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Synthesis and Reactivity of a Heterometallic CO_2 Complex

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Reduction of CO_2 by $(COD)RhH_3OsP_3$ (COD = 1,5-cyclooctadiene; P = PMe_2Ph) proceeds at 1 atm and 25 °C in benzene or THF to give $H_2Os(CO)P_3$, $[(COD)Rh]_2OsH_2CO_2P_3$ (I), and H_2O. The metal-containing products are characterized by NMR and vibrational spectroscopy (including products from $^{13}CO_2$), as well as an X-ray structure determination of compound I. Crystal data (−155 °C): a = 10.338 (4) Å, b = 23.184 (11) Å, c = 19.943 (8) Å, β = 123.20 (1)°, with Z = 4 in space group $P2_1/c$. Space-filling models of I show that only the oxygens of the coordinated CO_2 are accessible to external reagents, and Na^+ (as the BPh_4^- salt) is shown to bind in THF with a large formation constant but to exchange raidly on the NMR time scale with free I. Reaction of I with $ZnBr_2$ in THF also gives a 1:1 adduct, which has been characterized by NMR and vibrational spectroscopy, as well as X-ray diffraction. Crystal data (at −150 °C): a = 19.677 (11) Å, b = 11.267 (5) Å, c = 22.376 (15) Å, β = 103.59 (3)°, with Z = 4 in space group $P2_1/a$. Zinc achieves a tetrahedral geometry by binding to both oxygens of CO_2. The major structural change in I upon binding the $ZnBr_2$ electrophile is a shortening of the Os–C distance by 0.048 Å. Small changes of the identity of the metal or ligands in $(COD)RhH_3OsP_3$ are shown to quench its reactivity toward CO_2.

Introduction

The search for an inexpensive and abundant source of carbon has prompted much research interest in the activation and reduction of carbon dioxide.[1] The potential for activation of the stable CO_2 molecule via coordination to a transition metal has been envisaged and has resulted in the systematic pursuit of transition-metal/CO_2 complexes.[2,3] Indeed, the idea of first binding the dipolar CO_2 molecule to a heterobimetallic polyhydride complex and then reducing it with the available hydride ligands motivated our earlier communication of the synthesis, characterization, and structure of $[(COD)Rh]_2(\mu\text{-}H)_2(\mu_3\text{-}CO_2)OsP_3$ (I)[4] (COD = 1,5-cyclooctadiene; P = PMe_2Ph).

Herein, we report further details on the synthesis and reactivity of I. Since the CO_2 moiety in I is firmly attached to a rather robust three-metal system and appears to be in an activated state (∠O–C–O = 116°, C–O = 1.30 Å), I offered the rare opportunity to evaluate the reactivity of a CO_2 molecule bound to a transition metal. Described here are the outcome of the reaction of I with the electrophiles Na^+, Li^+, and $ZnBr_2$. These reactions are of special relevance with respect to the established role of alkali-metal ions in the transition-metal-mediated reduction of CO_2 to CO and CO_3^{2-}.[5,6]

Experimental Section

All manipulations were carried out by using standard Schlenk and glovebox procedures under prepurified nitrogen or vacuum. Solvents were dried and deoxygenated by NaK/benzophenone (THF, Et_2O, C_6D_6, pentane) and distilled prior to use. Anhydrous $ZnBr_2$ (Fisher Scientific) was purified by sublimation under vacuum. $NaBPh_4$ (Eastman Kodak Co.) was used as received. $LiBPh_4$ was prepared by a literature method.[7] ^{1}H and ^{31}P NMR spectra were recorded on a Nicolet NT-360 spectrometer (25 °C) at 360 and 146 MHz, respectively. ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (25 °C) at 74 MHz. ^{103}Rh NMR spectra were recorded on a Bruker WH400 spectrometer. CO_2 (anaerobic purity, Matheson) and $^{13}CO_2$ (99% enriched, Aldrich) were used as received. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer.

Synthesis of $[(COD)Rh]_2OsH_2P_3CO_2$ (I). A degassed 15-mL THF solution containing 250 mg (0.31 mmol) of $(COD)RhH_3OsP_3$[8] (P = PMe_2Ph) was pressurized with excess CO_2 (1.5 atm). Over a period of 8 h, the original, dark red solution became yellow. After the solution was stirred for a total of 12 h, THF and excess CO_2 were removed under vacuum. The ^{1}H NMR spectrum of the resulting solid in C_6D_6 showed $OsH_2(CO)P_3$[9] and I as the major (>95%) reaction products. A small amount of OsH_4P_3 was also present as a hydrolysis product of the extremely water-sensitive $(COD)RhH_3OsP_3$. $OsH_2(CO)P_3$ was extracted from the reaction mixture with cold (0 °C) pentane (3 × 15 mL). A yellow powder remained, which was recrystallized from acetone by slow evaporation in a glovebox to give a modest yield (66 mg, 38%) of yellow-orange crystals of compound I. In the solid state, I can be handled in air. Solutions of I, however, darken and deposit metal after standing overnight in the atmosphere. ^{1}H 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, selective coupling to the unique phosphorus gives J_{H-P} = 11 Hz, selective 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),

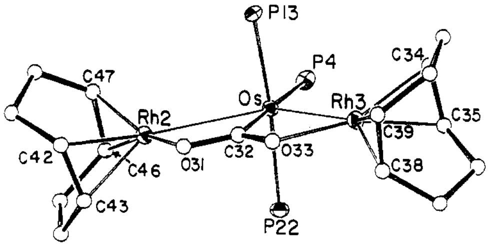

Figure 1. ORTEP drawing of $[(COD)Rh]_2OsH_2CO_2(PMe_2Ph)_3$, showing selected atom labeling. Methyl and phenyl groups, as well as hydrogens, have been omitted. One hydrogen atom bridges each of the two Rh–Os vectors.

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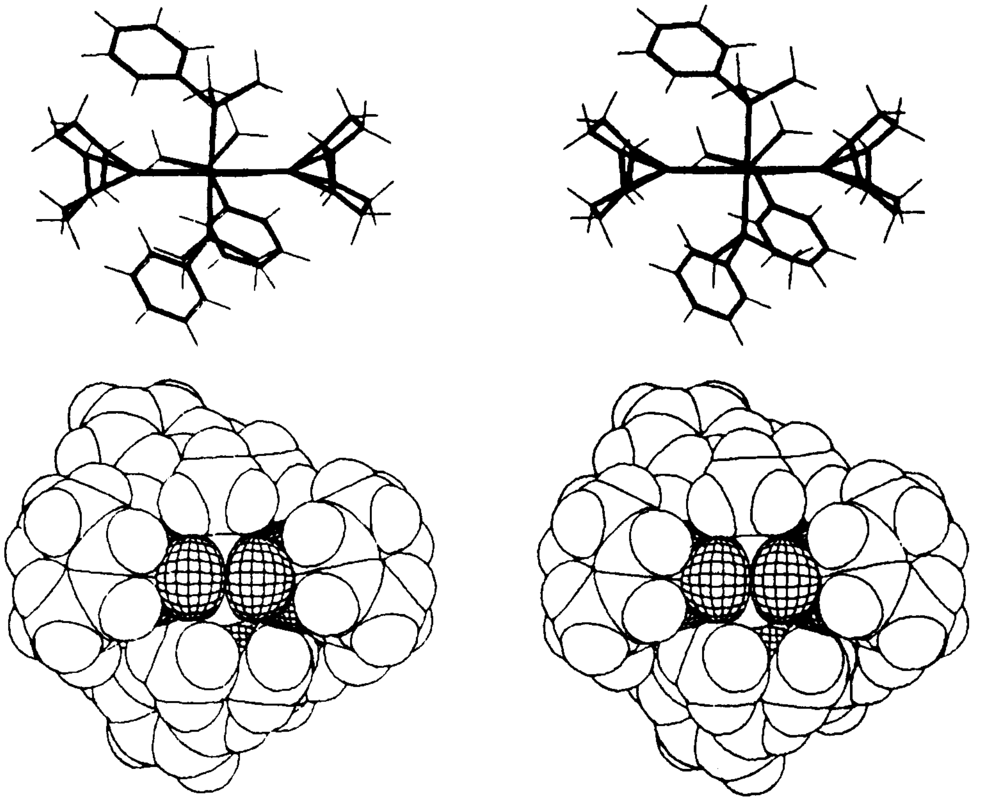

Figure 2. Stereo stick and space-filling drawings of $[(COD)Rh]_2OsH_2CO_2(PMe_2Ph)_3$, with all hydrogens placed with d(C–H) = 1.08 Å. This view is down the Os–C(32) vector. The centrally positioned, cross-hatched atoms are oxygen.

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): δ −36.5 (d of t, $J_{P-P} = 22$ Hz, $J_{P-Rh} = 1.5$ Hz, 2 P), −39.5 (t, $J_{P-P} = 22$ Hz, 1 P). $^{13}C\{^1H\}$ NMR of $[(COD)Rh]_2(^{13}CO_2)H_2Os(PMe_2Ph)_3$ (74 MHz, C_6D_6): 193 ppm (d of t, J_{C-P}(trans) = 64 Hz, J_{C-P}(cis) = 11 Hz), 130 (m, Ph–P), 87 (d, COD, $J_{C-Rh} = 13$ Hz), 71 (d, COD, $J_{C-Rh} = 13$ Hz), 33 (s, COD), 30 (s, COD), 29 (t, $J_{Me-P} = 10$ Hz), 23 (d, $J_{Me-P} = 10$ Hz). ^{103}Rh INEPT ($\Xi = 3.16$ MHz, 12.6 MHz, C_6D_6): δ 970 (−1:1 d, $J_{Rh-H} = 24$ Hz). IR (Nujol mull, μ-CO_2): 1365 and 1260 cm^{-1} ($^{13}CO_2$, 1332 and 1225 cm^{-1}).

Crystallography of $[(COD)Rh]_2OsH_2CO_2(PMe_2Ph)_3$. A suitable crystal was grown from slow evaporation of saturated acetone solutions, transferred to the goniostat by using standard inert-atmosphere handling techniques, and cooled to −155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected in the usual manner[10] using a continuous θ–2θ scan (6° ≤ 2θ ≤ 45°) with fixed backgrounds. Parameters of the crystal, data collection, and refinement appear in Table I. Data were reduced to a unique set of intensities and associated σ's in the usual manner after correction for absorption. The R for averaging of equivalent reflections was 0.054. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. The refinement model employed anisotropic thermal parameters on only the metals and phosphorus in order to maintain an acceptable (12:1) data-to-parameter ratio. Anisotropic refinement of carbon and oxygen thermal parameters gave no change in the R factor. Many of the hydrogen atom positions were visible in a difference Fourier phased on the non-hydrogen atoms. Positions were calculated for all hydrogens by assuming idealized geometry (with d(C–H) = 0.95 Å), and they were included as fixed atom contributors (with a thermal parameter 1 unit larger than that of the attached carbon atom) in the final cycles. There was no indication of the location of the hydridic hydrogen atoms, since the final difference Fourier contained residual peaks near the metals of ca. 1.4 e/Å^3. All other features were random. The results of the structural study are given in Tables II and III and Figures 1 and 2. Additional details are available as supplementary material.

Table I. Crystal Data for $[(COD)Rh]_2OsH_2(CO)_2(PMe_2Ph)_3$ and Its $ZnBr_2$ Adduct

compd	$[(COD)Rh]_2OsH_2$-$(CO_2)(PMe_2Ph)_3$	$[(COD)Rh]_2OsH_2(CO_2)$-$(PMe_2Ph)_3ZnBr_2$
empirical formula	$C_{41}H_{59}O_2P_3OsRh_2$	$C_{41}H_{59}Br_2O_2P_3OsRh_2Zn$
color	yellow-orange	golden
cryst dimens, mm	0.022 × 0.070 × 0.060	0.15 × 0.11 × 0.066
space group	$P2_1/c$	$P2_1/a$
cell dimens	(at −155 °C)	(at −150 °C)
a, Å	10.338 (4)	19.667 (11)
b, Å	23.184 (11)	11.267 (5)
c, Å	19.943 (8)	22.376 (15)
β, deg	123.20 (1)	103.59 (3)
molecules/cell	4	4
V, Å^3	3999.42	4822.06
calcd dens, g/cm^{-3}	1.782	1.782
wavelength, Å	0.71069	0.71069
mol wt	1072.85	1294.00
linear abs coeff, cm^{-1}	41.28	55.662
max abs	0.565	0.313
min abs	0.842	0.517
no. of unique intensities	5184	6276
no. of intensities with $F > 0.0$	4453	5726
no. of intensities with $F > 2.33\sigma(F)$	2746	
no of intensities with $F > 3.0\sigma(F)$		4981
final resids		
$R(F)$	0.0489	0.0518
$R_w(F)$	0.0458	0.0472
GOF for last cycle	0.85	1.02
max Δ/σ for last cycle	0.05	0.05

Reaction of I with $NaBPh_4$. To a 5-mm NMR tube containing 50 mg (0.05 mmol) of I in 0.4 mL of THF-d_8 was added 20 mg (0.07 mmol) of $NaBPh_4$. ^{1}H NMR spectroscopy indicated quantitative conversion to the adduct $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3NaBPh_4$. This complex has slight solubility in C_6D_6 as judged by ^{1}H NMR spectroscopy and can be obtained in good yield as an air- and moisture-sensitive yellow powder upon addition of pentane to the THF solution. ^{1}H NMR (360 MHz, THF-d_8): δ −17.3 (m, 2 H), 1.05 (d, $J_{Me-P} = 5$ Hz, 6 H), 1.55 (m, COD, 4 H), 1.70 (m, COD, 4 H), 2.10 (vt, $J_{Me-P} = 2$ Hz, 12 H), 2.20 (m, COD, 8 H), 4.18 (br s, vinyl COD, 4 H), 4.25 (br s, vinyl COD, 4 H), 6.5–8.0

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Table II. Fractional Coordinates and Isotropic Thermal Parameters for $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3$

	10^4x	10^4y	10^4z	$10B_{iso}$,[a] Å^2
Os(1)	1732 (1)	2116.5 (4)	1965.1 (5)	10
Rh(2)	4281 (2)	1386 (1)	3208 (1)	14
Rh(3)	732 (2)	3240 (1)	2273 (1)	13
P(4)	530 (6)	1792 (2)	628 (3)	13
C(5)	1779 (23)	1572 (9)	286 (12)	19 (4)
C(6)	−746 (24)	2304 (9)	−175 (12)	25 (4)
C(7)	−618 (22)	1118 (9)	340 (11)	16 (4)
C(8)	87 (22)	632 (9)	799 (11)	18 (4)
C(9)	−644 (22)	104 (8)	614 (11)	16 (4)
C(10)	−2075 (25)	70 (10)	−43 (13)	28 (5)
C(11)	−2869 (24)	533 (10)	−540 (12)	24 (4)
C(12)	−2071 (23)	1049 (9)	−318 (12)	21 (4)
P(13)	8 (6)	1676 (2)	2211 (3)	15
C(14)	−446 (20)	2064 (9)	2865 (10)	14 (3)
C(15)	696 (21)	975 (8)	2737 (11)	13 (4)
C(16)	−2014 (21)	1511 (8)	1366 (11)	15 (4)
C(17)	−2734 (21)	996 (8)	1312 (10)	12 (4)
C(18)	−4275 (24)	904 (9)	683 (12)	24 (4)
C(19)	−5045 (24)	1335 (9)	121 (12)	23 (4)
C(20)	−4351 (22)	1848 (9)	179 (11)	18 (4)
C(21)	−2832 (19)	1932 (7)	790 (10)	7 (3)
P(22)	3723 (6)	2595 (2)	1952 (3)	15
C(23)	4996 (25)	3062 (9)	2828 (13)	26 (5)
C(24)	5230 (23)	2174 (10)	1973 (12)	27 (4)
C(25)	3224 (21)	3113 (8)	1168 (11)	14 (4)
C(26)	3489 (21)	3039 (8)	551 (11)	16 (4)
C(27)	3013 (22)	3451 (9)	−61 (12)	18 (4)
C(28)	2339 (25)	3958 (10)	−27 (13)	26 (4)
C(29)	2091 (20)	4046 (8)	560 (10)	9 (3)
C(30)	2505 (22)	3639 (9)	1147 (11)	19 (4)
O(31)	3969 (13)	2099 (6)	3722 (7)	14 (2)
C(32)	2855 (22)	2396 (9)	3136 (11)	16 (4)
O(33)	2498 (13)	2881 (6)	3332 (7)	14 (2)
C(34)	−1591 (22)	3464 (9)	1398 (11)	17 (4)
C(35)	9406 (24)	3793 (9)	1258 (12)	25 (4)
C(36)	−241 (24)	4432 (9)	1473 (12)	24 (4)
C(37)	1181 (26)	4526 (10)	2319 (13)	29 (5)
C(38)	1429 (24)	4024 (10)	2905 (13)	25 (4)
C(39)	339 (23)	3789 (9)	2984 (12)	19 (4)
C(40)	−1337 (22)	4029 (9)	2562 (12)	19 (4)
C(41)	7617 (23)	3686 (9)	1783 (12)	23 (4)
C(42)	5824 (20)	1039 (8)	4377 (10)	9 (3)
C(43)	6638 (22)	1415 (9)	4181 (12)	18 (4)
C(44)	7668 (24)	1179 (9)	3931 (12)	25 (4)
C(45)	6923 (25)	738 (10)	3262 (13)	27 (5)
C(46)	5147 (23)	799 (9)	2736 (12)	19 (4)
C(47)	4143 (23)	511 (9)	2887 (12)	19 (4)
C(48)	4656 (25)	129 (10)	3615 (13)	28 (5)
C(49)	5923 (26)	374 (10)	4413 (13)	28 (5)

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3$

Os(1)–Rh(2)	2.9679 (20)	O(33)–C(32)	1.309 (22)
Os(1)–Rh(3)	2.9880 (21)	C(34)–C(35)	1.428 (27)
Os(1)–P(4)	2.364 (5)	C(34)–C(41)	1.488 (27)
Os(1)–P(13)	2.327 (5)	C(35)–C(36)	1.53 (3)
Os(1)—P(22)	2.351 (5)	C(36)–C(37)	1.53 (3)
Os(1)–C(32)	2.062 (19)	C(37)–C(38)	1.57 (3)
Rh(2)–O(31)	2.062 (13)	C(38)–C(39)	1.336 (2)
Rh(2)–C(42)	2.133 (17)	C(39)–C(40)	1.556 (2)
Rh(2)–C(43)	2.128 (19)	C(40)–C(41)	1.541 (2)
Rh(2)–C(46)	2.111 (20)	C(42)–C(43)	1.407 (2)
Rh(2)–C(47)	2.108 (20)	C(42)–C(49)	1.543 (2)
Rh(3)–O(33)	2.065 (12)	C(43)–C(44)	1.505 (2)
Rh(3)–C(34)	2.120 (19)	C(44)–C(45)	1.51 (3)
Rh(3)–C(35)	2.140 (21)	C(45)–C(46)	1.54 (3)
Rh(3)–C(38)	2.101 (22)	C(46)–C(47)	1.399 (2)
Rh(3)–C(39)	2.105 (20)	C(47)–C(48)	1.53 (3)
O(31)–C(32)	1.300 (21)	C(48)–C(49)	1.51 (3)

Rh(2)–Os(1)–Rh(3)	125.11 (6)	C(42)–Rh(2)–C(47)	81.6 (7)
Rh(2)–Os(1)–P(4)	116.01 (14)	C(43)–Rh(2)–C(46)	82.7 (8)
Rh(2)–Os(1)–P(13)	90.32 (14)	C(43)–Rh(2)–C(47)	99.2 (8)
Rh(2)–Os(1)–P(22)	84.05 (14)	C(46)–Rh(2)–C(47)	38.7 (7)
Rh(2)–Os(1)–C(32)	62.7 (6)	Os(1)–Rh(3)–O(33)	69.3 (4)
Rh(3)–Os(1)–P(4)	118.78 (14)	Os(1)–Rh(3)–C(33)	69.3 (4)
Rh(3)–Os(1)–P(13)	87.05 (14)	Os(1)–Rh(3)–C(34)	114.1 (5)
Rh(3)–Os(1)–P(22)	89.65 (14)	Os(1)–Rh(3)–C(35)	116.3 (6)
Rh(3)–Os(1)–C(32)	62.4 (6)	Os(1)–Rh(3)–C(38)	146.5 (6)
P(4)–Os(1)–P(13)	96.19 (18)	Os(1)–Rh(3)–C(39)	151.9 (5)
P(4)–Os(1)–P(22)	93.47 (18)	O(33)–Rh(3)–C(34)	155.4 (6)
P(4)–Os(1)–C(32)	178.0 (5)	O(33)–Rh(3)–C(35)	163.4 (7)
P(13)–Os(1)–P(22)	170.22 (18)	O(33)–Rh(3)–C(38)	85.1 (7)
P(13)–Os(1)–C(32)	85.4 (5)	O(33)–Rh(3)–C(39)	86.8 (6)
P(22)–Os(1)–C(32)	84.9 (5)	C(34)–Rh(3)–C(35)	39.2 (7)
Os(1)–Rh(2)–O(31)	69.4 (3)	C(34)–Rh(3)–C(38)	98.3 (8)
Os(1)–Rh(2)–C(42)	156.7 (5)	C(34)–Rh(3)–C(38)	98.3 (8)
Os(1)–Rh(2)–C(43)	142.5 (6)	C(34)–Rh(3)–C(39)	81.8 (8)
Os(1)–Rh(2)–C(46)	113.3 (5)	C(35)–Rh(3)–C(38)	83.2 (8)
Os(1)–Rh(2)–C(47)	114.5 (5)	C(35)–Rh(3)–C(39)	90.9 (8)
O(31)–Rh(2)–C(42)	89.2 (6)	C(38)–Rh(3)–C(39)	37.0 (7)
O(31)–Rh(2)–C(43)	86.2 (6)	Rh(2)–O(31)–C(32)	106.3 (11)
O(31)–Rh(2)–C(46)	163.3 (6)	Rh(3)–O(33)–C(32)	106.1 (11)
O(31)–Rh(2)–C(47)	156.9 (6)	Os(1)–C(32)–O(31)	121.6 (14)
C(42)–Rh(2)–C(43)	38.6 (7)	Os(1)–C(32)–O(33)	122.1 (13)
C(42)–Rh(2)–C(46)	89.9 (7)	O(31)–C(32)–O(33)	116.3 (16)

(m, BPh_4, P–Ph). $^{31}P\{^1H\}$ NMR (146 MHz, THF-d_8): δ −37.4 (d, J_{P-P} = 25 Hz, 2 P), −40.5 (t, J_{P-P} = 25 Hz, 1 P). $^{31}C\{^1H\}$ NMR of $[(COD)Rh]_2OsH_2(^{13}CO_2)(PMe_2Ph)_3NaBPh_4$ (74 MHz, THF-d_8): δ 198 (d of t, $J_{^{13}C-P}$ = 66 Hz, $J_{^{13}C-P}$ = 10 Hz). Absorption bands of BPh_4^- mask the CO stretching vibrations in this compound.

Reaction of I with $ZnBr_2$. To a 5-mm NMR tube containing 75 mg (0.07 mmol) of I in 0.4 mL of THF-d_8 was added 20 mg (0.10 mmol) of anhydrous $ZnBr_2$. The ^1H NMR spectrum shows quantitative conversion to the complex $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3ZnBr_2$. This complex is insoluble in C_6D_6. Layering a concentrated THF solution with pentane yields small golden crystals overnight (80% yield). ^1H NMR (360 MHz, THF-d_8): δ −17.9 (m, 2 H), 1.10 (d, J_{Me-P} = 5 Hz, 6 H), 1.60 (m, COD, 4 H), 1.70 (m, COD, 4 H), 2.20 (vt, J_{Me-P} = 2 Hz, 12 H), 2.25 (m, COD, 8 H), 4.10 (br s, vinyl COD, 4 H), 4.80 (br s, vinyl COD, 4 H), 7.0–8.0 (m, P–Ph). $^{31}P\{^1H\}$ NMR (146 MHz, THF-d_8): δ −38.4 (t, J_{PP} = 26 Hz, 1 P), −39.4 (d, J_{PP} = 26 Hz, 2 P). $^{13}C\{^1H\}$ NMR of $[(COD)Rh]_2OsH_2(^{13}CO_2)(PMe_2Ph)_3ZnBr_2$ (74 MHz, THF-d_8): δ 201 (d of t, $J_{^{13}C-P}$ = 66 Hz, $J_{^{13}C-P}$ = 11 Hz). IR (Nujol mull, μ_4,η^3-CO_2): 1280 and 1250 cm^{-1}.

Crystallography of $[(COD)Rh]_2OsH_2CO_2(PMe_2Ph)_3ZnBr_2\cdot THF$. A suitable crystal, grown as described above, was transferred to the goniostat by using standard inert-atmosphere handling techniques. The crystal was cooled to −150 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited monoclinic symmetry and systematic extinctions corresponding to the space group $P2_1/a$. The successful solution and refinement of the structure confirmed this choice.

Data collection (6° ≤ 2θ ≤ 45°) was undertaken in the usual manner[10] with parameters given in Table I. The *R* for the averaging was 0.0459 for 4418 reflections measured more than once. An absorption correction was carried out, after which the *R* for the averaging was almost the same: 0.0454 for 4418 reflections measured more than once. The structure was solved by locating the heavy atoms by direct methods; the lighter atoms were located in subsequent difference Fourier maps. When all of the expected atoms were located, six peaks well separated from the main molecule remained in the difference Fourier map. These were apparently THF in two orientations and were modeled by the six atoms numbered C(53)–C(58). The two expected hydride atoms were not located: the difference Fourier map contained several peaks of about 1.5 e/Å in the vicinity of the heavy atoms. Since many of the other hydrogen atoms were evident, they were introduced in calculated fixed positions during the final full-matrix least-squares refinement of the structure. All nonhydrogen atoms were refined by using anisotropic thermal parameters. The results of this X-ray study are given in Tables IV and V and Figure 3.

Synthesis of $(COD)IrH_3Os(PMe_2Ph)_3$. Inside a glovebox, a 20-mL THF solution of $K[OsH_3P_3]$[8] (250 mg, 0.39 mmol) containing excess KH was filtered directly into a flask containing 130 mg (0.19 mmol) of $[(COD)IrCl]_2$.[11] The resulting bright orange solution was stirred for 3.5 h, and then solvent was removed under vacuum, leaving an orange oil. This material was dissolved in 15 mL of benzene and the mixture filtered to remove KCl. Benzene was removed under vacuum and the solid

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Table IV. Fractional Coordinates and Isotropic Thermal Parameters for $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3ZnBr_2$

	$104x$	10^4y	10^4z	$10B_{iso}$,[a] Å^2
Os(1)	2022.6 (2)	390.7 (4)	2224.4 (2)	14
Rh(2)	3355.3 (5)	218 (1)	3203.8 (4)	16
Rh(3)	1794.6 (5)	−631 (1)	950.7 (4)	15
Zn(4)	3815 (1)	−1651 (1)	1748 (1)	20
Br(5)	4576 (1)	−533 (1)	1334 (1)	28
Br(6)	3881 (1)	−3666 (1)	1960 (1)	36
O(7)	3422 (4)	−675 (8)	2406 (4)	20
O(8)	2800 (4)	−1000 (7)	1484 (4)	18
C(9)	2829 (6)	−496 (10)	2023 (5)	17
P(10)	1042 (2)	1449 (3)	2393 (2)	18
P(11)	2519 (2)	2124 (3)	1912 (2)	19
P(12)	1633 (2)	−1463 (3)	2496 (2)	16
C(13)	449 (7)	762 (12)	2800 (7)	27
C(14)	420 (7)	1947 (13)	1704 (7)	29
C(15)	1218 (6)	2789 (12)	2857 (5)	20
C(16)	927 (6)	3910 (11)	2670 (5)	16
C(17)	1072 (7)	4878 (12)	3058 (7)	27
C(18)	1514 (8)	4799 (13)	3624 (7)	32
C(19)	1803 (7)	3693 (13)	3835 (6)	30
C(20)	1650 (7)	2724 (11)	3442 (6)	26
C(21)	2944 (8)	3213 (12)	2500 (7)	31
C(22)	3244 (7)	1885 (13)	1548 (7)	27
C(23)	1949 (6)	3099 (11)	1338 (6)	18
C(24)	1745 (7)	4200 (12)	1494 (6)	24
C(25)	1287 (7)	4855 (12)	1047 (7)	30
C(26)	1036 (6)	4454 (13)	466 (6)	27
C(27)	1270 (7)	3359 (12)	309 (6)	24
C(28)	1723 (6)	2690 (11)	735 (6)	20
C(29)	2196 (7)	−2723 (11)	2448 (6)	23
C(30)	828 (7)	−2030 (12)	2032 (6)	23
C(31)	1538 (7)	−1722 (11)	3292 (6)	22
C(32)	2140 (8)	−1765 (13)	3747 (6)	32
C(33)	2113 (9)	−2021 (14)	4349 (7)	40
C(34)	1474 (10)	−2250 (14)	4489 (7)	42
C(35)	880 (9)	−2242 (13)	4030 (7)	36
C(36)	906 (7)	−1993 (12)	3443 (6)	28
C(37)	4236 (7)	−798 (15)	3663 (6)	33
C(38)	4460 (7)	218 (13)	3451 (6)	29
C(39)	4745 (9)	1275 (20)	3868 (9)	63
C(40)	4212 (7)	2122 (13)	3995 (7)	34
C(41)	3464 (7)	1615 (13)	3849 (6)	33
C(42)	3273 (7)	573 (12)	4118 (5)	22
C(43)	3761 (8)	−154 (13)	4577 (6)	31
C(44)	4187 (10)	−1028 (18)	4322 (7)	55
C(45)	936 (6)	103 (11)	297 (6)	18
C(46)	724 (6)	−933 (11)	547 (5)	15
C(47)	628 (6)	−2122 (11)	223 (5)	15
C(48)	1225 (7)	−2454 (11)	−67 (6)	22
C(49)	1923 (6)	−1956 (12)	309 (6)	23
C(50)	2194 (6)	−884 (11)	151 (6)	16
C(51)	1849 (7)	−73 (12)	−344 (6)	21
C(52)	1088 (7)	191 (11)	−352 (6)	21
C(53)	3473 (15)	−4482 (25)	3928 (13)	93 (7)
C(54)	4062 (19)	−4425 (32)	3659 (18)	125 (10)
C(55)	4364 (38)	−4134 (66)	4361 (40)	271 (29)
C(56)	4083 (34)	−4277 (54)	4869 (31)	206 (20)
C(57)	3853 (20)	−3890 (36)	5325 (19)	136 (11)
C(58)	3396 (16)	−4407 (26)	4588 (14)	96 (7)

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

product triturated with pentane (2 × 10 mL), leaving an orange powder in 60% yield. ^1H NMR (360 MHz, C_6D_6): δ −8.45 (m, 3H), 1.58 (d, J_{Me-P} = 7 Hz, 18 H), 1.80 (m, COD, 4 H), 2.42 (br m, COD, 4 H), 4.54 (m, vinyl COD, 4 H), 7.0–8.0 (m, Ph-P). $^{31}P\{^1H\}$ NMR (146 MHz, C_6D_6): δ −16.4 (s).

Synthesis of $(PMe_2Ph)_2RhH_3Os(PMe_2Ph)_3$. Inside a glovebox, a 15-mL THF solution containing $K[OsH_3P_3]$ (160 mg, 0.25 mmol) and excess KH was filtered directly into a flask containing 102 mg (0.12 mmol) of $[(PMe_2Ph)_2RhCl]_2$.[12] The resulting dark, burgundy-colored solution was stirred for 1 h, and then the solvent was removed under vacuum. This resulting material was dissolved in 10 mL of benzene and the mixture filtered to remove KCl. Benzene was removed under vacuum and the solid triturated with pentane (1 × 15 mL) to afford a burgundy powder in 65% yield. ^1H NMR (360 MHz, C_6D_6): δ −8.30 (m, 3 H), 1.65 (m, P-Me, 12 H) 1.75 (d, J_{Me-P} = 7 Hz, 18 H), 7.25 (m, P-Ph), 8.0 (m, P-Ph). $^{31}P\{^1H\}$ NMR (146 MHz, C_6D_6): δ 14.2 (d of q, J_{P-Rh} = 164 Hz, J_{P-P} = 6 Hz, 2 P), −19.8 (d of t, J_{Rh-P} = 7 Hz, J_{P-P} = 6 Hz, 3 P).

Table V. Selected Bond Distances (Å) and Angles (deg) for $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3ZnBr_2$

Os(1)–Rh(2)	3.0028 (20)	Zn(4)–O(8)	2.081 (7)
Os(1)–Rh(3)	3.0079 (22)	O(7)–C(9)	1.290 (14)
Os(1)–P(10)	2.374 (3)	O(8)–C(9)	1.322 (14)
Os(1)–P(11)	2.363 (3)	C(37)–C(38)	1.352 (21)
Os(1)–P(12)	2.353 (3)	C(37)–C(44)	1.523 (21)
Os(1)–C(9)	2.014 (12)	C(38)–C(39)	1.536 (21)
Rh(2)–O(7)	2.080 (8)	C(39)–C(40)	1.494 (23)
Rh(2)–C(37)	2.129 (13)	C(40)–C(41)	1.542 (20)
Rh(2)–C(38)	2.114 (13)	C(41)–C(42)	1.411 (20)
Rh(2)–C(41)	2.112 (13)	C(42)–C(43)	1.478 (19)
Rh(2)–C(42)	2.129 (12)	C(43)–C(44)	1.491 (22)
Rh(3)–O(8)	2.097 (7)	C(45)–C(46)	1.401 (17)
Rh(3)–C(45)	2.125 (12)	C(45)–C(52)	1.551 (17)
Rh(3)–C(46)	2.116 (11)	C(46)–C(47)	1.513 (17)
Rh(3)–C(49)	2.128 (13)	C(47)–C(48)	1.517 (17)
Rh(3)–C(50)	2.135 (11)	C(48)–C(49)	1.538 (18)
Br(5)–Zn(4)	2.3097 (22)	C(49)–C(50)	1.398 (18)
Br(6)–Zn(4)	2.3162 (25)	C(50)–C(51)	1.473 (18)
Zn(4)–O(7)	2.124 (8)	C(51)–C(52)	1.524 (18)

Rh(2)–Os(1)–Rh(3)	125.24 (4)	Os(1)–Rh(3)–O(8)	68.04 (22)
Rh(2)–Os(1)–P(10)	121.31 (9)	Os(1)–Rh(3)–C(45)	114.9 (3)
Rh(2)–Os(1)–P(11)	85.34 (9)	Os(1)–Rh(3)–C(46)	112.2 (3)
Rh(2)–Os(1)–P(12)	92.04 (9)	Os(1)–Rh(3)–C(49)	153.3 (4)
Rh(2)–Os(1)–C(9)	62.1 (3)	Os(1)–Rh(3)–C(50)	147.4 (3)
Rh(2)–Os(1)–P(10)	113.41 (9)	O(8)–Rh(3)–C(45)	163.6 (4)
Rh(3)–Os(1)–P(11)	90.89 (9)	O(8)–Rh(3)–C(46)	157.2 (4)
Rh(3)–Os(1)–P(12)	85.43 (9)	O(8)–Rh(3)–C(49)	90.0 (4)
Rh(3)–Os(1)–C(9)	63.1 (3)	O(8)–Rh(3)–C(50)	88.1 (4)
P(10)–Os(1)–P(11)	92.30 (12)	C(45)–Rh(3)–C(46)	38.6 (5)
P(10)–Os(1)–P(12)	94.49 (12)	C(45)–Rh(3)–C(49)	90.5 (5)
P(10)–Os(1)–C(9)	176.3 (3)	C(45)–Rh(3)–C(50)	82.2 (5)
P(11)–Os(1)–P(12)	173.12 (11)	C(46)–Rh(3)–C(49)	82.1 (5)
P(11)–Os(1)–C(9)	86.6 (3)	C(46)–Rh(3)–C(50)	98.4 (5)
P(12)–Os(1)–C(9)	86.5 (3)	C(49)–Rh(3)–C(50)	38.3 (5)
Os(1)–Rh(2)–O(7)	67.98 (22)	Br(5)–Zn(4)–Br(6)	127.33 (8)
Os(1)–Rh(2)–C(37)	149.2 (4)	Br(5)–Zn(4)–O(7)	111.82 (24)
Os(1)–Rh(2)–C(38)	149.2 (4)	Br(5)–Zn(4)–O(8)	111.29 (25)
Os(1)–Rh(2)–C(41)	112.4 (4)	Br(6)–Zn(4)–O(7)	112.17 (25)
Os(1)–Rh(2)–C(42)	116.0 (4)	Br(6)–Zn(4)–O(8)	114.06 (25)
O(7)–Rh(2)–C(37)	86.9 (4)	O(7)–Zn(4)–O(8)	62.1 (3)
O(7)–Rh(2)–C(38)	87.5 (4)	Rh(2)–O(7)–Zn(4)	162.1 (4)
O(7)–Rh(2)–C(41)	158.5 (5)	Rh(2)–O(7)–C(9)	105.4 (7)
O(7)–Rh(2)–C(42)	161.9 (4)	Zn(4)–O(7)–C(9)	92.3 (7)
C(37)–Rh(2)–C(38)	37.2 (6)	Rh(3)–O(8)–Zn(4)	161.1 (4)
C(37)–Rh(2)–C(41)	97.6 (6)	Rh(3)–O(8)–C(9)	105.5 (7)
C(37)–Rh(2)–C(42)	82.8 (5)	Zn(4)–O(8)–C(9)	93.4 (6)
C(38)–Rh(2)–C(41)	83.6 (6)	Os(1)–C(9)–O(7)	124.5 (9)
C(38)–Rh(2)–C(42)	93.1 (5)	Os(1)–C(9)–O(8)	123.3 (8)
C(41)–Rh(2)–C(42)	38.9 (5)	O(7)–C(9)–O(8)	112.2 (10)

Synthesis of $(COE)_2RhH_3Os(PMe_2Ph)_3$ (COE = Cyclooctene). Inside a glovebox, a 15-mL THF solution of $K[OsH_3P_3]$ (105 mg, 0.16 mmol), containing excess KH was filtered directly into a flask containing 58 mg (0.08 mmol) of $[(COE)_2RhCl]_2$.[13a] This orange-red solution was stirred for 1.5 h. Subsequent removal of solvent under vacuum leaves a red oil. This material was dissolved in 10 mL of benzene and the mixture filtered to remove KCl. Benzene was removed under vacuum and the solid material triturated with pentane (2 × 10 mL) to give a red-orange powder in 60% yield. ^1H NMR (360 MHz, C_6D_6): δ −9.8 (m, 3 H), 0.80 (s, COE), 1.6–1.7 (m, COE) 1.75 (d, J_{Me-P} = 7 Hz, 18 H), 2.7 (m, COE), 3.5 (m, COE), 7.1–8.0 (m, Ph-P). $^{31}P\{^1H\}$ (146 MHz, C_6D_6): δ −24.0 (d, J_{P-Rh} = 7 Hz).

Synthesis of $(PMePh_2)_2RhH_3Os(PMe_2Ph)_3$. Inside a glovebox, a 25-mL THF solution containing $K[OsH_3P_3]$ (320 mg, 0.49 mmol) and excess KH was filtered directly into a flask containing 266 mg (0.25 mmol) of $[(PMePh_2)_2RhCl]_2$.[12] This resulting green-brown solution, which is dichroic (appearing red by transmitted light), was stirred for 1.5

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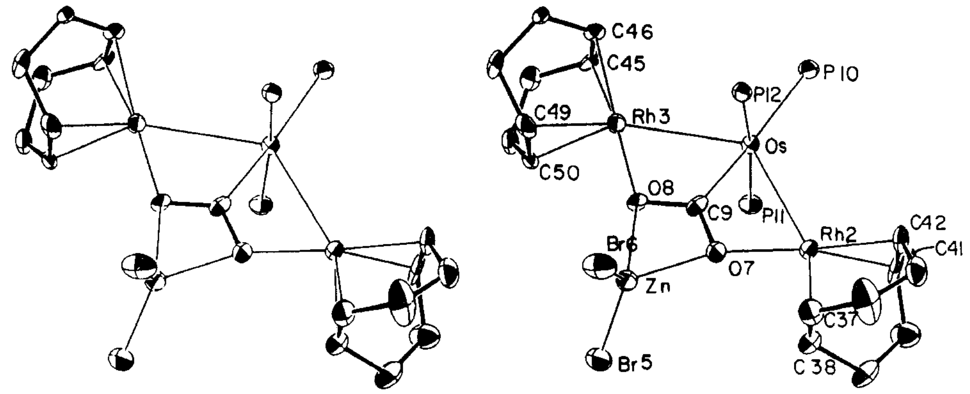


Figure 3. Stereo ORTEP drawing of $[(COD)Rh]_2OsH_2CO_2(PMe_2Ph)_3ZnBr_2$, showing selected atom labeling. Methyl and phenyl groups and all hydrogens have been omitted. One hydrogen atom bridges each of the Rh–Os vectors.

h, after which time the solvent was removed under vacuum. This brown oily product was dissolved in 10 mL of benzene and the mixture filtered to remove KCl. Benzene was removed under vacuum and the solid material triturated with pentane (2 × 10 mL), leaving a brown-red powder in 70% yield. ^1H NMR (360 MHz, C_6D_6): δ −8.0 (m, 3 H), 1.42 (br s, P–Me, 6 H), 1.50 (d, $J_{Me-P} = 7$ Hz, 18 H), 7.0 (m, P–Ph), 7.6 (m, P–Ph), 7.8 (m, P–Ph). $^{31}P\{^1H\}$ NMR (146 MHz, C_6D_6): δ 30.5 (d of q, $J_{P-Rh} = 167$ Hz, $J_{P-P} = 7$ Hz, 2 P), −19.1 (d of t, $J_{P-Rh} = 7$ Hz, $J_{P-P} = 7$ Hz, 3 P).

Results

$(COD)RhH_3OsP_3$ (COD = 1,5 cyclooctadiene; P = PMe_2Ph) reacts with CO_2 (1 atm) at room temperature according to eq 1.

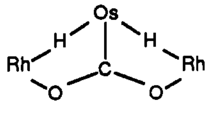
$$2(COD)RhH_3OsP_3 + 2CO_2 \rightarrow \underset{\text{II}}{H_2Os(CO)P_3} + \underset{\text{I}}{[(COD)Rh]_2OsH_2P_3CO_2} + H_2O \quad (1)$$

In this reaction, one CO_2 molecule is reduced to CO and H_2O, while a second CO_2 molecule is captured by some intermediate generated in the first step of this reaction. The reaction proceeds equally well in benzene or THF and gives I in isolated yields based on the above stoichiometry of 35–45%. Monitoring the reaction by ^1H NMR spectroscopy shows no detectable intermediates over the course of 12 h with signals for $(COD)RhH_3OsP_3$ disappearing while those for I and $H_2Os(CO)P_3$ appear. Using less than stoichiometric CO_2 results in only incomplete consumption of $(COD)RhH_3OsP_3$.

The ^{31}P and ^1H NMR spectroscopic data for complex I indicate a material containing two hydrides, one *mer*-OsP_3 unit and two Rh(COD) units, with the two Rh(COD) units being symmetry-equivalent (but the vinyl groups inequivalent). Two of the three phosphine ligands are also symmetry-equivalent. Selective heteronuclear spin-decoupling studies show each hydride to couple to one rhodium ($J_{H-Rh} = 24$ Hz). The INEPT ^{103}Rh NMR spectrum shows more directly this doublet splitting of two *equivalent* rhodium sites. The rhodium chemical shift (δ 970) is comparable to those of $[Rh(COD)H]_4$ (δ 786)[13b] and $(COD)Rh(O_3SCF_3)\{Bu^t{}_2P(CH_2)_5PBu^t{}_2\}Rh(COD)(O_3SCF_3)$ (δ 933).[13c]

Carrying out this reaction with $^{13}CO_2$ (99% enriched) yields $H_2Os(^{13}CO)P_3$ (thus establishing CO_2 as the source of the carbonyl ligand) and ^{13}C-labeled I. The $^{13}C\{^1H\}$ NMR signal of labeled I is a doublet of triplets at 193 ppm, the multiplet structure indicating strong coupling (64 Hz) to one (presumably) trans phosphine and weaker coupling (11 Hz) to two cis phosphines. The infrared bands (assigned, by comparison to the material synthesized by using $^{13}CO_2$, as 1365 and 1260 cm^{-1}) demonstrate the reduced nature of the CO_2 moiety (cf. 1337 and 2349 cm^{-1} for gaseous CO_2).

These spectroscopic characteristics are consistent with the molecular structure for I determined by X-ray diffraction (Figure 1). Compound I, $[(COD)Rh]_2OsH_2CO_2(PMe_2Ph)_3$, is a stereochemically rigid species with a planar (±0.03 Å) PRh_2OsCO_2 unit. The coordination geometry at osmium is made up of two orthogonal planes: the angle between the $OsRh_2P(4)C(32)O(31)O(32)$ plane and the $OsP(4)P(13)P(22)C(32)$ plane is 92.4°. CO_2 is bound by carbon (to Os) and both oxygens (one to each Rh) and bent to an OCO angle of 116.3 (16)°. Since the hydride ligands were not evident in the final electron density map, molecular mechanics calculations[14] were employed as a guide to their location. Using the crystallographic coordinates for all non-hydrogen atoms, stable minima were calculated for two hydrides, each located 1.8 ± 0.02 Å from osmium and one rhodium (i.e., bridging, A). These hydrogen positions yield a (square) planar



A

coordination geometry about rhodium. A corresponding search for terminal hydrides on rhodium gave only positions of dramatically higher energy.

Reactivity of I. Since I is the first example of a neutral hydrido carbon dioxide complex, we sought to find conditions in which the coordinated CO_2 could be further reduced by hydride migration to form C–H bonds or even to split O–C bonds. Thermolysis (70 °C, 24 h) and photolysis (100 W, 8 h) (even under a dihydrogen atmosphere) leaves I unchanged. Such behavior is in sharp contrast to that of other carbon dioxide complexes,[2,3] which readily lose CO_2 upon heating. The tightly bound CO_2 moiety is also resistant to exchange with labeled CO_2. When a C_6D_6 solution of $[(COD)Rh]_2OsH_2(^{13}CO_2)P_3$ is pressurized with $^{12}CO_2$ (500 psi) for 24 h, the $^{13}C\{^1H\}$ NMR spectrum reveals complete retention of the labeled CO_2. Attempts to reduce the bound CO_2 with external hydride sources also proved unsuccessful. The hydride reagents $LiBEt_3H$, $LiBH_4$, and $Cp_2Zr(H)Cl$ gave no reaction, while the use of $LiAlH_4$ resulted in decomposition of I to intractable products.

The lack of reactivity of I toward H_2 and external nucleophiles seems to be due to steric shielding of the $H_2OsRh_2CO_2$ moiety by the phosphine and olefin ligands. Indeed, space-filling drawings (Figure 2) reveal that the trimetallic core, as well as the CO_2 carbon, is deeply embedded in a hydrocarbon ligand sphere. The space-filling diagram does, however, reveal that the oxygen atoms are "exposed" (Figure 2) and could possibly be approached with external electrophiles.

Reaction of I with Electrophiles. Structure of $[(COD)Rh]_2OsH_2(CO_2)P_3ZnBr_2 \cdot THF$. Addition of a slight excess of $NaBPh_4$ to a THF-d_8 solution of I in an NMR tube causes the resonance for the hydride signal to shift upfield by 0.5 ppm to −17.3 ppm. The use of a deficiency of $NaBPh_4$ shifts the hydride resonance upfield by less than 0.5 ppm, while addition of a large excess of $NaBPh_4$ does not alter the hydride signal from −17.3 ppm. More notably, the $^{13}C\{^1H\}$ NMR spectrum of $^{13}CO_2$-enriched I shows a shift for the CO_2 unit of 5 ppm further downfield (to 198 ppm)

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upon addition of $NaBPh_4$. Solutions containing Li^+ ($LiBPh_4$) in THF show no spectral evidence of interaction with I. This lack of interaction is probably due to strong THF solvation of Li^+.[15] When anhydrous $ZnBr_2$ is added, the spectral changes are even larger than those with added Na^+. The hydride signal is now shifted upfield to −17.9 ppm, while in the $^{13}C\{^1H\}$ NMR spectrum, the labeled resonance has shifted downfield by 8 ppm to 201 ppm. The C–O vibrational frequency also drops on binding the electrophile. To confirm that the spectral changes observed were truly diagnostic of a Lewis acid–base type interaction between I and added electrophile and to establish with certainty the binding site for the electrophile, an X-ray structure determination of the $ZnBr_2$ adduct was undertaken.

The electrophile $ZnBr_2$ is shown by X-ray crystallography to bind to both oxygen atoms of the coordinated CO_2 of I (Figure 3) with complete displacement of THF from the coordination sphere of Zn^{2+}. The pseudotetrahedral Zn center lies in the same plane as the Rh_2OsCO_2 unit. Overall, binding of the electrophile causes no gross structural rearrangements although some distances and angles do change. The Os–C distance of 2.01 Å is reminiscent of a hetero carbene type interaction. The C–O distances of 1.30 Å are lengthened from that of free CO_2 (1.16 Å) and ketones (1.22 Å) but still considerably shorter than that of C–O single bonds (1.45 Å). The hydrides are presumed (on the basis of ^1H NMR data) to each be bridging a Rh–Os (3.00 Å) vector.

Generality of the Reaction of $(COD)RhH_3OsP_3$ with CO_2. In an attempt to establish what characteristics of $(COD)RhH_3OsP_3$ (II) promote its reduction of CO_2, selected analogues were synthesized and their reactivity with CO_2 evaluated. The iridium analogue, $(COD)IrH_3OsP_3$, is produced in 60% yield by the reaction of $K[OsH_3P_3]$ with $[(COD)IrCl]_2$. The spectral data for this complex are similar to those of II, lacking only the additional Rh coupling. Under conditions identical with those in which II reacts with CO_2, no reaction was observed between $(COD)IrH_3OsP_3$ and CO_2. The use of higher CO_2 pressures (500 psi) likewise gave no reaction.

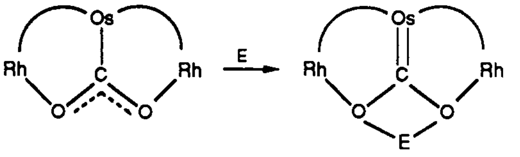
Replacing the COD ligand in II with two PMe_2Ph groups was achieved by reacting $K[OsH_3P_3]$ with $[(PMe_2Ph)_2RhCl]_2$. The resulting $(PMe_2Ph)_2RhH_3OsP_3$ represents an extremely basic, unsaturated species and as such was anticipated to have interesting reactivity with CO_2. However, this complex also proved inert to CO_2 at both ambient and elevated (500 psi for 24 h) CO_2 pressures. The analogue $(PMePh_2)_2RhH_3OsP_3$ was similarly unreactive. Since replacement of COD in II with two PMe_2Ph ligands curtailed any CO_2 reactivity, a more subtle change, the replacement of COD by two cyclooctenes (COE), was investigated. The complex $(COE)_2RhH_3OsP_3$ was synthesized by the reaction of $K[OsH_3P_3]$ with $[(COE)_2RhCl]_2$. Again, no reaction was observed with CO_2 under a variety of conditions.

Discussion

This study reveals the formation of a heterometallic carbon dioxide complex from the reaction of CO_2 with a heterobimetallic polyhydride complex under mild (1 atm CO_2 and 25 °C) conditions. In this reaction, one CO_2 molecule is also reduced to CO, captured as $OsH_2(CO)P_3$ ($^{13}CO_2$ produces $OsH_2(^{13}CO)P_3$), and H_2O.

After futile attempts to promote intramolecular reduction of the coordinated CO_2 in I with the available hydride ligands as well as failure to realize CO_2 reduction with external hydride reagents, we turned our attention toward using electrophiles to promote CO_2 reduction. The electrophile-promoted reduction of CO_2 to CO and CO_3^{2-} is one of the better studied reactions in the field of carbon dioxide chemistry. Studies by Cooper[5,6] have shown that, in the presence of Li^+, $W(CO)_5^{2-}$ will reduce CO_2 to CO and CO_3^{2-} through the intermediacy of Li^+-stabilized carbon dioxide adducts. Another example of electrophile-promoted reduction of carbon dioxide comes from the group of Bianchini.[16] Interestingly, this group has found that the complex $HCo(np_3)$ (np_3 = tris(2-(diphenylphosphino)ethyl)amine) will reduce CO_2 to CO (as $[(np_3)CoCO]BPh_4$) and phosphine oxide ($O{=}PPh_2CH_2CH_2N(CH_2CH_2PPh_2)_2$) *only* in the presence of Na^+. Other examples where alkali-metal cations play a prominent role in CO_2 transformation chemistry include Darensbourg's studies[17,18] of alkali metal ion promoted CO_2 insertions and Floriani's K^+-stabilized Co/CO_2 complex.[2c]

The spectral changes we observe upon addition of $NaBPh_4$ and $ZnBr_2$ are consistent with a Lewis acid–base interaction between the CO_2 oxygens and added electrophiles, E (eq 2). Indeed, the X-ray study does reveal that added $ZnBr_2$ coordinates to the CO_2 moiety in I forming a μ_4,η^3 coordination mode previously unobserved for CO_2.



(2)

A comparison of structural parameters of the CO_2 complex and its $ZnBr_2$ adduct shows identical Rh—C, C═C, and Os—P distances. While there may be a slight lengthening of the Rh–Os and Rh–O distances in the $ZnBr_2$ adduct, these are only of magnitude 2–5σ and are therefore at most modest in size. The O–C distances, because they carry esd's of up to 0.02 Å, show no persuasive evidence of lengthening in the $ZnBr_2$ adduct. One parameter that is altered is the OCO angle, which closes from 116.3 (16) to 112.2 (10)° upon adduct formation. The Zn–O bond distance of 2.10 Å is indicative of a weak interaction by comparison to the Zn–O distances found for coordinated THF in the complexes $CpMo(CO)_3ZnBr(THF)_2$[19] (2.11 Å), $ZnCl_3(THF)^-$[20] (2.12 Å), and $Zn(OAr)_2(THF)_2$[21] (2.08 Å). The Rh–O distance is quite comparable to that in $(COD)_2Rh_2(\mu\text{-}OMe)_2$.

The Os–C distance shortens 0.048 Å (2.1σ_{diff}) on adduct formation. We suggest that binding zinc to oxygen makes carbon more electron deficient, with the result that multiple Os–C bonding increases in a compensatory effort. Thus, eq 2 has been drawn so as to emphasize enhanced carbene character of the Os–C bond in the electrophile adduct. It must be pointed out, however, that *both* Os–C distances indicate varying degrees of multiple bonding. A typical Os—C single-bond length is 2.22 (2)Å[22] and an $Os{=}CH_2$ distance is 1.92 (1) Å.[23] This is corroborated by the downfield ^{13}C NMR shift (i.e., toward more carbene character).

Finally, in an attempt to extend the range of compounds that would react with CO_2, a number of analogues of $(COD)RhH_3OsP_3$ were synthesized and their reactivity with CO_2 explored. Replacing rhodium with iridium we hoped would, due to the less reactive nature of iridium, permit the isolation and characterization of the intermediates involved in the formation of $[(COD)Rh]_2OsH_2CO_2P_3$. Unfortunately, the less reactive nature of iridium is indeed evident, with no reaction with CO_2 (500 psi, 12 h, THF) being observed. Next, we had hoped that increasing the basicity at the rhodium center would be beneficial for CO_2 activation; the COD ligand in II was replaced with two PMe_2Ph (or $PMePh_2$) ligands. Under a variety of conditions, this complex, unsaturated at rhodium, also showed no reaction with 500 psi CO_2 in THF for 12 h. Surprisingly, the most subtle change, replacing COD in II with two cyclooctene ligands also halts any reaction with CO_2 (500 psi, 12 h, THF). The totality of these negative results suggests some special balance of factors is achieved with the

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(COD)Rh unit, yet we still lack understanding and rational control of such factors.

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Registry No. I, 106017-47-4; $OsH_2(CO)(PMe_2Ph)_3$, 41574-21-4; $OsH_4(PMe_2Ph)_3$, 24228-57-7; $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3NaBPh_4$, 124042-08-6; $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3ZnBr_2 \cdot THF$, 124021-23-4; $(COD)IrH_3Os(PMe_2Ph)_3$, 124021-24-5; $(PMe_2Ph)_2RhH_3Os(PMe_2Ph)_3$, 124021-25-6; $(COE)_2RhH_3Os(PMe_2Ph)_3$, 124021-26-7; $(PMePh_2)_2RhH_3Os(PMe_2Ph)_3$, 124021-27-8; $(COD)RhH_3Os(PMe_2Ph)_3$, 106017-48-5; $K[OsH_3(PMe_2Ph)]$, 106061-75-0; $[(COD)IrCl]_2$, 12112-67-3; $[(PMe_2Ph)_2RhCl]_2$, 124021-28-9; $[(COE)_2RhCl]_2$, 12279-09-3; $[(PMePh_2)_2RhCl]_2$, 124021-29-0; Os, 7440-04-2; Rh, 7440-16-6.

Supplementary Material Available: For $[(COD)Rh]_2OsH_2(CO_2)(PMe_2Ph)_3$ and its $ZnBr_2$ adduct, tables of anisotropic thermal parameters (2 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Notes

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(Phthalocyaninato)osmium(II) and Bisaxially Coordinated (Phthalocyaninato)osmium(II) Compounds

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Bisaxially coordinated complexes $MacML_2$ and bridged systems $[MacML]_n$ with phthalocyanine (Pc) or 1,2- or 2,3-naphthalocyanine as the macrocycle (Mac) and transition metals, e.g. iron or ruthenium, as the central metal atom (M) have been systematically investigated by us regarding their semiconducting properties.[1,2] The third metal in the eighth group of the periodic table of elements, osmium, has rarely been used until today, however. On the other hand, (porphyrinato)osmium complexes with octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) as macrocyclic ligands have been much better studied than their analogous ruthenium complexes.[3-6]

Osmium phthalocyanine derivatives have been described several times in the literature.[7-15] The pure unsubstituted $PcOs^{II}$ and bisaxially coordinated $PcOsL_2$ compounds with N-heterocyclic or isocyanide ligands or bridged PcOs compounds $[PcOsL]_n$ carrying bidentate ligands have not yet been reported.

Synthesis and Characterization of (Phthalocyaninato)osmium(II) ($PcOs^{II}$)

All of the procedures that have been described so far for the synthesis of PcOs deliver only insufficiently characterized products and/or require the use of the highly poisonous OsO_4 as the starting metal compound. For the synthesis of pure $PcOs^{II}$ we therefore followed the route that we have already described for the synthesis of pure $PcRu^{II}$[16] (Scheme I).

Table I. Electronic Absorption Maxima (nm) of $PcM(py)_2$ (M = Fe, Ru, Os) in Chloroform

complex	Q band			Soret band
$PcFe(4\text{-pic})_2$[21,25]	656	594	410	328
$PcRu(py)_2$[21,24]	625	573	377	313
$PcOs(py)_2$[a]	616	563	369	308

[a] Bands also appear at 460, 436, and 416 nm.

o-Cyanobenzamide[17] was reacted with $OsCl_3$ in molten naphthalene. After column chromatography a uniform product (TLC) is obtained. The FD mass spectrum does not show the expected molecular ion for PcOs (*m/e* = 702), but instead the peak for a dimeric molecule (*m/e* = 1407) with the characteristic isotopic pattern for osmium.[18] According to its IR spectrum, the crude product might actually be a bisaxially coordinated species, where derivatives of phthalic acid or the cyclized *o*-cyanobenzamide is axially coordinated. The crude $PcOsL_x$ is then heated slowly up to 400 °C under a stream of nitrogen, and this temperature is maintained for about 1 h. Reaction control is carried out by simultaneous thermogravimetry/differential thermal analysis (TG/DTA). Separation of the axially coordinated ligands is observed between 160 and 385 °C.

The FD mass spectrum of the resulting blue-black powder shows the expected molecular ion (*m/e* = 702) with the characteristic isotopic pattern for osmium. A signal for the dimeric $[PcOs]_2^+$ as for the crude $PcOsL_x$ cannot be detected. The infrared spectrum of PcOs is almost identical with that of PcRu[19-21] with only a few bands shifted to higher or lower frequencies, respectively.

This striking similarity can be explained by the nearly identical covalent radii of ruthenium(II) and osmium(II).[22] PcOs exhibits a dark conductivity of 2.5×10^{-5} S/cm (pressed powder, two-probe technique). This value is rather high compared with those of most metal phthalocyanines, but it is within the same range as the conductivity of PcRu.[19]

Bisaxially Coordinated (Phthalocyaninato)osmium(II) Complexes

Bis(pyridine)(phthalocyaninato)osmium(II) ($PcOs(py)_2$). $PcOs(py)_2$ can be synthesized from the crude $PcOsL_x$ or pure PcOs

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