Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Hexakis(3,5-di-*tert*-butylphenyl)ethane (**1b**)

	x	y	z	U^a
C(1)	-290 (5)	-290 (5)	-290 (5)	49 (2)
C(2)	0	-1204 (4)	0	100 (2)
C(3)	700 (3)	-1645 (3)	0	83 (2)
C(4)	729 (3)	-2478 (3)	0	62 (1)
C(5)	0	-2877 (4)	0	59 (2)
C(6)	1528 (3)	-2921 (3)	0	78 (2)
C(7)	1983 (9)	-2778 (10)	762 (6)	145 (3)
C(8)	2011 (9)	-2625 (11)	-728 (10)	169 (3)
C(9)	1459 (3)	-3817 (4)	-68 (16)	127 (2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

symmetry (Figure 1), but the molecular axis, which includes the central carbon-carbon bond, is oriented along the four body diagonals of the cubic unit cell with equal probability (Figure 2).[9] The phenyl rings are represented as averages perpendicular to the faces of the cube. The disorder is apparent from the large anisotropic thermal parameters tangential to the plane of the benzene ring (e.g., C(2): $U_{11} = 183$ (5), $U_{22} = 39$ (3), $U_{33} = 77$ (4) $Å^2 \times 10^3$). The C(1)-C(2) benzylic bond length of 1.670 (7) Å as well as the C(1)-C(2)-C(3) and C(1)-C(2)-C(3A) angles of 137.0 (4)° and 103.9 (4)° are artifacts of averaging the four phenyl orientations. The solvent molecules are located at the intersections of the three mirror planes (Wyckoff position *b*) and are highly disordered.

The ethane carbon atoms, by contrast with the phenyl carbons, are not represented at average positions. Furthermore, these atoms are well defined, with relatively small thermal parameters ($U_{11} = U_{22} = U_{33} = 49$ (4) $Å^2 \times 10^3$). The estimated standard deviation associated with the central carbon-carbon bond length, 1.67 (3) Å, is significantly higher than that for other bond lengths in the molecule. Among the contributing reasons are the following. First, the ethane carbon lies on a special position and hence has an inherent indeterminacy associated with this position.[10] Second, the ethane carbons are related by a center of symmetry; this correlation leads to an error in bond length equal to $2\sigma(x)$. Third, there is a greater error in the position of the ethane carbon due to the reduced occupancy; this follows from the proportionality of $\sigma(x)$ and $\sigma(\mathrm{d}\rho/\mathrm{d}x)$.[10,11]

In light of the present findings and of the previous computational studies,[1,3] the claim for bond shortening of r_c in **1a**[2] may now be safely dismissed.[12]

Acknowledgment. We thank the National Science Foundation (CHE-8510067) for support of this work.

Supplementary Material Available: Bond lengths, bond angles, with standard deviations for **1b** (Tables II and III), final anisotropic thermal parameters (Table IV), and atomic parameters for hydrogen (Table V) and for cyclohexane (Table VI) (2 pages); listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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[9] It is not uncommon for "globular" ethanes to exhibit a cubic solid phase in which the ethane bond is disordered among the four threefold axes. See: (a) Hexamethylethane: Koide, T. *Bull. Chem. Soc. Jpn.* **1967**, 40, 2026. (b) Hexachloroethane: Atoji, M.; Oda, T.; Watanabe, T. *Acta Crystallogr.* **1953**, *6*, 868. (c) Hexabromoethane: Koide, T.; Tsujino, M.; Sawada, K.; Oda, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2998.

[10] Cruickshank, D. W. J.; Rollett, J. S. *Acta Crystallogr.* **1953**, *6*, 705.

[11] Jeffrey, G. A.; Rollett, J. S. *Proc. R. Soc. London, A* **1952**, *213*, 86.

[12] Doubts concerning the reliability of this r_c value have previously been expressed by us (ref 3, footnote 11) and by others (Olah, G. A.; Field, L. D.; Watkins, M. I.; Malhotra, R. *J. Org. Chem.* **1981**, *46*, 1761. Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982; p 150).

High Yields of Formal CH Insertion Products in the Reactions of Polyfluorinated Aromatic Nitrenes

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Aryl azides continue to be widely used as photoaffinity labeling (PAL) reagents for biomolecules.[2] Unfortunately, photolysis of phenyl azide or its simple derivatives in a model solvent such as toluene leads only to trace amounts of aniline and azobenzene and large quantities of intractable tars.[3] An adduct of phenylnitrene and toluene, the useful product of PAL studies, is not formed in detectible quantities. We recently reported the formation of modest yields (~30%) of a formal insertion adduct in the reaction of triplet (*m*-nitrophenyl)nitrene with frozen polycrystalline toluene at the benzylic position.[4] Adduct formation did not occur upon direct photolysis or in only very low yield on triplet-sensitized photolysis of *m*-nitrophenyl azide in toluene solution. In this paper we report the effect of temperature and phase on the photochemistry of pentafluorophenyl and 2,6-difluorophenyl azides. Our interest in fluorine-substituted aryl azides was motivated by Reiser and Leyshon's report that electron-withdrawing substituents enhance the reactivity of triplet aryl nitrenes.[5] Fluorine is also an ideal substituent for PAL as it is nearly isosteric with hydrogen[6] and thus should not interfere with substrate recognition.

Photolysis of **1a** and **1b** in toluene at 25 °C gives small amounts of tar, the fluorinated anilines **3a** and **3b**, azo compound **5b**, and the adducts **4a** and **4b** and their isomers (Table I and II).[7] The ratio of isomers formed by photolysis of **1a** in toluene at 25 °C was in agreement with the reports of Abramovitch, Challand, and Scriven[8] who deoxygenated pentafluoronitrosobenzene in toluene. At -78 °C, some tar is still formed on photolysis of **1a** and **1b**, there is an increase in yields of the azo compounds **5a,b**, but there is a decrease in the yields of the nitrene-toluene adducts. Simply lowering the temperature of a solution-phase photolysis does not lead to an increased yield of the desired adducts. Sensitized photolysis of **1a** and **1b** at 25 °C led to a decrease in the amount of tar produced, high yields of anilines **3a** and **3b**, low yields of insertion adducts **4a**, **4a′**, and isomerically pure **4b**. The generation of triplet nitrenes in solution by sensitized photolysis does not lead to appreciable yields of the adducts desired in a PAL experiment. However, photolysis of frozen polycrystalline toluene containing **1a** or **1b** gave almost quantitative yields of insertion adducts **4a** and **4b** which were essentially isomerically pure. Tar was not present in the low-temperature photolysis reaction mixture. Thus the combination of fluorine substitution and low-temperature irradiation appears to be an ideal strategy for efficient PAL (Scheme I).

The origin of the enhanced yields of adducts formed in matrices was revealed by EPR analysis. Photolysis of **1a** and **1b** in polycrystalline toluene at -196 °C leads to triplet nitrenes **2a** and **2b** which are indefinitely stable in the dark at this temperature.

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[1] Camille and Henry Dreyfuss Teacher-Scholar.

[2] Bailey, H. *Photogenerated Reagents in Biochemistry and Molecular Biology*; Elsevier: New York, 1983.

[3] See: Smith, P. A. in *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: San Diego, CA, 1985; p 95.

[4] Torres, M. J.; Zayas, J.; Platz, M. S. *Tetrahedron Lett.* **1986**, *27*, 791.

[5] Reiser, A.; Leyshon, L. *J. Am. Chem. Soc.* **1970**, *92*, 7487.

[6] The atomic radii in covalent bonds for H and F are 0.37 and 0.72 Å, respectively: Gordon, A. J.; Ford, R. A. *Chemist's Companion*; Wiley: New York, 1972; pp 82-85.

[7] The benzylic insertion adducts **4a** and **4b** were differentiated from their aromatic insertion isomers by GC-MS analysis and by independent synthesis. Compounds were analyzed for by GC; products were identified by coinjection with authentic samples.

[8] (a) Abramovitch, R. A.; Challand, S. R.; Scriven, E. F. V. *J. Org. Chem.* **1972**, *37*, 2705. (b) Abramovitch, R. A.; Challand, S. R.; Scriven, E. F. V. *J. Am. Chem. Soc.* **1972**, *94*, 1374.

0002-7863/86/1508-8307$01.50/0

Scheme I

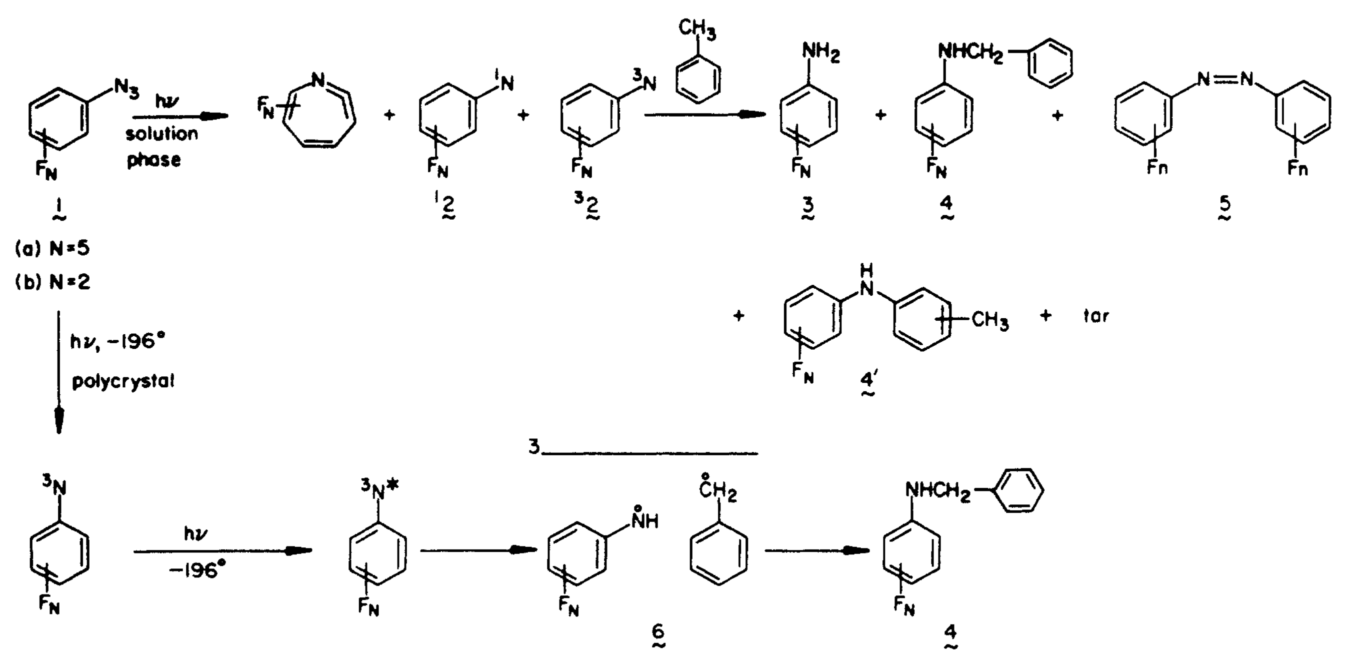

Table I. The Distribution of Products Formed on Photolysis of **1a** in Toluene[a]

	reaction products (absolute yield, %)		
T (±2 °C)	**3a**	**4a**	**5a**
25[b]	12	52[c]	
25[d]	17	8.3	
-78[b]	9.8	33[c]	17
-196[b,e]	5.9	77[c]	7.9

[a] λ = 350-nm Rayonet photochemical reactor, 4 h, all products analyzed by GC. [b] 4.03×10^{-2} M **1a** and naphthalene (internal standard) in toluene. [c] Yield includes isomers **4a**'. [d] 4.10×10^{-2} M **1a**, 2.00×10^{-2} M 2-acetonaphthone (sensitizer), and naphthalene (internal standard) in toluene, λ = 365 nm. [e] After photolysis, the frozen solution was kept at -196 °C in the dark for 46 h before it was thawed to room temperature.

Table II. The Distribution of Products Formed on Photolysis of **1b** in Toluene[a]

	reaction products (absolute yield, %)		
T (±2 °C)	**3b**	**4b**	**5b**
25[b]	17	13[c]	3
25[d]	54	5	10
-78[b]	16	trace[c]	24
-196[b,e]	trace	94	6

[a] λ = 350 nm Rayonet photochemical reactor, 4 h, all produts analyzed by GC. [b] 4.0×10^{-2} M **1b** and naphthalene (internal standard) in toluene. [c] Yield includes its isomers **4b**'. [d] 1.0×10^{-2} M **1b**, 1.0×10^{-1} M naphthophenone (sensitizer), and diphenylmethane (internal standard) in toluene. [e] After photolysis, the frozen solution was kept in -196 °C in the dark for 40 h before it was thawed to room temperature.

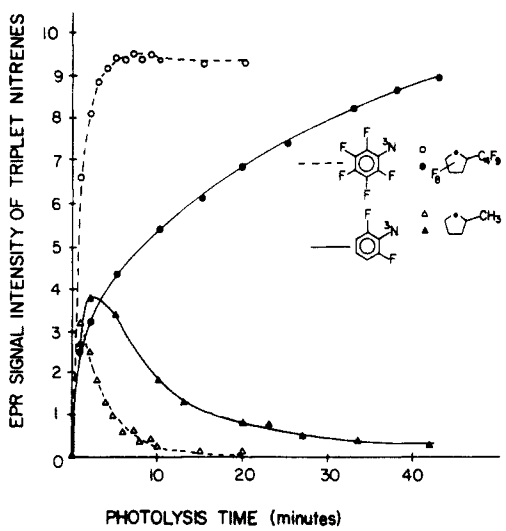

Figure 1. Time dependence of the EPR signals of ^{3}**2a,b** in 2-MeTHF and perfluoro-2-n-butyltetrahydrofuran at -196 °C during continuous irradiation.

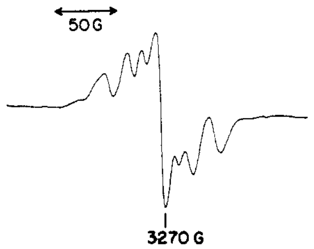

Figure 2. EPR spectrum of the RP derived from the photoreaction of (2,6-difluorophenyl)nitrene and ethanol.

Prolonged photolysis of ^{3}**2a** and ^{3}**2b** in frozen toluene, ethanol, or 2-methyltetrahydrofuran destroys these nitrenes as evidenced by the disappearance of their associated EPR resonance peaks near 7000 G (Figure 1). Triplet nitrenes **2a** and **2b** are completely stable to prolonged photolysis in a glass of perfluoro-2-n-butyltetrahydrofuran (where H atom abstraction is impossible). The disappearance of ^{3}**2a** and ^{3}**2b** is accompanied by the formation of EPR spectra attributed to the polyfluoroanilino–benzyl radical pairs **6a** and **6b** centered near 3250 G. Radical pair spectra were also observed in 2-methyltetrahydrofuran and ethanol glasses (Figure 2), but significantly no radical pair EPR spectra were observed in the perfluorinated glass or in toluene-d_8 or in ethanol-d_6.

The near quantitative yields of adducts **4a** and **4b** formed in frozen toluene are a direct consequence of the matrix conditions. Solid-state conditions impart long lifetimes to triplet nitrenes because dimerization leading to azo compounds **5a** and **5b** is retarded. Under these conditions the nitrenes can accumulate and undergo secondary photolysis. Fluorine is an ideal substituent for low-temperature PAL because fluorinated arylnitrenes do not photoisomerize to benzazirines or ketenimines[9] as per phenyl-

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(9) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1982**, 1192. Ketenimines and benzazirines are not useful in PAL because they only react with nucleophiles and polymerize to form tars.

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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(10) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783.

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

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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]

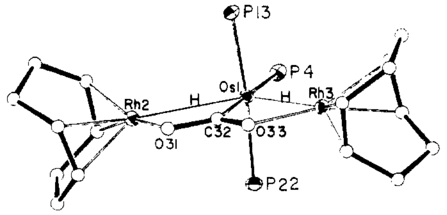
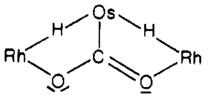
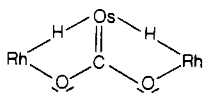


Figure 1. ORTEP drawing of the inner coordination sphere of $(COD)_2Rh_2OsH_2CO_2(PMe_2Ph)_3$. The hydrides are shown in the positions determined by molecular mechanics calculations. Selected bond distances: Os(1)–Rh (2) 2.9679 (20), Os(1)–Rh(3) 2.9880 (21), Os(1)–C(32) 2.062 (19), Rh(2)–O(31) 2.062 (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)°.

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 $J(H\text{–}Rh)$ = 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 sp^3 carbon,[14] thus favoring a blend of the following electronic structures:





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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(1) Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Intl. Ed. Engl.* **1986**, *25*, 262.

(2) Geerts, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 590.

(3) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 1759 and references therein.

(4) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8310.

(5) Skupinski, W. A.; Huffman, J. C.; Bruno, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8128.

(6) Lundquist, E. G.; Caulton, K. G., submitted for publication in *Inorg. Synth.*

(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, $J_{Me\text{–}P}$ = 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, $J_{P\text{–}Rh}$ = 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, $J_{p\text{–}p}$ = 16 Hz, 2 P), −37.0 ppm (t, $J_{p\text{–}p}$ = 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 $J_{H\text{–}Rh}$ = 24 Hz, selectively coupling to the unique phosphorus gives $J_{H\text{–}P}$ = 11 Hz, selectively coupling to the two equivalent phosphorus ligands gives $J_{H\text{–}P'}$ = 7 Hz; 1.05 (d, $J_{Me\text{–}P}$ = 6 Hz, 6 H), 1.55 (m, COD, 4 H), 1.65 (m, COD, 4 H), 2.12 (virtual triplet, $J_{Me\text{–}P}$ = 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, $J_{p\text{–}p}$ = 22 Hz, 2 P), −39.5 (t, $J_{p\text{–}p}$ = 22 Hz, 1 P).

(11) Crystallographic data (−155 °C): a = 10.338 (4) Å, b = 23.184 (11) Å, c = 19.943 (8) Å, β = 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.

(13) Terminal hydrides on osmium would be inconsistent with the large observed Rh–H coupling.

(14) Motyl, K. M.; Norton, J. R.; Schauer, C. K.; Andersen, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325.

(15) Delavaux, B.; Chaudret, B.; Devillers, J.; Dahan, F.; Commerges, G.; Poilblanc, R. *J. Am. Chem. Soc.* **1986**, *108*, 3703.

(16) $^{13}C\{^1H\}$ NMR (C_6D_6): 191 ppm (d of t, $J_{CO\text{–}P}$ = $J_{CO\text{–}P'}$ = 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, $J_{C\text{–}P\,trans}$ = 64, $J_{C\text{–}P\,cis}$ = 11 Hz), 130 (m, Ph–P), 87 (d, $J_{C\text{–}Rh}$ = 13 Hz), 71 (d, COD, $J_{C\text{–}Rh}$ = 13 Hz), 33 (s, COD), 30 (s, COD), 29 (t, $J_{Me\text{–}P}$ = 10 Hz), 23 ppm (d, $J_{Me\text{–}P}$ = 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.

0002-7863/86/1508-8309$01.50/0