Reaction of Carbon Monoxide with Hydridobis[di(tertiary phosphine)]rhodium(I) Complexes. Synthesis and Structure of the Metal-Metal Bonded Carbonyl-Bridged Dimers $[Rh(CO)(diphosphine)]_2(\mu\text{-}CO)_2$

Brian R. James,* Devinder Mahajan, Steven J. Rettig, and Gregory M. Williams

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

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Reaction of the hydridorhodium(I) complexes $RhH(P\text{-}P)_2$ with carbon monoxide leads to formation of the dimeric carbonyl-bridged complexes $[Rh(CO)(P\text{-}P)]_2(\mu\text{-}CO)_2$ with concomitant elimination of hydrogen, where P-P represents the di(tertiary phosphines): 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, and 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, abbreviated as dppe, dppp, and diop, respectively. The $Rh_2(dppp)_2(CO)_4\cdot{}^1/_2C_6H_6$ complex exists as two crystallographically independent binuclear molecules possessing approximate C_2 symmetry (triclinic, space group $P\bar{1}$, a = 17.222 (3) Å, b = 21.513 (4) Å, c = 15.479 (3) Å; α = 90.929 (11)°, β = 108.358 (9)°, γ = 86.303 (12)°; Z = 4; R = 0.047 and R_w = 0.056 for 8068 reflections with $I \geq 3\sigma(I)$). The structure is described in terms of two square pyramids (with phosphorus apical) sharing an edge formed by the two bridging carbonyl ligands, the mean angle between basal planes being 82.6°; a formal metal-metal single bond is indicated. Important bond lengths are Rh-Rh = 2.725 (1) and 2.709 (1) Å, Rh-P(basal) = 2.340 (3)-2.399 (3) Å, Rh-P(apical) = 2.316 (3)-2.340 (3) Å, Rh-CO(bridging) = 2.036 (9)-2.067 (10) Å, and Rh-CO(terminal) = 1.920 (11)-1.944 (11) Å. Low-temperature $^{31}P\{H\}$ NMR spectra are consistent with the rigid structure; at room temperature the pairs of phosphorus atoms become chemically equivalent, probably via carbonyl site exchange since the ^{13}C NMR spectrum is a single, broad resonance. Spectroscopic data for all three complexes indicate the same structure in each case. Like the corresponding bis(triphenylphosphine) species, the complexes are active catalysts for hydrogenation, isomerization, and hydroformylation of terminal olefins.

Introduction

Di(tertiary phosphine) complexes of Rh(I) are known to catalyze a variety of organometallic reactions, including the decarbonylation of aldehydes,[1,2] reduction of aromatic nitro compounds,[2] hydroformylation,[3] and hydrogenation of olefinic substrates[4] including asymmetric catalysis when chiral diphosphines are used.[5] In order to develop the chemistry of rhodium(I) diphosphine compounds, particularly with regard to asymmetric catalysis, we have been studying the reactions of such species with small gas molecules.[6] One aim of the work was to develop syntheses for complexes of the type RhH(CO)(P-P), analogous to the very effective hydroformylation catalyst systems involving $RhH(CO)(PPh_3)_n$ (n = 1-3).[7] This paper reports our findings on the reaction of carbon monoxide with $RhH(P\text{-}P)_2$ complexes[6] [P-P = dppe, dppp, (+)-diop].[8]

Table I. Spectroscopic Data for $[Rh(CO)(P\text{-}P)]_2(\mu\text{-}CO)_2$ Complexes[a]

P-P	$\delta(^{31}P)$	J_{Rh-P}[b]	$\delta(^1H)$	ν_{CO}
dppe	38.1	138	2.24 (br 8 H), 7.08 (m, 24 H), 7.68 (m, 16 H)	1960, 1720
dppp	9.7	154	1.66 (m, 4 H), 2.36 (m, 8 H), 7.08 (m, 24 H), 7.52 (m, 16 H)	1967, 1718
dppp[c]	2.0 13.9	181 109		
diop	3.7	160	1.38 (s, 12 H), 3.11 (br m, 8 H), 4.16 (br m, 4 H), 7.16 (br m, 24 H), 7.56 (br m, 16 H)	1960, 1740

[a] NMR spectra recorded in toluene-d_8 at 30 °C; ^{31}P relative to $P(OMe)_3$, downfield positive; ^1H relative to Me_4Si; chemical shifts in ppm; coupling constants in Hz. IR in cm^{-1} (KBr). [b] The separation of the two intense peaks is written simply as J_{Rh-P} and will incorporate the longer range, smaller couplings. Some remarkably similar spectra for related rhodium compounds have been analyzed as AA'A''A'''XX' systems (Mague, J. T.; Sanger, A. R. *Inorg. Chem.* 1979, *18*, 2060). [c] At -65 °C.

Experimental Section

General Data. All operations were carried out under Ar or CO atmospheres using standard Schlenk techniques. Benzene, toluene, and hexane were distilled under N_2 from sodium benzophenone ketyl; ethanol was vacuum degassed. Infrared spectra were recorded as KBr disks on a Perkin-Elmer 598. A Varian XL-100 was used to record $^{31}P\{H\}$ NMR spectra with $P(OCH_3)_3$ as an external standard. ^1H and ^{13}C NMR were obtained with Varian XL-100 and Bruker WP-80 instruments. The stoichiometries of the gas/Rh solution reactions were measured with a constant-pressure apparatus described elsewhere.[9] Carbon

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[8] Abbreviations used: dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

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monoxide (C. P. grade) and H_2 (Prepurified) were Matheson products and were used as provided. H_2 was identified by GC (12-ft Porapak Q column at 30 °C) and mass spectrometry (AEI MS902).

Rhodium(III) trichloride trihydrate (41.37% Rh) was supplied by Johnson, Matthey Ltd. The diphosphines (Strem Chemicals) were recrystallized prior to use. The precursor hydridobis[di(tertiary phosphine)]rhodium(I) complexes, RhH(P-P)$_2$, were prepared by literature procedures.[6,10-12] Microanalyses were performed by Mr. P. Borda of this Department.

Preparation of [Rh(CO)(P-P)]$_2$(μ-CO)$_2$ Complexes. All of the carbonyl dimers were prepared as described below for the dppp compound.

The RhH(dppp)$_2$ complex (0.58 g, 0.63 mmol) was dissolved in 25 mL of benzene. Carbon monoxide was bubbled through the red-orange solution; the mixture turned bright yellow within 2 min. Bubbling of CO was continued until the reaction volume was approximately 5 mL. Addition of 25 mL of hexane resulted in precipitation of a lemon yellow solid. The product (0.33 g, 0.30 mmol, 95%) was collected on a fritted filter and thoroughly dried under a stream of CO. The dppp complex when dry is only slightly sensitive to oxygen, while the dppe and diop analogues are much more reactive and can tolerate exposure to air for only very brief periods of time. Anal. Calcd for $Rh_2(dppp)_2(CO)_4 \cdot {}^1/_2 C_6H_6$, $C_{64}H_{51}O_4P_4Rh_2$:[13] C, 61.34; H, 4.65. Found: C, 61.55; H, 4.75. Analyses for the dppe and diop complexes were consistently low in carbon (up to ~1.0%), which we attribute to their sensitivity in handling. The spectroscopic data for the three complexes (Table I and text) show them to be pure compounds.

Crystals of $Rh_2(dppp)_2(CO)_4$ for structural analysis were grown under a CO atmosphere by layering hexanes over a benzene solution of the dimer. After 15 days, a crystal was wet mounted in a capillary tube in a glovebag filled with CO.

X-ray Crystallographic Analysis of $Rh_2(dppp)_2(CO)_4 \cdot {}^1/_2C_6H_6$. Crystallographic data are given in Table II. The crystal was mounted in a general orientation, lattice constants being determined by least squares on $(2 \sin \theta)/\lambda$ values for 25 reflections (with $30 < 2\theta < 35°$) measured with Mo Kα_1 radiation (λ = 0.709 30 Å). The intensities of the reflections (−2,3, −7), (690), and (802) (monitored each hour of X-ray exposure time) decreased uniformly by 7% during the data collection. An isotropic decay correction was applied during the data processing,[14] but no absorption correction was applied due to the irregularity of the crystal surface.

The centrosymmetric space group $P\bar{1}$ was indicated by the E statistics and by the Patterson function, from which the coordinates of the Rh and P atoms of each of the two crystallographically independent complex molecules were determined. The remaining non-hydrogen atoms were positioned from subsequent Fourier syntheses. The 17 independent phenyl rings were refined as rigid groups (D_{6h} symmetry, C–C = 1.392 Å), and all other non-hydrogen atoms were refined with anisotropic thermal parameters, to an R value of 0.054. Hydrogen atom positions and isotropic thermal parameters were then calculated (C–H = 0.98 Å, $B_H = B_C + 1.0$ Å^2) and included as fixed contributions in subsequent cycles of refinement. The phenyl hydrogen atoms were incorporated into the rigid groups.

Neutral atom scattering factors from ref 15 were used for all atoms except hydrogen, which were taken from ref 16. Anomalous scattering factors from ref 17 were used for Rh and P atoms. Mean and maximum parameter shifts on the final cycle of refinement corresponded to 0.07σ and 0.83σ, the largest shift being associated with the temperature factor of C(3) in ring 1. The largest peak on the final difference map (0.94 e Å^{-3}) was in the vicinity of phenyl ring 1, which displays a high degree of thermal motion. No evidence of orientational disorder of ring 1 was noted, the residual density in this region probably arising from inadequacies in the rigid-group model.

Table II. Crystallographic Data[a]

compd	$Rh_2(dppp)_2(CO)_4 \cdot {}^1/_2C_6H_6$
formula	$C_{58}H_{52}O_4P_4Rh_2 \cdot {}^1/_2C_6H_6$
fw	1181.81
cryst system	triclinic
a, Å	17.222 (3)
b, Å	21.513 (4)
c, Å	15.479 (3)
α, deg	90.929 (11)
β, deg	108.358 (9)
γ, deg	86.303 (12)
V, Å^3	5432 (2)
Z	4
D_{calcd}, g cm^{-3}	1.445
space group	$P\bar{1}$ (reduced cell)
$F(000)$	2412
cryst dimens, mm	0.16 × 0.25 × 0.28
bounding planes	irregular
μ(Mo Kα), cm^{-1}	7.59
diffractometer	Enraf-Nonius CAD4-F
scan type	ω-2θ
ω scan speed, deg min^{-1}	1.44–10.06
scan range, deg in ω	$0.70 + 0.35 \tan \theta$
data collected	$\pm h, +k, \pm l$
2θ(max), deg	48
no. of unique reflections	16890
no. of reflections with $I \geq 3\sigma(I)$	8068
no. of variables	565
R(obsd reflctns)	0.047
R_w(obsd reflctns)	0.056
goodness of fit	1.909

[a] Temperature 22 °C, Mo Kα radiation (λ = 0.710 73 Å), graphite monochromator, takeoff angle 2.7°, aperture $(2.0 + \tan \theta) \times 4.0$ mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (S = scan count, B = normalized background count), function minimized $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Final positional and equivalent isotropic thermal parameters [$U_{eq} = {}^1/_3\text{trace}(U_{diag})$] for the nongroup atoms are given in Table III and rigid-group parameters in Table IV. Bond lengths and angles appear in Table V and intraannular torsion angles in Table VI. Calculated coordinates and temperature factors for H atoms, anisotropic thermal parameters, a listing of torsion angles, and observed and calculated structure factors amplitudes (Tables VII–X) are included as supplementary material.

Results and Discussion

Synthesis. One route for making the hydrogenation/hydroformylation catalyst, RhH(CO)(PPh$_3$)$_3$,[7] is by treatment of RhH(PPh$_3$)$_4$ with carbon monoxide;[18] we repeated and confirmed this literature report and also measured the rapid CO uptake at 1 atm and 25 °C in toluene solution ($t_{1/2} \approx 1$ min) to be 1.0 ± 0.1 mol/Rh, consistent with the simple reaction shown in eq 1.

$$RhH(PPh_3)_4 + CO \rightarrow RhH(CO)(PPh_3)_3 + PPh_3 \quad (1)$$

$$2RhH(P\text{-}P)_2 + 4CO \rightarrow Rh_2(P\text{-}P)_2(CO)_4 + 2(P\text{-}P) + H_2 \quad (2)$$

Carbonylation of the corresponding bis(diphosphine) hydride complexes is now shown to form the carbonyl-

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[13] The sample used to obtain the elemental analysis was from the same batch of crystals used for the structural analysis.

[14] The computer programs used include locally written ones for data processing and locally modified versions of the following: ORFLS, full matrix, least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier Syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson.

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Table III. Final Positional (fractional $\times 10^4$, Rh and P $\times 10^5$) and Isotropic Thermal Parameters (10^3U, Å^2) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq}
Rh(1)	25140 (4)	44248 (4)	43858 (5)	40
Rh(2)	25338 (4)	42966 (3)	61412 (5)	36
Rh(3)	73072 (4)	14345 (3)	4800 (5)	32
Rh(4)	83253 (4)	6075 (3)	16789 (5)	33
P(1)	26496 (16)	52993 (13)	35905 (18)	50
P(2)	35456 (16)	38085 (13)	40001 (17)	45
P(3)	25775 (15)	50299 (12)	72861 (18)	43
P(4)	13277 (15)	38645 (12)	62769 (18)	43
P(5)	65269 (14)	9274 (11)	−8379 (16)	36
P(6)	75582 (15)	22583 (11)	−3399 (16)	39
P(7)	80925 (15)	5243 (12)	30816 (16)	39
P(8)	97406 (15)	5640 (12)	22896 (17)	42
O(1)	4074 (4)	4735 (4)	5862 (5)	63
O(2)	1211 (4)	5189 (4)	4934 (5)	72
O(3)	975 (6)	3899 (5)	3077 (6)	113
O(4)	3839 (5)	3281 (4)	7068 (6)	89
O(5)	8621 (4)	702 (3)	−135 (5)	59
O(6)	8258 (4)	1944 (3)	2321 (4)	54
O(7)	5844 (5)	1861 (4)	1123 (5)	71
O(8)	7926 (4)	−740 (3)	1093 (5)	66
C(1)	3393 (6)	4592 (4)	5585 (6)	44
C(2)	1786 (6)	4828 (5)	5096 (7)	45
C(3)	1556 (7)	4064 (5)	3553 (8)	64
C(4)	3331 (6)	3639 (5)	6730 (7)	50
C(5)	8276 (6)	855 (4)	377 (7)	42
C(6)	8094 (5)	1547 (4)	1791 (6)	35
C(7)	6391 (6)	1703 (5)	878 (7)	45
C(8)	8054 (6)	−237 (5)	1294 (6)	44
C(9)	3687 (6)	5369 (5)	3555 (7)	58
C(10)	4091 (6)	4803 (5)	3235 (7)	58
C(11)	4375 (5)	4284 (5)	3939 (7)	50
C(12)	1561 (6)	5355 (5)	7254 (8)	61
C(13)	965 (6)	4874 (5)	7326 (8)	66
C(14)	624 (6)	4491 (5)	6453 (8)	62
C(15)	6960 (6)	960 (5)	−1762 (6)	45
C(16)	7005 (6)	1630 (5)	−2057 (6)	46
C(17)	7696 (6)	1998 (4)	−1408 (6)	43
C(18)	8849 (6)	907 (5)	4011 (6)	49
C(19)	9738 (6)	667 (5)	4124 (6)	49
C(20)	10113 (6)	893 (5)	3441 (6)	49

bridged dimeric species $[Rh(CO)(P\text{-}P)]_2(\mu\text{-}CO)_2$. The stoichiometry of eq 2 was studied, and the *net* absorption of gas was close to the 1.5 equiv/Rh in each of the three systems examined.[19] Hydrogen was identified by mass spectrometry and by GC in the atmosphere above the final reaction solutions. The bright yellow carbonyl dimer products are readily precipitated in high yield by addition of hexane to carbonylated toluene solutions of the hydrides (eq 2). Solutions of the carbonyl dimers are oxygen sensitive but are stable under CO, and the complexes are best isolated by drying under a stream of CO. By layering CO-saturated hexanes over benzene solutions of $Rh_2(dppp)_2(CO)_4$, crystals suitable for X-ray structural analysis were obtained.

It is worth mentioning that our early studies on reaction 2 were clouded by data obtained for the dppe system, since on leaving the fully formed in situ $Rh_2(dppe)_2(CO)_4$ product to stand at 25 °C under Ar (after pumping off the CO atmosphere and the H_2 byproduct), the precursor hydride was slowly regenerated over a few days in up to about 70% yield (readily monitored by IR). We had therefore not initially considered loss of hydride as H_2, and since the ν(Rh–H) band in the IR disappeared in the carbonylation reaction, we had envisioned, and hoped for, reversible formation of a formyl species via a net CO insertion reaction promoted by the presence of the two chelating diphosphine ligands, not unlike the behavior of a hydrido(porphyrinato)rhodium(III) system.[20] We were, of course, unable to detect by NMR any hydrogen in the product either as hydride or formyl. The source of hydrogen for the regeneration of $RhH(dppe)_2$ has not yet been elucidated. The hydride is still produced if C_6D_6 is used as solvent or if $RhD(dppe)_2$ is used as the precursor. Solutions of $RhD(dppe)_2$ on standing under Ar for several days generate small amounts (~20%) of $RhH(dppe)_2$, possibly by reversible intramolecular orthometallation involving the phosphine phenyl group, but this cannot as such account for formation of the hydride from the in situ $Rh_2(dppe)_2(CO)_4$/dppe solution. It is interesting to note that the rhodium(0) species $Rh(dppe)_2$, generated electrochemically from $Rh(dppe)_2^+$, forms $RhH(dppe)_2$ by hydrogen atom abstraction from unactivated sp^3 C–H bonds.[21] Our rhodium complex, particularly when pictured as the metal–metal bond-cleaved monomer, rhodium(0) unit, $Rh(CO)_2(dppe)$, could decompose by a pathway involving C–H bond cleavage within the phosphine ligand, but as yet we have no direct evidence for any dehydrogenated dppe. Impurities in the solvent are other potential sources of hydride.

Crystal Structure of $Rh_2(dppp)_2(CO)_4\cdot{}^1/_2C_6H_6$ (1). The structure of complex 1 consists of well-separated complex and benzene molecules. The two crystallographically independent $Rh_2(dppp)_2(CO)_4$ molecules (shown in Figure 1) are essentially identical although there are some statistically significant differences between corresponding structural parameters (presented side-by-side in Table V for ease of comparison). Each of the molecules possesses approximate C_2 symmetry, the most obvious departure from which being the deviation between C_2-related intraannular torsion angles about the Rh–P bonds (see Table VII).

The inner coordination sphere of $Rh_2(dppp)_2(CO)_4$ may be thought of as two square pyramids sharing an edge of the basal plane defined by the two bridging carbonyl ligands. The average dihedral angle between basal mean planes is 82.6°. On the basis of the acute Rh–C_b–Rh angles (82.0 (4)–83.5 (4)°) and the Rh–Rh separations (2.725 (1) and 2.709 (1) Å), which lie within the 2.617 (3)–2.8415 (7) Å range previously reported[22,23] for Rh–Rh single bonds, a formal metal–metal single bond is indicated. Thus each Rh atom in the present structure attains pseudooctahedral geometry via formation of a bent Rh–Rh single bond. The geometry of the inner coordination sphere is very similar to that observed for $[IrI(CO)(PMe_2Ph)]_2(\mu\text{-}t\text{-}BuS)_2$ in which an Ir–Ir bond is strongly suggested.[24]

At each of the four independent Rh atoms, the "apical" Rh–P bond is significantly shorter than the "basal" Rh–P bond, the mean[25] distances being 2.330 (11) and 2.366 (25) Å, respectively. The observed Rh–P bond lengths are slightly longer than similar bonds in formally five-coordinate Rh(I) species, e.g., 2.303 (2)–2.330 (2) Å in $Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$,[26] and are in good agreement with the Rh–P distances of 2.357–2.387 Å in the psuedooctahedral Rh(I) complex $RhCl(O_2)(PPh_3)_3$.[27]

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[19] The range of gas-uptake values was 1.35–1.47 equiv; the reactions are fast at 25 °C and 1 atm CO pressure ($t_{1/2} \approx$ a few minutes).

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Table IV. Rigid-Group Parameters[a]

ring	x	y	z	δ	ϵ	η
1	2302 (4)	6678 (4)	4264 (6)	−1.819 (10)	−2.358 (7)	−0.567 (9)
2	1493 (4)	5335 (3)	1520 (4)	1.837 (7)	−2.483 (6)	1.695 (7)
3	4455 (3)	2691 (2)	5386 (3)	−1.118 (4)	3.030 (4)	−2.598 (5)
4	3148 (3)	3109 (2)	2053 (3)	1.000 (4)	3.048 (4)	1.079 (4)
5	3284 (3)	4504 (3)	9354 (4)	−0.183 (5)	−2.820 (5)	−1.975 (5)
6	3622 (3)	6248 (2)	7519 (3)	−2.176 (4)	2.963 (4)	0.027 (4)
7	1408 (3)	2847 (2)	7827 (3)	−2.023 (5)	2.689 (4)	−2.230 (5)
8	267 (3)	3087 (2)	4559 (3)	1.251 (5)	−2.703 (4)	0.791 (5)
9	6306 (2)	−520 (2)	−565 (3)	1.071 (7)	−2.077 (4)	−0.415 (7)
10	4652 (3)	1389 (2)	−1924 (3)	−0.123 (4)	−2.590 (4)	0.262 (4)
11	6055 (3)	3311 (2)	−914 (3)	−2.248 (4)	−2.624 (3)	−1.620 (4)
12	9121 (3)	3079 (2)	570 (3)	−1.856 (12)	1.902 (4)	−0.659 (12)
13	8229 (3)	−841 (2)	3981 (3)	−2.015 (6)	2.296 (4)	−2.466 (6)
14	6332 (3)	1082 (2)	3150 (3)	−0.560 (5)	−2.481 (5)	−0.392 (6)
15	10505 (3)	−848 (3)	2450 (4)	1.819 (8)	2.147 (5)	0.115 (8)
16	10805 (3)	1278 (3)	1277 (3)	−2.833 (5)	2.639 (4)	0.830 (5)
17	3287 (5)	503 (3)	3838 (5)	2.462 (7)	3.043 (7)	−0.553 (6)

ring	B_1	B_2	B_3	B_4	B_5	B_6
1	5.3 (3)	16.4 (8)	23.9 (12)	14.6 (7)	10.0 (4)	7.0 (3)
2	4.6 (2)	7.1 (3)	11.1 (5)	12.9 (6)	11.6 (5)	7.2 (3)
3	4.2 (2)	5.5 (3)	6.8 (3)	7.3 (3)	7.0 (3)	5.7 (3)
4	3.8 (2)	5.2 (3)	6.4 (3)	6.1 (3)	7.1 (3)	5.5 (3)
5	4.1 (2)	4.8 (2)	7.1 (3)	7.7 (3)	9.1 (4)	7.2 (4)
6	3.5 (2)	4.4 (2)	5.5 (3)	5.4 (3)	4.6 (2)	4.3 (2)
7	4.1 (2)	7.1 (3)	8.5 (4)	6.8 (3)	6.0 (3)	4.8 (2)
8	3.9 (2)	4.8 (2)	6.6 (3)	6.3 (3)	7.3 (3)	6.2 (3)
9	3.1 (2)	4.2 (2)	4.8 (2)	4.8 (2)	4.3 (2)	3.9 (2)
10	3.4 (2)	4.5 (2)	5.3 (3)	5.2 (3)	4.7 (2)	3.6 (2)
11	3.1 (2)	4.6 (2)	5.0 (2)	5.5 (3)	5.1 (2)	4.2 (2)
12	3.3 (2)	4.2 (2)	4.4 (2)	5.5 (3)	7.6 (3)	5.5 (3)
13	3.3 (2)	4.1 (2)	5.2 (3)	5.4 (3)	5.2 (3)	4.4 (2)
14	3.8 (2)	5.2 (3)	6.0 (3)	7.3 (3)	8.3 (4)	6.6 (3)
15	3.9 (2)	6.8 (3)	8.7 (4)	9.3 (4)	7.0 (3)	5.0 (2)
16	4.0 (2)	6.5 (3)	8.8 (4)	7.1 (3)	5.9 (3)	4.7 (2)
17	10.0 (4)	11.3 (5)	11.7 (5)	12.9 (6)	12.5 (6)	9.5 (4)

[a] See: LaPlaca, S. J.; Ibers, J. A. *Acta.Crystallogr.* **1965**, *18*, 511, for definition of group parameters. x, y, and z are fractional coordinates of the ring centroids (×10^4). B_i is the temperature factor of atom C_i in the phenyl ring in Å^2.

The carbonyl bridges all display a small degree of asymmetry; at each Rh atom the shorter Rh–C_b distance (mean 2.046 (13) Å) is associated with a mean Rh–C_b–O angle of 140.5 (5)° and the longer Rh–C_b distance (mean 2.067 (7) Å) with a mean Rh–C_b–O angle of 136.7 (5)°. This relationship between Rh–C_b distances and Rh–C_b–O angles in unsymmetrical bridging systems is as expected.[28] Unsymmetrical bridging of Rh–Rh bonds by carbonyl ligands has been noted previously and has been ascribed to steric effects.[23] Both the Rh–C_b distances and the mean C_b–O distance of 1.170 (10) Å are in good agreement with those observed in related structures,[23,29–34] while the Rh–C_b–O angles are generally somewhat larger and the mean Rh–C_b–Rh angle of 82.7 (8)° is generally smaller than those previously reported.[23,26,29–34] Of interest, however, the solvated dimeric complex $[Rh(PPh_3)_2]_2(\mu\text{-}CO)_2\cdot 2CH_2Cl_2$ (ν_{CO} = 1739 cm^{-1}) has a "bridging core" [Rh–Rh = 2.63 Å, Rh–C_b = 2.05 Å, Rh–C_b–Rh angle = 82°][34] that is remarkably similar to that found here for **1**, despite the very different geometries at the metal centers. The ν_{CO} at 1710 cm^{-1} for the bridging carbonyl in **1** is anomalously low. A similar low value of 1745 cm^{-1} in the $Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ complex has been associated with shorter Rh–C_b distances (1.958 (8) and 1.961 (8) Å) and stronger π-back-bonding from the metal to the carbon.[26] However, the Rh–C_b distances in the present structure are longer (2.036–2.075 Å), and the uncorrected C–O distances are in good agreement (1.167 (9) Å in the dppm complex[26] and 1.170 (10) Å in our dppp structure).

The mean Rh–C (terminal) distance of 1.933 (11) Å is significantly longer than the typical values of 1.831 (7) and 1.836 (7) Å reported for the $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ cation;[23] the longer distance presumably reflects the position of the terminal carbonyls that are each trans to a bridged carbonyl. The mean C_t–O distance of 1.133 (16) Å and Rh–C_t–O angles of 174.7 (12) to 179.4 (9)° are normal.

Each of the four unique six-membered chelate rings have distorted chair conformations (torsion angles given in Table VII). All other bond lengths and angles (Tables V and VI) assume normal values.

NMR Data. The NMR spectra of the carbonyl diphosphine dimers generally (Table I) are in full accord with the crystal structure of the dppp complex. Proton-decoupled ^{31}P data show that the four phosphorus atoms are chemically equivalent at ambient temperature. Each species exhibits a complex pattern consistent with an AA′A″A‴XX′ spin system (Figure 2). Minor differences in secondary coupling constants distinguish the spectrum of the dppe complex from those of the dppp and diop species. As well, the dppe complex shows a much larger coordination shift, consistent with the known deshielding effect of the five-membered ring.[35] At −65 °C, the dppp

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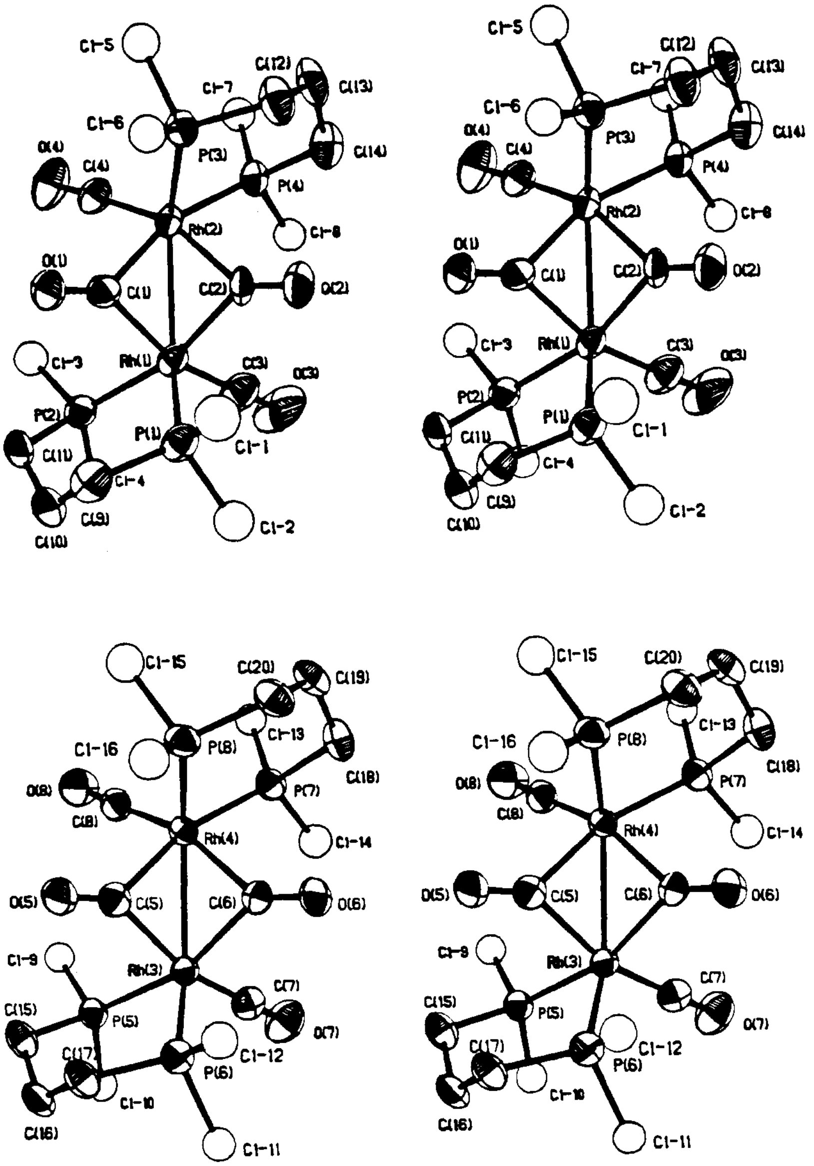

Figure 1. Stereoscopic views of the two crystallographically independent molecules of $Rh_2(dppp)_2(CO)_4$. Probability thermal ellipsoids of 50% are shown. For the sake of clarity, only the first carbon atom of each phenyl ring is shown. In each case the view is approximately along the noncrystallographic twofold axis.

dimer shows a pair of doublets, each with a minor amount of fine splitting, while neither the diop nor the dppe species had reached a low-temperature limiting spectrum at −60 °C. In the rigid molecular framework, one pair of equivalent phosphorus atoms can be described as trans to the rhodium–rhodium bond, while the second equivalent pair is in the cis configuration. Carbonyl site exchange between terminal and bridging positions will cause the pairs of phosphorus atoms to become chemically equivalent, and this notion is corroborated by the ^{13}C NMR spectrum of the dppp dimer that shows the four carbon monoxide ligands to be equivalent at ambient temperature, a single, broad resonance being observed at 212 ppm for the carbonyl ligands.

Comparison with Bis(triphenylphosphine) Analogues. The carbonyl diphosphine dimers described in this work are analogous to the triphenylphosphine analogue $[Rh(CO)(PPh_3)_2]_2(\mu\text{-}CO)_2$, **2**, first described by Wilkinson's group.[36,37] Other workers have also reported on this yellow dimer,[38-40] particularly in regard to it being a component in catalyzed hydroformylation reactions,

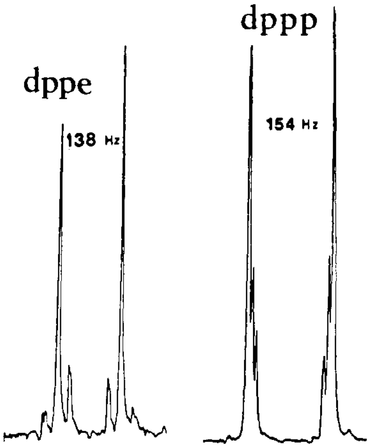

Figure 2. $^{31}P\{H\}$ NMR spectra of $[Rh(P\text{-}P)(CO)_2]_2$ in toluene-d_8 at 30 °C. The diop complex shows the same splitting pattern with $J_{Rh\text{-}P}$ = 160 Hz (Table I).

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Table V. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

molecule A		molecule B	
	Bond Lengths		
Rh(1)-Rh(2)	2.725 (1)	Rh(3)-Rh(4)	2.709 (1)
Rh(1)-P(1)	2.329 (3)	Rh(4)-P(8)	2.316 (3)
Rh(1)-P(2)	2.368 (3)	Rh(4)-P(7)	2.340 (3)
Rh(1)-C(1)	2.036 (9)	Rh(4)-C(6)	2.049 (9)
Rh(1)-C(2)	2.057 (10)	Rh(4)-C(5)	2.067 (10)
Rh(1)-C(3)	1.944 (11)	Rh(4)-C(8)	1.942 (11)
Rh(2)-P(3)	2.340 (3)	Rh(3)-P(6)	2.336 (3)
Rh(2)-P(4)	2.399 (3)	Rh(3)-P(5)	2.355 (3)
Rh(2)-C(1)	2.068 (10)	Rh(3)-C(6)	2.075 (9)
Rh(2)-C(2)	2.036 (10)	Rh(3)-C(5)	2.063 (10)
Rh(2)-C(4)	1.929 (11)	Rh(3)-C(7)	1.920 (11)
O(1)-C(1)	1.175 (10)	O(6)-C(6)	1.160 (10)
O(2)-C(2)	1.181 (10)	O(5)-C(5)	1.163 (10)
O(3)-C(3)	1.115 (11)	O(8)-C(8)	1.138 (10)
O(4)-C(4)	1.128 (11)	O(7)-C(7)	1.152 (11)
	Bond Angles		
Rh(2)-Rh(1)-P(1)	130.62 (8)	Rh(3)-Rh(4)-P(8)	129.46 (7)
Rh(2)-Rh(1)-P(2)	114.62 (7)	Rh(3)-Rh(4)-P(7)	115.94 (7)
Rh(2)-Rh(1)-C(1)	48.9 (3)	Rh(3)-Rh(4)-C(6)	49.4 (3)
Rh(2)-Rh(1)-C(2)	47.9 (3)	Rh(3)-Rh(4)-C(5)	49.0 (3)
Rh(2)-Rh(1)-C(3)	110.6 (3)	Rh(3)-Rh(4)-C(8)	110.0 (3)
P(1)-Rh(1)-P(2)	94.41 (10)	P(8)-Rh(4)-P(7)	95.03 (9)
P(1)-Rh(1)-C(1)	98.0 (3)	P(8)-Rh(4)-C(6)	98.7 (3)
P(1)-Rh(1)-C(2)	98.8 (3)	P(8)-Rh(4)-C(5)	96.2 (3)
P(1)-Rh(1)-C(3)	102.7 (3)	P(8)-Rh(4)-C(8)	105.3 (3)
P(2)-Rh(1)-C(1)	86.4 (3)	P(7)-Rh(4)-C(6)	85.8 (3)
P(2)-Rh(1)-C(2)	162.6 (3)	P(7)-Rh(4)-C(5)	164.9 (3)
P(2)-Rh(1)-C(3)	98.8 (4)	P(7)-Rh(4)-C(8)	95.3 (3)
C(1)-Rh(1)-C(2)	80.6 (4)	C(6)-Rh(4)-C(5)	82.5 (4)
C(1)-Rh(1)-C(3)	158.2 (4)	C(6)-Rh(4)-C(8)	155.7 (4)
C(2)-Rh(1)-C(3)	89.4 (4)	C(5)-Rh(4)-C(8)	91.5 (4)
Rh(1)-Rh(2)-P(3)	131.68 (7)	Rh(4)-Rh(3)-P(6)	132.08 (7)
Rh(1)-Rh(2)-P(4)	113.52 (7)	Rh(4)-Rh(3)-P(5)	110.97 (7)
Rh(1)-Rh(2)-C(1)	47.9 (3)	Rh(4)-Rh(3)-C(6)	48.5 (3)
Rh(1)-Rh(2)-C(2)	48.6 (3)	Rh(4)-Rh(3)-C(5)	49.1 (3)
Rh(1)-Rh(2)-C(4)	109.7 (3)	Rh(4)-Rh(3)-C(7)	110.5 (3)
P(3)-Rh(2)-P(4)	92.97 (9)	P(6)-Rh(3)-P(5)	93.47 (9)
P(3)-Rh(2)-C(1)	102.6 (3)	P(6)-Rh(3)-C(6)	104.2 (2)
P(3)-Rh(2)-C(2)	96.3 (3)	P(6)-Rh(3)-C(5)	95.5 (3)
P(3)-Rh(2)-C(4)	104.8 (3)	P(6)-Rh(3)-C(7)	107.2 (3)
P(4)-Rh(2)-C(1)	161.2 (3)	P(5)-Rh(3)-C(6)	159.1 (3)
P(4)-Rh(2)-C(2)	87.7 (3)	P(5)-Rh(3)-C(5)	85.4 (3)
P(4)-Rh(2)-C(4)	98.9 (3)	P(5)-Rh(3)-C(7)	95.5 (3)
C(1)-Rh(2)-C(2)	80.3 (4)	C(6)-Rh(3)-C(5)	81.9 (4)
C(1)-Rh(2)-C(4)	87.3 (4)	C(6)-Rh(3)-C(7)	90.0 (4)
C(2)-Rh(2)-C(4)	157.5 (4)	C(5)-Rh(3)-C(7)	157.2 (4)
Rh(1)-P(1)-C(9)	113.5 (3)	Rh(4)-P(8)-C(20)	113.8 (3)
Rh(1)-P(1)-C1-1	120.7 (3)	Rh(4)-P(8)-C1-16	119.7 (2)
Rh(1)-P(1)-C1-2	115.6 (3)	Rh(4)-P(8)-C1-15	113.7 (3)
Rh(1)-P(2)-C(11)	111.1 (3)	Rh(4)-P(7)-C(18)-	113.1 (3)
Rh(1)-P(2)-C1-3	117.1 (3)	Rh(4)-P(7)-C1-14	116.8 (3)
Rh(1)-P(2)-C1-4	120.6 (3)	Rh(4)-P(7)-C1-13	118.6 (3)
Rh(2)-P(3)-C(12)	112.9 (3)	Rh(3)-P(6)-C(17)	111.8 (3)
Rh(2)-P(3)-C1-5	116.2 (3)	Rh(3)-P(6)-C1-11	115.7 (2)
Rh(2)-P(3)-C1-6	121.3 (2)	Rh(3)-P(6)-C1-12	120.3 (2)
Rh(2)-P(4)-C(14)	109.6 (3)	Rh(3)-P(5)-C(15)	112.4 (3)
Rh(2)-P(4)-C1-7	122.3 (3)	Rh(3)-P(5)-C1-10	121.7 (2)
Rh(2)-P(4)-C1-8	117.1 (3)	Rh(3)-P(5)-C1-9	115.5 (2)
Rh(1)-C(1)-Rh(2)	83.2 (4)	Rh(4)-C(6)-Rh(3)	82.1 (3)
Rh(1)-C(1)-O(1)	140.2 (8)	Rh(4)-C(6)-O(6)	140.3 (7)
Rh(2)-C(1)-O(1)	136.4 (7)	Rh(3)-C(6)-O(6)	137.3 (7)
Rh(1)-C(2)-Rh(2)	83.5 (4)	Rh(4)-C(5)-Rh(3)	82.0 (4)
Rh(1)-C(2)-O(2)	136.3 (8)	Rh(4)-C(5)-O(5)	136.6 (8)
Rh(2)-C(2)-O(2)	140.3 (8)	Rh(3)-C(5)-O(5)	141.3 (8)
Rh(1)-C(3)-O(3)	174.7 (12)	Rh(4)-C(8)-O(8)	177.2 (9)
Rh(2)-C(4)-O(4)	175.0 (10)	Rh(3)-C(7)-O(7)	179.4 (9)

where H_2/CO atmospheres lead to equilibration with active $RhH(CO)_n(PPh_3)_2$, $n = 1$ or 2, species.[7,37] Reductive elimination of H_2 via a four-center transition state readily accounts for formation of the dimers from the precursor monohydrides:[4,37]

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$$2\text{RhH} \rightleftharpoons \left[\begin{array}{c} \text{H}\cdots\text{H} \\ \vdots \qquad \vdots \\ \text{Rh}\cdots\text{Rh} \end{array}\right] \rightleftharpoons \text{Rh-Rh} + \text{H}_2 \qquad (3)$$

Presumably, since the precursor hydrides $RhH(P\text{-}P)_2$ do not spontaneously evolve H_2, reaction 2 probably occurs via dimerization of RhH(CO)(P-P) species to generate $[Rh(CO)(P\text{-}P)]_2$ and H_2, followed by addition of CO ligands. The corresponding $RhH(CO)(PPh_3)_2$ complex can certainly form 2 via this route, in which the intermediate metal-metal bonded orange dimer $[Rh(CO)(PPh_3)_2]_2$ with no bridging ligands, 3, has been isolated.[37] The related solvated complex $[Rh(CO)(PPh_3)_2]_2 \cdot 2CH_2Cl_2$ that contains two bridging carbonyls[34,37] (vide supra) can be formed by loss of CO from solutions of 2. Our carbonyl diphosphine dimers such as 1 also lose CO under vacuum, but the product(s) have not yet been characterized.

No crystallographic or ^{31}P NMR data have been reported for the carbonyl bis(triphenylphosphine) dimers 2 and 3, but the IR data for 2 (2017, 1992, 1800, 1770 cm^{-1}, Nujol)[37] showed the presence of both terminal and bridging carbonyls, and presumably the structure is analogous to that described here for 1. The higher frequency of the carbonyls in 2 compared to 1 probably reflects the stronger π-acceptor/weaker σ-donor ability of two PPh_3 ligands relative to the diphosphine.

Preliminary experiments reveal that, like the triphenylphosphine analogues, the carbonyl bis(diphosphine) dimers such as 1 are effective under mild conditions (50 °C, 1 atm in benzene) for hydrogenation, isomerization, and hydroformylation of terminal olefins.[41]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of British Columbia Computing Centre for financial support, Dr. J. Trotter for use of the departmental X-ray facilities, Johnson, Matthey Ltd for the loan of rhodium, and Dr. T. W. Dekleva for valuable discussions.

Registry No. $[Rh(CO)(dppp)]_2(\mu\text{-}CO)_2 \cdot {}^1/_2C_6H_6$, 86853-77-2; $[Rh(CO)(dppe)]_2(\mu\text{-}CO)_2$, 86853-78-3; $[Rh(CO)(diop)]_2(\mu\text{-}CO)_2$, 86862-66-0; $RhH(dppp)_2$, 70196-25-7; $RhH(dppe)_2$, 29189-87-5; $RhH(diop)_2$, 51222-55-0; carbon monoxide, 630-08-0; Rh, 7440-16-6.

Supplementary Material Available: Table VI, selected bond lengths (Å) and angles (deg) for the coordinated dppp ligands, Table VII, intraannular torsion angles, Table VIII, calculated coordinates and thermal parameters for non-group hydrogen atoms; Table IX, anistropic thermal parameters; Table X, torsion angles; and Table XI, observed and calculated structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

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[41] James, B. R.; Williams, G. M.; Young, C. G., work in progress.

Communications

Preparation and Reactions of Tetrahydrido(pentamethylcyclopentadienyl)iridium: A Novel Iridium(V) Polyhydride

Thomas M. Gilbert and Robert G. Bergman*

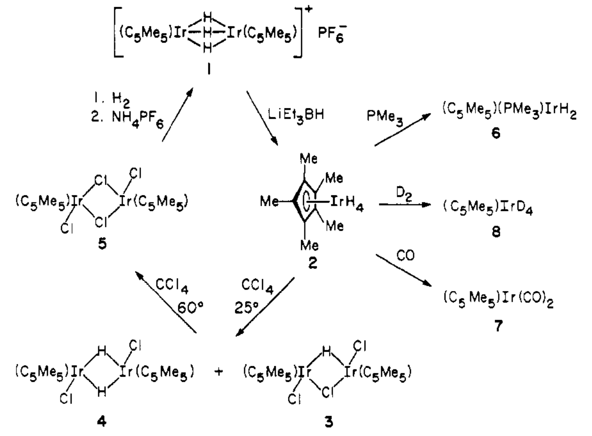
Department of Chemistry
University of California at Berkeley
and Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Received July 6, 1983

Summary: The complex $(C_5(CH_3)_5)IrH_4$ (2) has been synthesized and characterized by spectroscopic and analytical methods, including a single-crystal X-ray diffraction study. This compound is a rare example of a formal iridium(V) species; it can be converted to $[C_5(CH_3)_5](PMe_3)IrH_2$ on irradiation in the presence of PMe_3, leads to $C_5(CH_3)_5$-substituted chloro- and hydridochloroiridium dimers on treatment with CCl_4, gives $[C_5(CH_3)_5]Ir(CO)_2$ with CO, and undergoes thermal and photochemical H/D exchange in the presence of D_2 gas.

Few examples exist of organometallic complexes of late transition metals in high oxidation states. Comparison with high-valent complexes of early transition metals suggests that such compounds, especially those of group 8B, might be expected to possess unique properties and reactivities.

Scheme I



Phosphine-stabilized iridium(V) hydrides have been known since the early 1970s[1] and were shown somewhat later to catalyze H/D exchange with deuterated solvents at elevated temperatures.[2] Recently, Maitlis and coworkers demonstrated the accessibility of pentamethylcyclopentadienyl-substituted organoiridium(V)[3] and organorhodium(V)[4] complexes, noting intriguing products upon pyrolysis of the former. However, examples of this

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0276-7333/83/2302-1458$01.50/0