these complexes has been either to combine early and late transition metals or to make a complex where one of the metal centers is unsaturated or can easily dissociate a ligand (e.g., 1,5-cyclooctadiene (COD), solvent, hydrogen) to become unsaturated. This latter strategy motivated our recent synthesis of $(1,5\text{-COD})RhH_3Os(PMe_2Ph)_3$.[6,7] Here, we report the reaction of $(1,5\text{-COD})RhH_3Os(PMe_2Ph)_3$ with CO_2 resulting in the retention of the cyclooctadiene and the formation of the first heterometallic carbon dioxide complex formed from CO_2 itself.[8]

A dark red THF solution of 0.23 mmol of $(COD)RhH_3OsP_3$ ($P = PMe_2Ph$) reacts completely with CO_2 (1 atm, 4 mmol, 25 °C) within 8 h to give a yellow solution. The ^1H and ^{31}P NMR spectra of the products establish the formation of *cis,mer*-$H_2Os(CO)P_3$,[9] along with one other product. Extraction with pentane removes $H_2Os(CO)P_3$ and leaves a yellow powder which can be recrystallized by slow evaporation from acetone to afford yellow-orange crystals (38% isolated yield). The ^{31}P and ^1H NMR spectra of this material[10] are consistent with a product containing two hydrides, one *mer*-OsP_3 unit and two Rh(COD) units. Selective heteronuclear spin decoupling studies show each hydride to couple to one rhodium, with $J(H{-}Rh) = 24$ Hz. An X-ray structure determination[11] (Figure 1) reveals a three-metal system with a planar PRh_2OsCO_2 unit. While the hydride ligands were not located in final electron density maps, molecular mechanics calculations[12] reveal the lowest energy sites for two hydrides to be bridging the two Rh–Os vectors.[13] The C/O distances are longer than those in ketones, and the Os/C distance (2.062 (19) Å) is shorter than that (2.22 (2) Å) to an sp³ carbon,[14] thus favoring a blend of the following electronic structures:

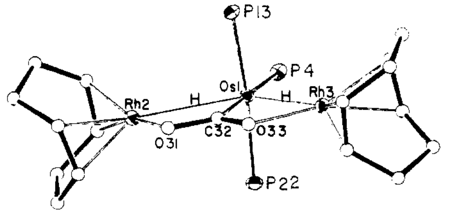
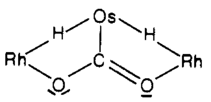
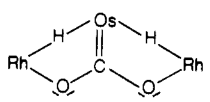


Figure 1. ORTEP drawing of the inner coordination sphere of $(COD)_2Rh_2OsH_2CO_2(PMe_2Ph)_3$. The hydrides are shown in the positions determined by molecular mechanics calculations. Selected bond distances: Os(1)–Rh (2) 2.9679 (20), Os(1)–Rh(3) 2.9880 (21), Os(1)–C(32) 2.062 (19), Rh(2)–O(31) 2.062 (13), Rh(3)–O(33) 2.065 (12), C(32)–O(31) 1.300 (21), C(32)–O(33) 1.309 (22) Å. Angles: Rh(2)–Os(1)–Rh(3) 125.11 (6)°, P(4)–Os(1)–C(32) 178.0 (5)°, Os(1)–C(32)–O(31) 121.6 (14)°, Os(1)–C(32)–O(33) 122.1 (13)°, O(31)–C(32)–O(33) 116.3 (16)°.





The Rh/Os distances in $(COD)_2Rh_2OsH_2CO_2(PMe_2Ph)_3$ nearly duplicate that of a hydride-bridged Rh/Ru bond in $RuRhHPh(PhPCH_2PPh_2)(Ph_2PCH_2PPh_2)(COD)$ (2.9413 (8) Å).[15]

On the basis of integration of the ^1H NMR spectrum of the products upon complete consumption of $(COD)RhH_3OsP_3$, we propose the following stoichiometry for the reaction described here:

$$2(COD)RhH_3OsP_3 + 2CO_2 \rightarrow (COD)_2Rh_2OsP_3H_2CO_2 + H_2Os(CO)P_3 + H_2O$$

Carrying out the reaction using $^{13}CO_2$ yields $H_2Os(^{13}CO)P_3$,[16] establishing CO_2 as the source of the carbonyl ligand and thus demonstrating that the reaction effects a net deoxygenation of CO_2. The ^{13}C NMR of $(COD)_2Rh_2OsH_2{}^{13}CO_2P_3$ also produced in this reaction shows the bound $^{13}CO_2$ as a doublet of triplets at 193 ppm.[17] This chemical shift falls close to the 195–210-ppm region found for all CO_2 complexes studied by ^{13}C NMR to date.[18] The coupling constants reveal stronger coupling (64 Hz) to the trans phosphorus than to those that are cis (11 Hz). The infrared C/O stretching vibrations (Nujol mull) of $(COD)_2Rh_2OsH_2CO_2P_3$ (1365 and 1260 cm⁻¹) were assigned, on the basis of their shift

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[7] $(1,5\text{-COD})RhH_3Os(PMe_2Ph)_3$ synthesized by the reaction of $K[OsH_3(PMe_2Ph)_3]$ with $[RhCl(COD)]_2$ in THF. ^1H NMR (360 MHz, C_6D_6): δ −9.15 (m, 3 H) 1.53 (d, $J_{Me-P} = 7$ Hz, 6 H), 1.78 (m, COD CH_2, 4 H) 2.40 (m, COD CH_2, 4 H), 4.85 (br s, COD vinyl, 4 H), 7.10–7.70 (m, P–Ph). $^{31}P\{^1H\}$ NMR (40.5 MHz, C_6D_6): −20.6 ppm (d, $J_{P-Rh} = 8.5$ Hz).

[8] An Ir/Os/CO_2 complex has been made by oxidation of CO bound to iridium with OsO_4. See: Audett, J. D.; Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 7352.

[9] Bell, B.; Chatt, J.; Leigh, J. G. *J. Chem. Soc., Dalton Trans.* **1973**, 997. $^{31}P(^1H)$ NMR (C_6D_6): −29.0 (d, $J_{p-p} = 16$ Hz, 2 P), −37.0 ppm (t, $J_{p-p} = 16$ Hz, 1 P).

[10] ^1H NMR (360 MHz, C_6D_6); δ −16.80 (m, 2 H); complete ^{31}P decoupling gives a doublet with $J_{H-Rh} = 24$ Hz, selectively coupling to the unique phosphorus gives $J_{H-P} = 11$ Hz, selectively coupling to the two equivalent phosphorus ligands gives $J_{H-P'} = 7$ Hz; 1.05 (d, $J_{Me-P} = 6$ Hz, 6 H), 1.55 (m, COD, 4 H), 1.65 (m, COD, 4 H), 2.12 (virtual triplet, $J_{Me-P} = 2$ Hz, 12 H), 2.30 (m, COD, 8 H), 4.00 (br s, vinyl COD, 4 H), 4.55 (br s, vinyl COD, 4 H), 7.0–8.1 (m, Ph–P, 15 H). $^{31}P\{^1H\}$ NMR (146 MHz, C_6D_6): −36.5 (d, $J_{p-p} = 22$ Hz, 2 P), −39.5 (t, $J_{p-p} = 22$ Hz, 1 P).

[11] Crystallographic data (−155 °C): $a = 10.338$ (4) Å, $b = 23.184$ (11) Å, $c = 19.943$ (8) Å, $\beta = 123.20$ (1)°, and $Z = 4$ in space group $P2_1/c$. $R = 0.0489$ for 2746 reflections with $F > 2.33\sigma(F)$, using a model with fixed (d(C–H) = 0.95 Å) hydrogens on carbon and anisotropic thermal parameters on metals and phosphorus.

[12] Program XHYDEX. See: Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

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[16] $^{13}C\{^1H\}$ NMR (C_6D_6): 191 ppm (d of t, $J_{CO-P} = J_{CO-P'} = 8$ Hz).

[17] $^{13}C\{^1H\}$ NMR of $[CODRh]_2(^{13}CO_2)H_2Os(PMe_2Ph)_3$ (74 MHz, C_6D_6): 193 (d of t, $J_{C-P\,trans} = 64$, $J_{C-P\,cis} = 11$ Hz). 130 (m, Ph–P), 87 (d, $J_{C-Rh} = 13$ Hz), 71 (d, COD, $J_{C-Rh} = 13$ Hz), 33 (s, COD), 30 (s, COD), 29 (t, $J_{Me-P} = 10$ Hz), 23 ppm (d, $J_{Me-P} = 10$ Hz).

[18] Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monye, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286. **Note Added in Proof**: Following submission of our manuscript, Tso and Cutler have revealed conversion of a CO-derived $ReCO_2H$ fragment to a μ-CH_2O moiety by reduction with hydride bound to oxophilic Zr(IV): Tso, C. T.; Cutler. A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

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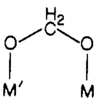
to 1332 and 1225 cm^{-1} in the ^{13}C analogue. These values support the conclusion of considerable single-bond character in the C/O bonds.

$(COD)_2Rh_2OsP_3H_2CO_2$ is the unique example of a neutral compound containing hydride as well as CO_2 ligands. We are, therefore, working to establish conditions that promote the formation of C–H bonds (e.g., formate or the *gem*-diolate I) or indeed the net scission of C/O bonds.



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Acknowledgment. Professor Michele Aresta contributed a remarkably stimulating environment for our contemplation of the results reported here. We thank the National Science Foundation (CHE 83-05281) for financial support and Johnson Matthey, Inc., for material support. Teresa Wright-Kester and Scott Horn are thanked for skilled technical assistance. Drs. A. G. Orpen and D. Ho and Professor A. Albinati provided valuable help with the molecular mechanics calculations.

Supplementary Material Available: Table of atomic positional and thermal parameters for $(COD)_2Rh_2OsH_2CO_2(PMe_2Ph)_3$ (1 page). Ordering information is given on any current masthead page.

Synthesis and Structure of the First Molybdenum–Pterin Complex

Sharon J. N. Burgmayer and Edward I. Stiefel*

Corporate Research Science Laboratories
Exxon Research and Engineering Company
Clinton Township, Annandale, New Jersey 08801

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Pterin derivatives have been found in an increasing number of enzymes.[1-3] In a significant number of cases, a metal–pterin complex is present. For example, Mo-co, the molybdenum cofactor contained in at least 10 distinct enzymes, has a 6-substituted sulfur-containing pterin associated with Mo.[2] In phenylalanine hydroxylase, biopterin (a 6-substituted tetrahydropterin) is directly associated with Fe.[3] Despite the presence of metal pterin units in these enzymes, there is no extant report and no structural information yet available about any isolated metal pterin complex. Although several reports are available concerning metal coordination by the related molecules, lumazine and flavin,[4] this paper reports the first characterization and structure determination for a metal–pterin complex.

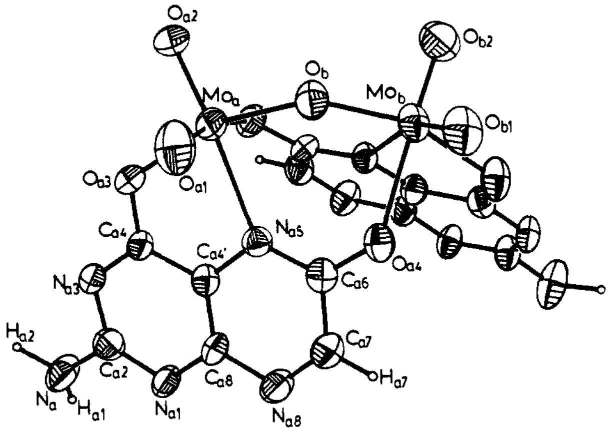

Figure 1. View of $Mo_2O_5(O_2N_5C_6H_3)_2^{2-}$ showing atomic labeling scheme. The atomic numbering scheme of both xanthopterinate ligands is identical. The second xanthopterinate ligand (unlabeled for pictorial clarity) has subscript b in the atomic labels. Thermal ellipsoids drawn at 50% probability. Atom H_{b1} is hidden from view.

Table I. Selected Bond Lengths and Angles Involving the $[Mo_2O_5(O_2N_5C_6H_3)_2]^{2-}$ Anion in Crystalline $[Na((CH_3)_2SO)_2]_2[Mo_2O_5(O_2N_5C_6H_3)_2]$

	Bond Lengths, Å		
Mo_a–O_b	1.883 (6)	Mo_b–O_b	1.884 (6)
Mo_a–O_{a1}	1.691 (7)	Mo_b–O_{b1}	1.710 (6)
Mo_a–O_{a2}	1.707 (5)	Mo_b–O_{b2}	1.684 (7)
Mo_a–O_{a3}	2.084 (5)	Mo_b–O_{b3}	2.081 (5)
Mo_a–N_{a5}	2.324 (6)	Mo_b–N_{b5}	2.324 (6)
Mo_a–O_{b4}	2.252 (6)	Mo_b–O_{a4}	2.246 (6)
$Mo_a \cdot\cdot Mo_b$	3.604 (1)		
	Bond Angles, deg		
$O_bMo_aO_{a1}$	99.6 (3)	$O_bMo_bO_{b1}$	104.9 (3)
$O_bMo_aO_{a2}$	104.2 (3)	$O_bMo_bO_{b2}$	99.4 (3)
$O_bMo_aO_{a3}$	155.5 (2)	$O_bMo_bO_{b3}$	155.3 (2)
$O_bMo_aN_{a5}$	84.7 (2)	$O_bMo_bN_{b5}$	84.3 (2)
$O_bMo_aO_{b4}$	84.9 (2)	$O_bMo_bO_{a4}$	84.8 (2)
$O_{a1}Mo_aO_{a2}$	105.1 (3)	$O_{b1}Mo_bO_{b2}$	105.3 (3)
$O_{a1}Mo_aO_{a3}$	93.5 (3)	$O_{b1}Mo_bO_{b3}$	91.4 (2)
$O_{a1}Mo_aN_{a5}$	92.2 (3)	$O_{b1}Mo_bN_{b5}$	158.3 (3)
$O_{a1}Mo_aO_{b4}$	167.5 (3)	$O_{b1}Mo_bO_{a4}$	84.6 (3)
$O_{a2}Mo_aO_{a3}$	92.1 (2)	$O_{b2}Mo_bO_{b3}$	93.8 (3)
$O_{a2}Mo_aN_{a5}$	158.6 (3)	$O_{b2}Mo_bN_{b5}$	92.3 (3)
$O_{a2}Mo_aO_{b4}$	84.9 (3)	$O_{b2}Mo_bO_{a4}$	167.6 (3)
$O_{a3}Mo_aN_{a5}$	74.1 (2)	$O_{b3}Mo_bN_{b5}$	74.4 (2)
$O_{a3}Mo_aO_{b4}$	78.4 (2)	$O_{b3}Mo_bO_{a4}$	78.3 (2)

Xanthopterin, 2-amino-4,6-dioxopteridine, is a yellow pigment first isolated from butterfly wings ("xanthos" and "pterin" are Greek for yellow and wing, respectively).[5] Under appropriate conditions,[6] xanthopterin reacts with molybdate to form the di-

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[6] (a) Xanthopterin hydrate (Aldrich) (0.397 g, 2.00 mmol), $Na_2MoO_4 \cdot 2H_2O$ (0.242 g, 1.00 mmol), and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.176 g, 0.143 mmol) were charged into a 100-mL Schlenk flask. Dimethyl sulfoxide, Me_2SO (50 mL), was added and the mixture was deaerated by multiple purges with argon on the vacuum manifold. Complete dissolution occurred when the mixture was heated to 80 °C. After stirring for 50 min between 85 and 90 °C, the yellow-orange solution was cooled. All Me_2SO was removed by distillation in vacuo. The resulting oil was redissolved in dry, deaerated dmf (20 mL) and the product was precipitated by addition of anhydrous deaerated diethyl ether. The yellow-orange microcrystalline solid was isolated by filtration to give 94% yield of $[Na(dmf)_2]_2Mo_2O_5(xanth)_2$. Satisfactory analysis was obtained for $C_{24}H_{34}N_{14}O_{13}Na_2Mo_2$ (C, H, N, Na, Mo). ^1H NMR (Me_2SO-d_6, in ppm downfield from TMS): δ 2.71, 2.87 (s, 12 H, CH_3 of DMF); 6.19 (s br, 2 H, -NH_2 of xanthopterinate); 7.84 (s, 1 H, H7 of xanthopterinate); 7.93 (s, 2 H, dmf). ^{13}C NMR (Me_2SO-d_6, in ppm from TMS): δ 30.8, 35.8, 162.5 (s, dmf resonances); 116.7, 149.2, 160.2, 161, 150.6, 172.5 (s, xanthopterinate resonances). $[Na(dmf)_2]_2Mo_2O_5(xanth)_2$ has one irreversible reduction at −1.295 V vs. Ag/AgCl in 0.1 M [TBA][PF_6]DMF. (b) $[TEA]_2Mo_2O_5(xanth)_2$ can be prepared by following the above procedure but substituting TEA_2MoO_4 for $Na_2MoO_4 \cdot 2H_2O$. ^1H NMR (Me_2SO-d_6): δ 1.18, (t, 12 H, CH_3 of TEA); 3.22 (q, 18 H, CH_2 of TEA), 6.10 (s, 2 H NH_2 of xanthopterinate); 7.77 (s, 1 H, N7 of xanthopterinate).

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