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Rh–Rh Bonds of Order 0, 1, and 2 in Dinuclear Rhodium(I) Phosphido and Arsenido Complexes: X-ray Crystal Structures of $[Rh(CO)(\textit{t}\text{-}Bu_2PH)]_2(\mu\text{-}\textit{t}\text{-}Bu_2P)(\mu\text{-}H)$ (Rh–Rh), $[Rh(COD)]_2(\mu\text{-}\textit{t}\text{-}Bu_2P)(\mu\text{-}Cl)$ (COD = 1,5-Cyclooctadiene), and $[Rh(\mu\text{-}\textit{t}\text{-}Bu_2As)(CO)_2]_2$

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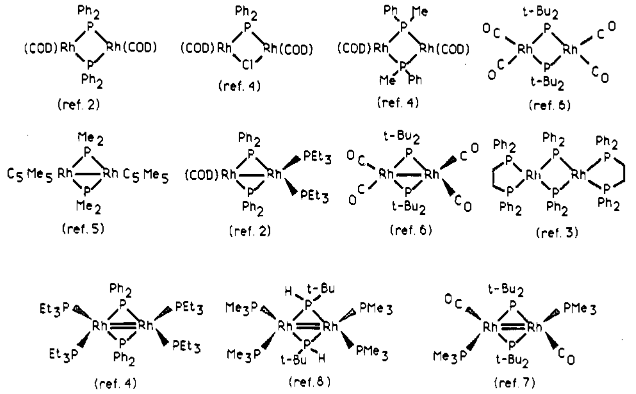
Reaction of *t*-Bu_2PH with $Rh_4(CO)_{12}$ in toluene under reflux yields $[Rh(CO)(\textit{t}\text{-}Bu_2PH)]_2(\mu\text{-}\textit{t}\text{-}Bu_2P)(\mu\text{-}H)$ (**1**) (61%). **1** has one *t*-Bu_2P unit, which bridges two virtually planar Rh(I) atoms. The hydride could not be located in the crystal structure, but the overall geometry indicates that it probably occupies a bridging site. There is a relatively long single Rh–Rh bond (2.906 (2) Å), and the phosphine (*t*-Bu_2PH) ligands are cis with respect to it. Reaction of Li(*t*-Bu_2P) with $[Rh(COD)Cl]_2$ (1:1) (COD = 1,5-cyclooctadiene) in THF yields $[Rh(COD)]_2(\mu\text{-}\textit{t}\text{-}Bu_2P)(\mu\text{-}Cl)$ (**2**) (55%). **2** has one *t*-Bu_2P group bridging two planar Rh(I) atoms. The chlorine atom is also bridging. There is no Rh–Rh bond in **2** (Rh–Rh = 3.395 Å (average)). Reaction of $Li(\textit{t}\text{-}Bu)_2As$ with $[Rh(CO)_2Cl]_2$ (2:1) in THF at −78 °C yields $[Rh(\mu\text{-}\textit{t}\text{-}Bu_2As)(CO)_2]_2$ (**3**) (25%) as well as $Rh_3(CO)_{11}(\mu\text{-}\textit{t}\text{-}Bu_2As)_2(\mu_4\text{-}\textit{t}\text{-}BuAs)$ (**4**) (35%). **4** has been described elsewhere. The structure of **3** consists of two *t*-Bu_2As groups, which bridge two planar Rh(I) atoms with no Rh–Rh bond (Rh–Rh = 3.884 (1) Å). The structures of **1–3** have been determined by single-crystal X-ray diffraction studies. **1** crystal data: $C_{38}H_{85}O_2P_3Rh_2$, $M_r = 872.83$, monoclinic, $P2_1/c$ (No. 14), $a = 12.335$ (1) Å, $b = 15.142$ (2) Å, $c = 22.304$ (2) Å, $\beta = 91.35$ (2)°, $U = 4164.9$ (5) Å^3, $D_c = 1.392$ g cm^{-3}, $Z = 4$, λ(Mo Kα) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 9.229 cm^{-1}. Methods: Multan, difference Fourier, full-matrix least squares. Refinement of 3605 reflections ($I > 3\sigma(I)$) out of 7250 unique observed reflections (2° < 2θ < 50°) gives R and R_w values of 0.070 and 0.075, respectively. The data/parameter ratio = 10.92. Hydrogen atoms were not located. **2** crystal data: $C_{24}H_{38}ClPRh_2$, $M_r = 598.81$, orthorhombic, *Pbcn* (No. 60), $a = 13.379$ (1) Å, $b = 29.020$ (2) Å, $c = 25.621$ (1) Å, $U = 9947.5$ (7) Å^3, $D_c = 1.599$ g cm^{-3}, $Z = 16$, λ(Mo Kα) = 0.71069 Å (graphite monochromator), $\mu = 14.87$ cm^{-1}. Refinement of 3342 reflections ($I > 3\sigma(I)$) out of 9559 measured (2° < 2θ < 50°) gave R and R_w values of 0.0502 and 0.0554, respectively. The data/parameter ratio = 6.62. All non-hydrogen atoms were anisotropic; hydrogen atoms were not located. **3** crystal data: $C_{20}H_{36}As_2O_4Rh_2$, $M_r = 696.16$, monoclinic, $I2/m$ (a nonstandard setting of $C2/m$, No. 12), $a = 11.102$ (2) Å, $b = 11.201$ (2) Å, $c = 11.575$ (1) Å, $\beta = 115.44$ (1)°, $U = 1299.8$ (5) Å^3, $D_c = 1.779$ g cm^{-3}, $Z = 2$, λ(Mo Kα) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 37.92 cm^{-1}. Refinement of 1612 reflections ($I > 3\sigma(I)$) out of 1672 unique observed reflections (2° < 2θ < 60°) gave R and R_w values of 0.033 and 0.040, respectively. The data/parameter ratio = 22.39. All non-hydrogen atoms were anisotropic; hydrogen atoms were not located. Reaction of the dilithio diphosphide $LiP(\textit{t}\text{-}Bu)(CH_2)_4(\textit{t}\text{-}Bu)PLi$ with $[Rh(COD)Cl]_2$ in THF at −78 °C gives dark red, crystalline $[Rh(COD)]_2(\mu\text{-}P(\textit{t}\text{-}Bu)(CH_2)_4(\textit{t}\text{-}Bu)P)$ (**5**) in 60% yield. NMR data indicate pseudotetrahedral Rh atoms with a Rh–Rh double bond. X-ray quality crystals of **5** could not be obtained.

Introduction

A variety of dinuclear phosphido-bridged complexes of Rh are now known. Diphenylphosphido-bridged complexes such as those shown in Chart I have been described by Meek[1-3] and Geoffroy.[4] Dimethylphosphido complexes have also been reported by Werner and co-workers.[5] Our interests in transition-metal phosphido chemistry have involved study of the effects of bulky ligands such as the di-*tert*-butylphosphido (*t*-Bu_2P^-)[6-8] and di-*tert*-butylarsenido (*t*-Bu_2As^-) units.[9] Of particular interest has been the observation that the Rh–Rh bond order in complexes of type $[Rh(\mu\text{-}PR_2)L_2]_2$ can vary from 0 through 1 to 2 according to the geometry[10] about the metal atoms and also the charge on the complex.[11]

We have extended our studies of Rh phosphido species, and this paper describes four new dinuclear phosphido- or arsenido-bridged complexes of Rh(I), **1–3** and **5** (Scheme I), which have a variety of formal Rh–Rh bond orders ranging from 0 through 1 and 2. The complexes have been characterized spectroscopically (IR, NMR), and in the cases of 1–3 the solid-state structures have been determined via X-ray crystallography. The various factors affecting the Rh–Rh bond orders in these complexes are discussed.

Chart I. Various Rh_2 Phosphido-Bridged Dinuclear Compounds



Results and Discussion

***t*-Bu_2P-Monobridged Complexes: $[Rh(\textit{t}\text{-}Bu_2PH)(CO)]_2(\mu\text{-}H)(\mu\text{-}\textit{t}\text{-}Bu_2P)$ (1) and $[Rh(COD)]_2(\mu\text{-}Cl)(\mu\text{-}\textit{t}\text{-}Bu_2P)$ (2). $[Rh(\textit{t}\text{-}Bu_2PH)(CO)]_2(\mu\text{-}H)(\mu\text{-}\textit{t}\text{-}Bu_2P)$ (1).** The reaction of $Rh_4(CO)_{12}$ with *t*-Bu_2PH in toluene under reflux results in a dark red solution from which yellow crystalline $[Rh(\mu\text{-}\textit{t}\text{-}Bu_2PH)(CO)]_2(\mu\text{-}H)(\mu\text{-}\textit{t}\text{-}Bu_2P)$ (**1**) can be obtained in ca. 60% yield by recrystallization from hexane at −20 °C. The complex is moderately air-sensitive in the solid state and more so when in solution. Spectroscopic data are consistent with the structure as determined via X-ray crystallography. Thus, the IR spectrum contains bands that can be assigned to the ν_{P-H} (2292 (m) cm^{-1}) and ν_{CO} and ν_{M-H} stretches (1942 (vs) and 1903 (sh) cm^{-1}) (although, of course, these assignments can be reversed). The ^1H NMR spectrum contains two doublets assigned to the *t*-Bu groups (δ 1.63, $J_{P-H} = 6.9$ Hz; δ 1.18, $J_{P-H} = 11.69$ Hz). In addition, there are signals assigned to the P–H protons of the terminal *t*-Bu_2PH groups (δ

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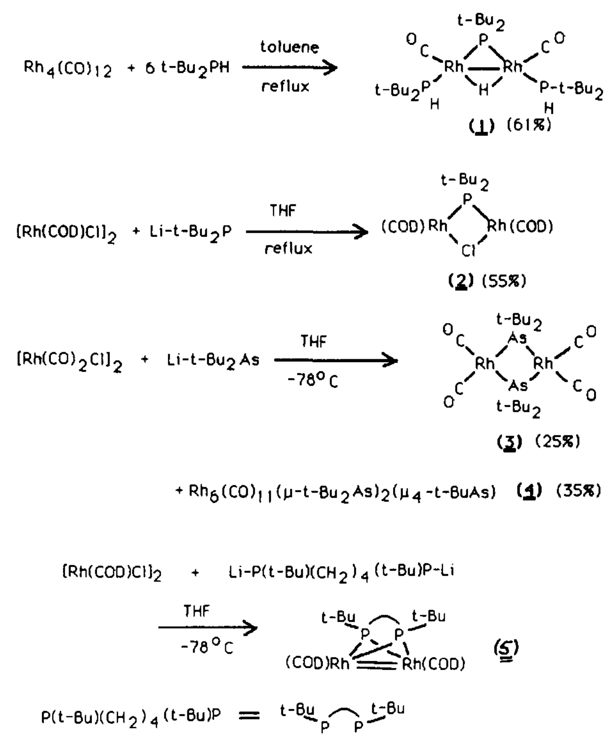
Table I. Crystal Data, Summary of Intensity Data Collection, and Structure Refinement for **1**–**3**

	$C_{38}H_{85}O_2P_3Rh_2$	$C_{24}H_{38}ClPRh_2$	$C_{20}H_{36}As_2O_4Rh_2$
color/habit	yellow/prism	yellow/rod	yellow/cube
mol wt	872.83	598.81	696.16
space group	$P2_1/c$, No. 14	*Pbcn*, No. 60	$I2/m$ (nonstandard setting of $C2/m$, No. 12)
cell constants			
a, Å	12.335 (1)	13.379 (1)	11.102 (2)
b, Å	15.142 (2)	29.020 (2)	11.201 (2)
c, Å	22.304 (2)	25.621 (1)	11.575 (1)
β, deg	91.35 (2)	90	115.44 (1)
cell vol, $Å^3$	4164.9 (5)	9947.5 (7)	1299.8 (5)
molecules/unit cell	4	16	4
D(calcd), g cm^{-3}	1.392	1.599	3.557
radiation: λ, Å	Mo Kα; 0.71069	Mo Kα; 0.71069	Mo Kα; 0.71069
max cryst dimens, mm	0.25 × 0.25 × 0.30	0.20 × 0.20 × 0.42	0.55 × 0.23 × 0.33
scan width, deg	0.8 + 0.35 tan *θ*	0.8 + 0.35 tan *θ*	0.8 + 0.35 tan *θ*
std reflcns	400, 040	$4\bar{4}6$, 0010	334, $63\bar{1}$
decay of stds, %	25	<2	0.6
no. of reflcns measd	7250	9559	1672
2*θ* range, deg	$2.0 < 2\theta < 50.0$	$2.0 < 2\theta < 50.0$	$2.0 < 2\theta < 60.0$
octants collcd	$+h,+k,\pm l$	$-h,+k,+l$	$+h,+k,\pm l$
no. of reflcns obsd ($I > 3\sigma(I)$)	3605	3342	1612
no. of params varied	310	505	72
data/param ratio	10.924	6.618	22.39
R	0.0699	0.0502	0.0333
R_w	0.0748	0.0554	0.0403

Scheme I



4.70, d, J_{P-H} = 308.7 Hz). Although the Rh hydride could not be observed at room temperature, in toluene-d_8 at −80 °C it appears as a complex multiplet to high field (δ −10.3, m). The $^{31}P\{^1H\}$ NMR spectrum shows a doublet of doublets in the normal phosphine region (δ 58.5, $^1J_{Rh-P}$ = 120.5 Hz, $^2J_{P-P}$ = 36.44 Hz) assigned to the *t*-Bu_2PH groups. The bridging phosphido unit appears well downfield at δ 264.3 as a multiplet. The low-field resonance is strongly indicative of a phosphide that bridges a metal–metal bond,[12] and this is consistent with the solid-state structure (Rh–Rh = 2.906 (2) Å).

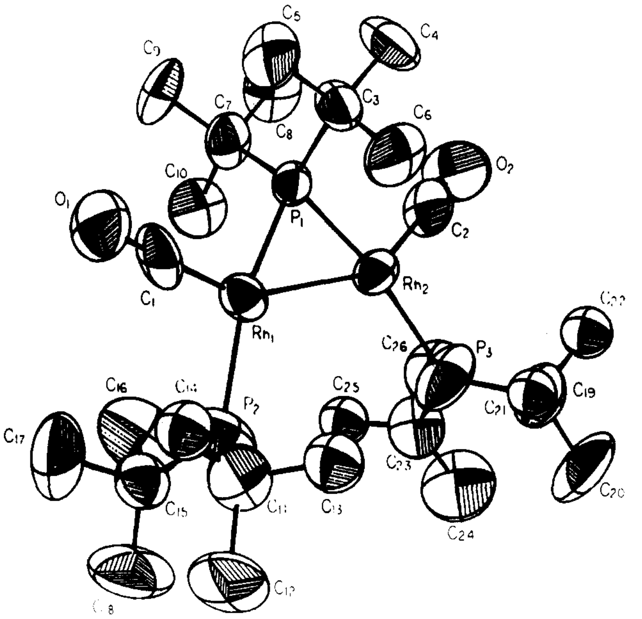


Figure 1. ORTEP view of **1** showing the atom-numbering scheme.

X-ray Structure of [Rh(*t*-Bu_2P)(CO)]$_2$(μ-H)(μ-*t*-Bu_2P) (1). Crystals of **1** lose crystallinity under vacuum; however, we were able to obtain a crystal structure by mounting them under a hexane-saturated atmosphere. The final refinement contains two severely disordered hexane molecules per unit cell. Crystal data, the summary of intensity data collection parameters, and refinement for **1** are given in Table I. Atomic positional parameters and selected bond lengths and angles for **1** are given in Tables II–IV, respectively. A view of the molecule with atom-numbering scheme is shown in Figure 1.

The overall structure consists of two distorted square-planar Rh(I) atoms bridged by one *t*-Bu_2P group. Although the hydride was not located in the structure, the geometry of the molecule clearly indicates that it occupies a bridging position between the two Rh atoms (see Figure 1). The Rh–Rh distance of 2.906 (2) Å is slightly longer than a normal Rh–Rh single bond (ca. 2.7–2.8 Å) although it is still within the upper limit that is normally considered a Rh–Rh bond (ca. 3.2 Å).[13]

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[12] Downfield shifts in the δ 50–200 range in the ^{31}P NMR of the Ph_2P groups bridging metal–metal bonds have been noted by several groups of workers. See: Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163 and references 1–5 therein. Similar downfield shifts have been noted for μ-*t*-Bu_2P complexes; see ref 6–11 and references therein.

[13] The upper limit on a Rh–Rh bond is probably ca. 3.2 Å—see: Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 209 and references therein.

Table II. Positional Parameters and Their Estimated Standard Deviations for **1**

atom	x	y	z	B,[a] Å^2
Rh1	0.64614 (9)	0.30613 (8)	0.76698 (5)	5.09 (2)
Rh2	0.8142 (1)	0.38601 (8)	0.84264 (5)	5.08 (2)
P1	0.8285 (3)	0.3098 (2)	0.7551 (2)	4.32 (8)
P2	0.4726 (4)	0.3212 (3)	0.8057 (3)	8.6 (1)
P3	0.7561 (6)	0.4627 (3)	0.9257 (2)	10.9 (2)
O1	0.5875 (9)	0.2086 (9)	0.6560 (5)	9.9 (4)
O2	1.049 (1)	0.410 (1)	0.8713 (6)	12.2 (4)
C1	0.611 (1)	0.247 (1)	0.7020 (7)	7.0 (4)
C2	0.959 (1)	0.404 (1)	0.8586 (7)	7.6 (4)
C3	0.878 (1)	0.380 (1)	0.6900 (6)	5.9 (3)
C4	1.002 (1)	0.399 (1)	0.6960 (7)	8.3 (5)
C5	0.853 (2)	0.333 (1)	0.6288 (6)	8.0 (5)
C6	0.812 (2)	0.4655 (9)	0.6937 (7)	8.3 (5)
C7	0.898 (1)	0.1982 (9)	0.7617 (7)	6.6 (4)
C8	1.023 (1)	0.208 (1)	0.775 (1)	10.1 (6)
C9	0.885 (2)	0.1422 (9)	0.7031 (8)	8.7 (5)
C10	0.841 (2)	0.150 (1)	0.8140 (7)	8.0 (5)
C11	0.382 (1)	0.397 (1)	0.7643 (8)	7.9 (5)
C12	0.267 (1)	0.412 (1)	0.793 (1)	11.0 (7)
C13	0.436 (2)	0.484 (1)	0.770 (2)	19 (1)
C14	0.368 (2)	0.372 (2)	0.699 (1)	22 (1)
C15	0.415 (1)	0.223 (1)	0.8401 (7)	7.1 (4)
C16	0.505 (2)	0.169 (1)	0.867 (1)	13.1 (7)
C17	0.376 (2)	0.160 (1)	0.787 (1)	16.6 (9)
C18	0.312 (2)	0.230 (2)	0.875 (1)	13.7 (7)
C19	0.750 (1)	0.582 (1)	0.9218 (7)	7.5 (4)
C20	0.705 (2)	0.633 (1)	0.9724 (9)	14.3 (7)
C21	0.695 (4)	0.601 (2)	0.871 (1)	31 (1)
C22	0.854 (2)	0.615 (2)	0.911 (2)	30 (1)
C23	0.738 (2)	0.406 (1)	0.9948 (6)	8.1 (5)
C24	0.711 (2)	0.451 (2)	1.0513 (8)	15.2 (9)
C25	0.716 (3)	0.318 (1)	0.987 (1)	24 (1)
C26	0.856 (3)	0.394 (3)	1.013 (1)	25 (1)
C27	−0.027 (3)	0.454 (2)	0.477 (1)	17 (1)*
C28	0.900 (3)	0.508 (2)	0.464 (1)	20 (1)*
C29	1.026 (4)	0.370 (3)	0.473 (2)	26 (2)*
C30	1.112 (3)	0.386 (3)	0.518 (2)	26 (2)*
C33	0.486 (3)	0.616 (3)	0.447 (2)	23 (1)*
C34	0.536 (4)	0.544 (3)	0.479 (2)	27 (2)*
C35	0.389 (3)	0.478 (2)	0.510 (2)	23 (1)*
C36	0.394 (3)	0.565 (2)	0.473 (2)	21 (1)*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Values marked with an asterisk denote positions refined with fixed isotropic thermal parameters.

Table III. Bond Distances (Å) for **1**[a]

Rh1–Rh2	2.906 (2)	C7–C9	1.56 (2)
Rh1–P1	2.272 (4)	C7–C10	1.55 (2)
Rh1–P2	2.338 (5)	C11–C12	1.58 (2)
Rh1–C1	1.75 (2)	C11–C13	1.48 (3)
Rh2–P1	2.278 (4)	C11–C14	1.51 (3)
Rh2–P3	2.314 (5)	C15–C16	1.50 (3)
Rh2–C2	1.83 (2)	C15–C17	1.59 (3)
P1–C3	1.907 (14)	C15–C18	1.51 (3)
P1–C7	1.897 (14)	C19–C20	1.49 (3)
P2–C11	1.84 (2)	C19–C21	1.35 (4)
P2C15	1.82 (2)	C19–C22	1.40 (3)
P3–C19	1.81 (2)	C23–C24	1.48 (3)
P3–C23	1.780 (15)	C23–C25	1.38 (3)
O1–C1	1.20 (2)	C23–C26	1.52 (4)
O2–C2	1.14 (2)	C29–C30	1.48 (6)
O3–C4	1.56 (2)	C33–C34	1.43 (6)
C3–C5	1.56 (2)	C33–C36	1.50 (6)
C3–C6	1.53 (2)	C34–C36	1.79 (6)
C7–C8	1.57 (2)	C35–C36	1.56 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (deg) for **1**[a]

Rh2–Rh1–P1	50.39 (9)	C5–C3–C6	110 (1)
Rh2–Rh1–P2	113.1 (1)	P1–C7–C8	111 (1)
Rh2–Rh1–C1	148.7 (5)	P1–C7–C9	113 (1)
P1–Rh1–P2	163.4 (2)	P1–C7–C10	105 (1)
P1–Rh1–C1	98.3 (5)	C8–C7–C9	107 (1)
P2–Rh1–C1	98.2 (5)	C8–C7–C10	111 (1)
Rh1–Rh2–P1	50.22 (9)	C9–C7–C10	110 (1)
Rh1–Rh2–P3	116.3 (2)	P2–C11–C12	115 (1)
Rh1–Rh2–C2	148.5 (5)	P2–C11–C13	104 (1)
P1–Rh2–P3	166.3 (2)	P2–C11–C14	112 (2)
P1–Rh2–C2	98.4 (5)	C12–C11–C13	105 (2)
P3–Rh2–C2	95.2 (5)	C12–C11–C14	110 (2)
Rh1–P1–Rh2	79.4 (1)	C13–C11–C14	111 (2)
Rh1–P1–C3	115.8 (5)	P2–C15–C16	108 (1)
Rh1–P1–C7	114.4 (5)	P2–C15–C17	107 (1)
Rh2–P1–C3	113.9 (5)	P2–C15–C18	120 (1)
Rh2–P1–C7	115.4 (5)	C16–C15–C17	100 (2)
C3–P1—C7	113.8 (7)	C16–C15–C18	117 (2)
Rh1–P2–C11	115.3 (6)	C17–C15–C18	100 (2)
Rh1–P2–C15	116.6 (6)	P3–C19–C20	120 (1)
C11–P2–C15	118.7 (7)	P3–C19–C21	106 (2)
Rh2–P3–C19	118.4 (6)	P3–C19–C22	109 (2)
Rh2–P3–C23	120.0 (6)	C20–C19–C21	110 (2)
C19–P3–C23	120.9 (8)	C20–C19–C22	107 (2)
Rh1–C1–O1	177 (1)	C21–C19–C22	103 (3)
Rh2–C2–O2	175 (2)	P3–C23–C24	124 (2)
P1–C3–C4	112 (1)	P3–C23–C25	113 (1)
P1–C3–C5	111 (1)	P3–C23–C26	99 (2)
P1–C3–C6	105 (1)	C24–C23–C25	121 (2)
C4–C3–C5	110 (1)	C24–C23–C26	94 (2)
C4–C3–C6	110 (1)	C25–C23–C26	96 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Since the complex is diamagnetic, for electron-counting purposes one could consider the bonding in the $Rh_2(\mu\text{-}H)$ unit as a 3c–2e interaction or a protonated Rh–Rh bond. The μ-*t*-Bu_2P group bridges in a slightly asymmetrical fashion with Rh1–P1 and Rh2–P1 bond distances of 2.272 (4) and 2.278 (4) Å, respectively. These distances fall within the normal range of values for Rh–P (bridging phosphido) lengths.[6-8]

The Rh–P(phosphine) distances of 2.338 (5) and 2.314 (5) Å are also normal. The geometry of each Rh atom is essentially planar, and the dihedral angle between the planes defined by P2–Rh1–C1–P1 and P1–Rh2–C2–P3 is quite small (5.0°).[14] The coordination of the two bulky phosphines in a cis instead of trans fashion to one side of the molecule is reasonable since this minimizes their steric interactions with the bulky bridging phosphido group.

The geometry about each phosphorus atom of each *t*-Bu_2PH group is also of interest. The non-hydrogen atoms about P2 and P3 are virtually coplanar. (sum of the angles Rh1–P2–C15, Rh1–P2–C11, and C15–P2–C11 = 350.6). This deviation from a pseudotetrahedral geometry is no doubt due to the considerable steric bulk of the *t*-Bu groups vs. that of H.

$[Rh(COD)]_2(\mu\text{-}Cl)(\mu\text{-}t\text{-}Bu_2P)$ (2). The reaction of $[Rh(COD)Cl]_2$ with 1 equiv of *t*-Bu_2PLi in THF under reflux yields yellow $[Rh(COD)]_2(\mu\text{-}Cl)(\mu\text{-}t\text{-}Bu_2P)$ (**2**) in high yield (ca. 70%) Geoffroy and co-workers have recently described the similar reaction with Ph_2P^- to give the diphenylphosphido analogue of (**2**).[4] The complex is moderately air-stable but decomposes quickly in solution when exposed to the atmosphere. The $^{31}P\{^1H\}$ NMR spectrum shows only a simple triplet that is not shifted to low field (δ 44.3, $^1J_{Rh-P}$ = 113.7 Hz). This indicates a symmetrical

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(14) For **1** deviations in Å from the least-squares planes are as follows: Rh1, 0.021 (1); P1, −0.009 (3); P2, −0.009 (5); C1, −0.003 (15); Rh2, −0.022 (1); P1, 0.010 (3); P3, 0.010 (5); C2, 0.003 (16). For **2**, cent1 and cent2 are the midpoints of CC11, CC12 and CC15, CC16, respectively, and cent3 and cent4 are the midpoints of CC21, CC22 and CC25, CC26, respectively. The complete table of least-squares planes is available as supplementary material.[26] Deviations (Å) for plane 1: Rh1, −0.004 (1); P1, −0.111 (4); C1, 0.121 (5) cent1, 0.126 (3); cent2, −0.133 (3). Deviations (Å) for plane 2: Rh2, −0.017 (1); P1, −0.136 (4); Cl1, 0.154 (5); cent3, −0.164 (3); cent4, 0.164 (3). The dihedral angle between planes 1 and 2 = 136.7°. The analogous angle in the second independent molecule of **2** is 120.8°.

Table V. Positional Parameters and Their Estimated Standard Deviations for **2**

atom	x	y	z	B,[a] Å^2
Rh1	0.86594 (9)	0.04196 (5)	0.59995 (5)	2.79 (2)
Rh2	0.61816 (9)	0.04191 (5)	0.60069 (5)	3.00 (2)
Rh3	0.23320 (9)	0.24751 (5)	0.05901 (4)	2.78 (2)
Rh4	0.2561 (1)	0.25164 (4)	0.19404 (4)	2.62 (2)
Cl1	0.7413 (4)	0.0419 (2)	0.5320 (2)	4.49 (9)
Cl2	0.3283 (4)	0.2902 (2)	0.1208 (2)	5.3 (1)
P1	0.7428 (4)	−0.0001 (2)	0.6459 (1)	2.51 (7)
P2	0.2270 (3)	0.1939 (1)	0.1298 (2)	2.47 (8)
C1	0.744 (1)	−0.0637 (5)	0.6264 (7)	3.5 (3)
C2	0.743 (2)	0.0035 (6)	0.7203 (5)	3.6 (3)
C3	0.109 (1)	0.1566 (5)	0.1359 (7)	3.4 (4)
C4	0.344 (1)	0.1563 (7)	0.1270 (7)	3.8 (4)
CC11	0.966 (1)	0.060 (1)	0.661 (1)	7.5 (7)
C11	0.795 (2)	−0.0678 (8)	0.5721 (9)	7.8 (7)
CC12	0.999 (1)	0.0176 (7)	0.6363 (8)	4.4 (5)
C12	0.639 (2)	−0.0829 (7)	0.623 (1)	8.5 (7)
CC13	1.083 (1)	0.0130 (8)	0.5996 (9)	5.6 (5)
C13	0.808 (2)	−0.0957 (8)	0.661 (1)	7.8 (8)
CC14	1.086 (1)	0.053 (1)	0.558 (1)	7.7 (7)
CC15	0.976 (2)	0.0676 (6)	0.5419 (8)	4.7 (5)
CC16	0.929 (2)	0.1054 (5)	0.5654 (9)	8.1 (5)
CC17	0.962 (2)	0.1349 (8)	0.610 (1)	8.3 (8)
CC18	1.013 (2)	0.1078 (7)	0.654 (1)	6.5 (6)
C21	0.839 (1)	−0.0160 (7)	0.7464 (7)	4.2 (4)
CC21	0.554 (2)	0.1043 (8)	0.5678 (8)	6.1 (5)
CC22	0.505 (1)	0.0706 (9)	0.5447 (8)	6.4 (6)
C22	0.651 (1)	−0.0205 (8)	0.7455 (7)	4.9 (5)
C23	0.737 (2)	0.0569 (6)	0.7335 (7)	4.7 (4)
CC23	0.402 (1)	0.0522 (9)	0.555 (1)	6.7 (6)
CC24	0.404 (1)	0.0107 (9)	0.594 (1)	6.7 (6)
CC25	0.488 (1)	0.0147 (6)	0.6350 (8)	4.1 (4)
CC26	0.515 (1)	0.0571 (6)	0.6609 (6)	3.6 (4)
CC27	0.463 (2)	0.1031 (8)	0.6540 (9)	6.2 (6)
CC28	0.509 (2)	0.1334 (8)	0.6115 (9)	5.6 (6)
C31	0.097 (2)	0.1229 (7)	0.0886 (8)	4.9 (5)
CC31	0.208 (1)	0.3119 (5)	0.0135 (7)	3.9 (4)
C32	1.101 (1)	−0.1297 (7)	0.6874 (7)	4.5 (4)
CC32	0.294 (1)	0.2911 (6)	−0.0021 (8)	4.7 (4)
CC33	0.300 (2)	0.2654 (8)	−0.0546 (7)	7.0 (6)
C33	1.023 (1)	−0.1943 (8)	0.6359 (9)	5.5 (6)
CC34	1.269 (2)	−0.2162 (7)	0.4492 (8)	8.2 (7)
CC35	1.209 (1)	−0.2028 (7)	0.4962 (7)	4.5 (4)
CC36	1.114 (2)	−0.2242 (7)	0.5099 (8)	5.5 (5)
CC37	1.067 (2)	−0.262 (1)	0.477 (1)	9.8 (8)
CC38	1.105 (2)	−0.3089 (8)	0.488 (1)	5.8 (6)
CC41	0.258 (2)	0.3176 (5)	0.2354 (7)	5.1 (4)
C41	1.436 (1)	−0.1842 (7)	0.6401 (9)	4.8 (5)
C42	1.343 (2)	−0.1149 (8)	0.667 (1)	9.4 (7)
CC42	0.346 (1)	0.2964 (6)	0.2483 (8)	4.3 (4)
C43	1.364 (2)	−0.1368 (7)	0.5718 (8)	5.6 (5)
CC43	0.363 (2)	0.2688 (7)	0.2989 (8)	5.2 (5)
CC44	0.168 (2)	0.2810 (7)	−0.2016 (9)	5.3 (5)
CC45	0.250 (2)	0.2915 (6)	−0.2394 (5)	3.4 (3)
CC46	0.159 (1)	0.2341 (6)	0.2569 (7)	3.8 (4)
CC47	1.131 (1)	−0.2760 (6)	0.7900 (8)	4.5 (5)
CC48	1.166 (2)	−0.3222 (6)	0.769 (1)	6.4 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

phosphido bridge that spans a nonbonding Rh–Rh distance.[12] This is consistent with the X-ray structure since a Rh–Rh distance of 3.395 Å (average) is outside the normal limits for a Rh–Rh bonding interaction.[13]

X-ray Structure of [Rh(COD)]$_2$(μ-Cl)(μ-*t*-Bu$_2$P) (2). **2** crystallizes from toluene in the orthorhombic space group *Pbcn* (No. 60). There are two independent molecules in the asymmetric unit, and they have similar structural parameters. There are 16 molecules per unit cell. A view of one molecule is shown in Figure 2. Details of crystal data, collection parameters, and the refinement for **2** are given in Table I. Atomic positional parameters and selected bond lengths and angles for **2** are presented in Tables V–VII, respectively. The coordination geometry about each Rh atom is planar if one considers the midpoints of each olefinic bond in the cyclooctadiene ligands and the P and Cl atoms.[14] Molecules of **2** are therefore similar to those of **1** in the fact that they contain planar Rh(I) atoms bridged by two groups. However, there are two key structural differences between them. In **2** the Rh–Rh separations for the two independent molecules (3.315 (2), 3.475 (2) Å) are much larger than that in **1** (2.900 (4) Å); also, the

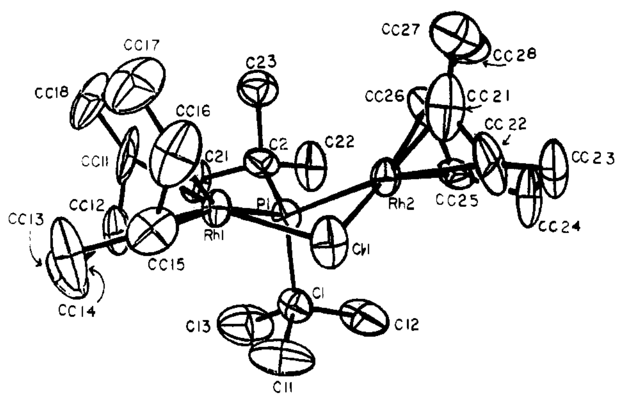

Figure 2. ORTEP view of one molecule of **2** showing the atom-numbering scheme.

Table VI. Selected Bond Lengths (Å) for One Molecule of **2**[a]

Rh1–Rh2	3.315 (2)	CC16–CC17	1.49 (2)
Rh1–Cl1	2.411 (3)	CC17–CC18	1.54 (2)
Rh1–P1	2.364 (3)	P1–C1	1.910 (15)
Rh1–CC11	2.128 (13)	P1–C2	1.911 (13)
Rh1–CC12	2.128 (11)	C1–C11	1.55 (3)
Rh1–CC15	2.222 (13)	C1–C12	1.51 (3)
Rh1–CC16	2.210 (11)	C1–C13	1.54 (3)
Rh2–Cl1	2.410 (3)	C2–C21	1.56 (3)
Rh2–P1	2.368 (3)	C2–C22	1.56 (3)
Rh2–CC21	2.175 (15)	C2–C23	1.59 (2)
Rh2–CC22	2.245 (11)	CC21–CC22	1.32 (2)
Rh2–CC25	2.108 (12)	CC21–CC28	1.52 (2)
Rh2–CC26	2.114 (10)	CC22–CC23	1.51 (2)
CC11–CC12	1.44 (2)	CC23–CC24	1.56 (2)
CC11–CC18	1.55 (2)	CC24–CC25	1.54 (2)
CC12–CC13	1.48 (2)	CC25–CC26	1.45 (2)
CC13–CC14	1.57 (2)	CC26–CC27	1.52 (2)
CC14–CC15	1.58 (2)	CC27–CC28	1.53 (2)
CC15–CC16	1.40 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Selected Bond Angles (deg) for One Molecule of **2**[a]

Cl1–Rh1–P1	82.90 (9)	Rh1–Cl1–Rh2	86.90 (8)
Cl1–Rh1–CC11	165.8 (6)	Rh1–P1–Rh2	88.95 (8)
Cl1–Rh1–CC12	153.4 (4)	Rh1–P1–C1	111.2 (3)
Cl1–Rh1–CC15	88.6 (4)	Rh1–P1–C2	117.9 (5)
Cl1–Rh1–CC16	88.6 (4)	Rh2–P1–C1	112.1 (4)
P1–Rh1–CC11	101.3 (5)	Rh2–P1–C2	117.5 (4)
P1–Rh1–CC12	101.2 (4)	C1–P1–C2	108.2 (5)
P1–Rh1–CC15	165.5 (4)	P1–C2–C21	114.2 (8)
P1–Rh1–CC16	153.5 (4)	P1–C2–C22	112.8 (9)
Cl1–Rh2–P1	82.84 (9)	P1–C2–C23	105.3 (7)
Cl1–Rh2–CC21	89.3 (4)	C21–C2–C22	108.5 (8)
Cl1–Rh2–CC22	89.6 (4)	C21–C2–C23	108 (1)
Cl1–Rh2–CC25	150.5 (4)	C22–C2–C23	108 (1)
Cl1–Rh2–CC26	167.9 (4)	Rh1–CC11–CC12	70.2 (8)
P1–Rh2–CC21	153.8 (4)	Rh1–CC11–CC18	113 (1)
P1–Rh2–CC22	167.9 (5)	CC12–CC11–CC18	126 (2)
P1–Rh2–CC25	100.8 (4)	Rh1–CC12–CC11	70.2 (7)
P1–Rh2–CC26	102.1 (3)	Rh1–CC12–CC13	113 (1)
CC22–Rh2–CC26	87.2 (5)	CC11–CC12–CC13	126 (1)
CC25–Rh2–CC26	40.0 (5)	CC12–CC13–CC14	112 (1)
P1–C1–C11	108.2 (7)	CC13–CC14–CC15	111 (1)
P1–C1–C12	111.2 (8)	Rh1–CC15–CC14	110.4 (9)
P1–C1–C13	115.8 (9)	Rh1–CC15–CC16	71.1 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

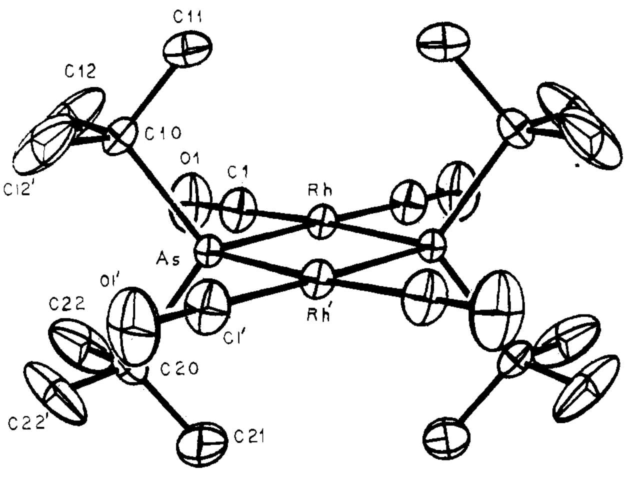

Figure 3. ORTEP view of 3.

central Rh_2PCl core in **2** adopts a butterfly type of configuration (see Figure 2).

The long Rh–Rh separation is consistent with the μ-Cl atom acting as a three-electron instead of a one-electron donor as in the case of the μ-H atom in **1**. Thus, the Rh atoms in **2** do not need to form a Rh–Rh bond to achieve 16-electron counts.

The butterfly configuration of the central core is not uncommon in dinuclear bridged Rh complexes. The dihedral angle between the Rh1–P1–Cl1 and Rh2–P1–Cl1 planes in the first molecule is 136.7° while that in the second independent molecule is 120.8° these values can be compared to an analogous angle of 124° in $[Rh(CO)_2Cl]_2$.[15] The relatively large differences in Rh–Rh lengths and dihedral angles in the two independent molecules of **2** may well represent only slight differences in energy; $[Rh(COD)Cl]_2$, for example, has a planar Rh_2Cl_2 core.[16] Of related interest in the observation by Geoffory and co-workers of the dinuclear Co(I) complex $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, which actually contains both planar and bent isomers in the same crystal structure.[17]

The other structural features of **2** require little additional comment. The cyclooctadiene ligands are in the boat or tub configuration, which is commonly observed for this ligand,[18] and the structural parameters of these groups are normal.

Bis(di-*tert*-butylarsenido) Complexes: $[Rh(\mu\text{-}t\text{-}Bu_2As)(CO)_2]_2$ (3). The reaction of Li-*t*-Bu_2As with $[Rh(CO)_2Cl]_2$ in THF yields the yellow crystalline dinuclear Rh(I) arsenido complex $[Rh(\mu\text{-}t\text{-}Bu_2As)(CO)_2]_2$ (**3**) in 25% yield. We have also isolated and characterized the Rh_6 cluster $Rh_6(CO)_{11}(\mu\text{-}t\text{-}Bu_2As)_2(\mu_4\text{-}t\text{-}BuAs)$ from this reaction, which we recently described.[9] Unlike the analogous Bu_2P^- system in which two isomers can be isolated under similar conditions,[6] only one isomer of **3** can be isolated by crystallization from hexane. In the solid state **3** has two planar 16e Rh atoms with no Rh–Rh bond (Rh–Rh = 3.8841 (1) Å). We have noted previously for *t*-Bu_2P complexes that the steric strain about the metal has a significant effect on its geometry and the degree of metal–metal bonding.[6-8,10] When the metals are sterically crowded, a tetrahedral coordination geometry is preferred and Rh–Rh bonds of order 2 are observed. When there is less steric strain, a planar metal geometry is permitted with no Rh–Rh bond. Clearly, in the case of **3** the replacement of P with As relieves the steric interactions in the molecule since As is larger than P (covalent radii: As = 1.22 Å, P = 1.10 Å).[19] Spectroscopic data for **3** are consistent with the structure as determined by X-ray crystallography. The IR spectrum shows strong terminal ν_{CO} absorptions at 2036 and 1993 cm^{-1}, and the ^1H NMR spectrum shows a singlet at δ 1.45 for the *t*-Bu_2As groups.

Table VIII. Positional Parameters and Their Estimated Standard Deviations for 3

atom	*x*	*y*	*z*	*B*,[a] Å^2
Rh	0.000	0.17338 (4)	0.000	2.781 (9)
As	−0.03793 (5)	0.000	0.11583 (5)	2.43 (1)
O1	0.0478 (5)	0.3619 (4)	−0.1626 (4)	7.7 (1)
C1	0.0297 (6)	0.2879 (5)	−0.1011 (5)	4.6 (1)
C10	0.2273 (6)	0.000	−0.0986 (6)	3.5 (1)
C11	−0.3152 (9)	0.000	−0.044 (1)	9.3 (4)
C12	−0.2568 (6)	0.1119 (8)	0.1562 (8)	9.4 (2)
C20	0.0923 (7)	0.000	0.3032 (6)	4.1 (2)
C21	0.231 (1)	0.000	0.304 (1)	10.3 (5)
C22	0.073 (1)	0.1124 (8)	0.3698 (6)	9.0 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table IX. Bond Distances (Å) for 3[a]

Rh–Rh	3.884 (1)	C10–C12	1.520 (6)
Rh–As	2.496 (4)	C20–C21	1.540 (9)
Rh–C1	1.859 (4)	C20–C22	1.537 (6)
As–C20	2.025 (5)	O1–C1	1.166 (4)
As–C10	2.025 (4)	C10–C11	1.517 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table X. Bond Angles (deg) for 3[a]

As–Rh–As′	77.85 (2)	As–C10–C11	105.2 (4)
As–Rh–C1′	172.5 (1)	As–C10–C12	111.5 (3)
As–Rh–C1	94.7 (1)	C11–C10–C12	108.7 (4)
C1–Rh–C1′	92.7 (2)	C12–C10–C12′	111.1 (6)
Rh–As–Rh′	102.15 (2)	As–C20–C21	105.1 (4)
Rh–As–C10	110.77 (8)	As–C20–C22	110.4 (3)
Rh–As–C20	111.58 (9)	C21–C20–C22	110.4 (4)
C10–As–C20	109.8 (2)	C22–C20–C22′	110.0 (6)
Rh–C1–O1	178.3 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

X-ray Structure of $[Rh(\mu\text{-}t\text{-}Bu_2As)(CO)_2]_2$ (3). Complex **3** crystallizes from hexane in the monoclinic space group *I*2/*m* with four molecules in the unit cell. One-fourth of a molecule represents the asymmetric unit. A view of the molecule is shown in Figure 3. Details of crystal data, intensity data collection, and refinement parameters are given in Table I. Atomic positional parameters, bond lengths, and bond angles are presented in Tables VIII–X, respectively. There is a twofold rotation axis passing through both Rh atoms and a mirror plane perpendicular to this which contains the unique As, C10, C11, C20, and C21 atoms. The combination of a twofold axis with a mirror plane results in a crystallographic center of inversion at the midpoint of the Rh–Rh vector. The Rh_2As_2 core is therefore crystallographically planar although the CO ligands are not required to be in this plane. The Rh–As distance is 2.496 (1) Å, which can be compared to an analogous length of 2.396 Å (average) in $Rh_6(CO)_{11}(\mu\text{-}t\text{-}Bu_2As)_2(\mu_4\text{-}t\text{-}BuAs)$ (**4**). In **4** the *t*-Bu_2As^- groups bridge Rh–Rh bonded interactions while in **3** they do not. This may account for the slightly larger Rh–As distance in **3**.

Rh–Rh Double-Bonded Species: $[Rh(COD)]_2(\mu\text{-}t\text{-}BuP(CH_2)_4P\text{-}t\text{-}Bu)$ (5). We have extended our studies of rhodium phosphido complexes to include those of diphosphido types of ligands. Thus, reaction of $[Rh(COD)Cl]_2$ with Li-*t*-BuP$(CH_2)_4$P-*t*-BuLi in hexane yields bright red crystalline $[Rh(COD)]_2(\mu\text{-}t\text{-}BuP(CH_2)_4P\text{-}t\text{-}Bu]$ (**5**) in 56% yield. We have so far been unable to obtain crystals of **5** suitable for X-ray diffraction studies. However, ^1H and ^{31}P NMR data clearly indicate a symmetrical dinuclear molecule with two Rh atoms separated by bonding distance. Thus, the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 is a simple triplet that is shifted well downfield (δ 238.76, $^1J_{Rh-P}$ = 98.47 Hz). The data are consistent with tetrahedrally coor-

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dinated Rh atoms and a Rh–Rh double bond as shown in Scheme I.

Experimental Section

All reactions were performed under oxygen-free nitrogen or under vacuum. Microanalyses were by the Schwartzkopf Microanalytical Laboratory, Woodside, NY. Hexane, THF, and diethyl ether were dried over sodium and distilled from sodium benzophenone ketyl under nitrogen before use. Toluene was freshly distilled from sodium metal under nitrogen. $Rh_4(CO)_{12}$,[20] $[Rh(COD)Cl]_2$,[21] t-Bu_2PH,[22] t-Bu_2AsH,[23] t-Bu_2PLi,[22] and t-Bu_2AsLi[23] were prepared as previously described. Melting points were in sealed capillaries under nitrogen (1 atm) and are uncorrected.

Instruments: IR, Perkin-Elmer 1330; NMR, Varian EM-390 (^1H, 90 MHz), FT-80 (^{31}P, 32.384 MHz), Bruker WM-90 (^{31}P, 36.43 MHz), Nicolet NT-200 (^1H and ^{31}P). IR spectra were as Nujol mulls (KBr plates) or in solution (matched KBr or CaF_2 cells). NMR spectra were recorded in C_6D_6 at ambient temperature and are referenced to Me_4Si (δ 0.0, ^1H) and 85% $H_3PO_4(aq)$ (δ 0.0, ^{31}P).

$[Rh(CO)(t\text{-}Bu_2PH)]_2(\mu\text{-}t\text{-}Bu_2P)(\mu\text{-}H)$ (1). Tetrarhodium dodecacarbonyl ($Rh_4(CO)_{12}$) (0.20 g, 0.27 mmol) was dissolved in toluene (50 mL) and t-Bu_2PH (0.22 mL, 1.6 mmol) added via syringe. The reaction mixture was heated under reflux under a nitrogen atmosphere for 12 h. During this time the color of the solution darkened considerably. The solution was cooled to room temperature, and volatile materials were removed under vacuum. The residue was extracted into hexane (2 × 25 mL) and the solution filtered and evaporated to ca. 10 mL under vacuum. Cooling (−40 °C) gave large yellow prisms of **1**, which were collected and dried under vacuum. Yield: 0.23 g (61%). Mp: 142–148 °C dec. ^1H NMR (PhMe-d_8) (−80 °C): δ 4.70 (d, J_{P-H} = 308.7 Hz, 2 H, t-Bu_2PH), 1.63 (d, J_{P-H} = 6.69 Hz, 18 H, μ-t-Bu_2P), 1.18 (d, J_{P-H} = 11.69 Hz, 36 H, t-Bu_2PH), −10.40 (m, 1 H, μ-H). $^{31}P\{^1H\}$ NMR (in THF, ambient temperature): δ 264.3 (μ-t-Bu_2P, t, t, $^1J_{Rh-P}$ = 113 Hz, $^2J_{P-P}$ = 190 Hz), 58.50 (dd, $^1J_{Rh-P}$ = 123 Hz, $^2J_{P-P}$ = 190 Hz, t-Bu_2PH, at 32.384 MHz). IR (Nujol mull, KBr plates): 2292 m, 1942 vs, 1903 sh cm^{-1}. Anal. Calcd for $C_{26}H_{57}O_2P_3Rh_2$: C, 44.57; H, 8.14; P, 13.29. Found: C, 44.33; H, 8.05; P, 12.89.

$[Rh(COD)]_2(\mu\text{-}t\text{-}Bu_2P)(\mu\text{-}Cl)$ (2) (COD = 1,5-Cyclooctadiene). $[Rh(COD)Cl]$ (0.63 g, 1.27 mmol) was suspended in hexane (80 mL) and the suspension cooled (0 °C). A solution of t-Bu_2PLi (2.0 mL of a 0.66 M THF solution, 1.32 mmol) was then added dropwise via a syringe. The mixture was then allowed to warm to room temperature (over 0.5 h). The mixture was then heated under reflux (16 h) until the suspended $[Rh(COD)Cl]_2$ had been consumed. The solution was then cooled to room temperature and volatile materials removed under vacuum. The residue was extracted into toluene (3 × 50 mL), and the extracts were combined and filtered. The solution was concentrated under vacuum (ca. 20 mL) and cooled (−40 °C) to give yellow crystals of **2**. They were collected and dried under vacuum. Yield: 0.42 g (55%). Mp: 185–190 °C dec. ^1H NMR: δ 1.62 (d, $^2J_{P-H}$ = 12 Hz, 36 H, t-Bu_2P), 2.20 (m, $\Delta\omega_{1/2}$ = 30 Hz, 16 H, COD), 4.41 (m, $\Delta\omega_{1/2}$ = 10.5 Hz), 4.99 (m, $\Delta\omega_{1/2}$ = 10.5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, ambient temperature): δ 43.21 (t, $^1J_{Rh-P}$ = 113.6 Hz, μ-t-Bu_2P). Anal. Calcd for $C_{24}H_{42}ClPRh_2$: C, 47.80; H, 6.97; P, 5.15. Found: C, 47.45; H, 6.53; P, 4.92.

$[Rh(\mu\text{-}t\text{-}Bu_2As)(CO)_2]_2$ (3) and $Rh_6(CO)_{11}(\mu\text{-}t\text{-}Bu_2As)_2(\mu\text{-}t\text{-}BuAs)$ (4). A solution of $Li(t\text{-}Bu)_2As$ (17.0 mL of a 0.047 M THF solution, 0.80 mmol) was added to a solution of $[Rh(CO)_2Cl]_2$ (0.146 g, 0.377 mmol) in THF (15 mL) at −78 °C. The reaction mixture rapidly turned black and was stirred at −78 °C for 20 min. The mixture was then allowed to warm slowly to room temperature (12 h). Volatile materials were removed under vacuum, and the residue was extracted into hexane (35 mL). The solution was filtered and evaporated to 10 mL. After 36 h at ambient temperature, the black crystals of $Rh_6(CO)_{11}(\mu\text{-}t\text{-}Bu_2As)_2(\mu_4\text{-}t\text{-}BuAs)$ (**4**) (35%) were obtained and the supernatant was decanted from them. Further evaporation (ca. 5 mL) and cooling (−20 °C) of the supernatant gave yellow crystals of $[Rh(\mu\text{-}t\text{-}Bu_2As)(CO)_2]_2$ (**3**). They were collected and dried under vacuum. Yield: 0.07 g (25%). Mp: crystals turn black at 170–175 °C and explode at 194–197 °C. IR (hexane solution, KBr cells): 2036 vs, 1993 s cm^{-1}. ^1H NMR (C_6D_6, 35 °C, 90 MHz): δ 1.45 (s, t-Bu_2As). The characterization and X-ray structure of $Rh_6(CO)_{11}(\mu\text{-}t\text{-}Bu_2As)_2(\mu_4\text{-}t\text{-}BuAs)$ has been described.[9]

$[Rh(COD)]_2(\mu\text{-}t\text{-}BuP(CH_2)_4P\text{-}t\text{-}Bu)$ (5). $[Rh(COD)Cl]_2$ (0.50 g, 1.004 mmol) was suspended in hexane (75 mL) and the mixture cooled to −100 °C. $Li(t\text{-}Bu)P(CH_2)_4P(t\text{-}Bu)Li$ (7.2 mL of a 0.14 M THF solution, 2.008 mmol) was added slowly. The temperature was then allowed to warm slowly (4 h) to room temperature. Volatile materials are removed under vacuum, and the residue was extracted into toluene (40 mL). The solution was filtered and concentrated under vacuum (ca. 15 mL). Cooling (−40 °C) gave bright red crystals of **5** after 24 h. They were collected and dried under vacuum. Yield: 0.38 g (56%). Mp: 225–227 °C dec. ^1H NMR: δ 1.16 (m, 18 H, t-BuP), 1.80 (m, 8 H, COD), 1.90 (m, 8 H, COD), 2.10 (m, 4 H, $P-(CH_2)_4-P$), 2.30 (m, 4 H, $P-(CH_2)_4-P$), 2.6–3.0 (br m, COD), 5.2 (m, COD). $^{31}P\{^1H\}$ NMR: δ 238.76 (t, $^1J_{Rh-P}$ = 98.47 Hz). IR: 1490 b w, 1350 m, 1320 w, 1290 b w, 1250 w, 1160 m, 1080 b m, 1000 m, 910 m, 870 w, 800 s, 790 s cm^{-1}. Anal. Calcd for $C_{24}H_{50}P_2Rh_2$: C, 51.4; H, 8.2; P, 8.7. Found: C, 52.3; H, 7.49; P, 8.69.

X-ray Experiments. General Procedures. Crystals of **1**–**3** were grown at low temperature from hexane (**1** at −40 °C, **3** at −20 °C) and toluene (**2** at −20 °C) and mounted in thin-walled glass capillaries under nitrogen. Crystals of **1** lose crystallinity under vacuum, and they were mounted under an atmosphere of hexane. For each compound final lattice parameters were determined from 25 strong reflections (26° > 2θ > 30°) carefully centered on an Enraf-Nonius CAD-4 diffractometer. Data were collected by the $\omega/2\theta$ scan technique at 23 ± 2 °C. Details of crystal data and a summary of intensity data collection parameters for all three compounds are given in Table I. Full details of data collection procedures were as described in ref 7. For all three structures the data were corrected for Lorentz and polarization effects, and for **3** an absorption correction was applied by using an empirical ψ-scan method (program EAC). (Transmission factors: minimum, 70.50%, maximum, 99.59;, average 87.34%.) No absorption correction was applied for **1** or **2**, since none was deemed necessary. All three structures were solved by using direct methods (MULTAN)[24] and successive difference Fourier maps using the Enraf-Nonius software package "SDP-PLUS"[27] on a PDP 11/44 computer. Scattering factors were taken from ref 25. For **1** and **2** weighting schemes employing non-Poisson contributions with ignorance factors of p = 0.07 (**1**) and P = 0.05 (**2**) were used. P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum w(|F_o| - |F_o|)^2$ where $w = 4(F_o)^2/[\sum(F_o)^2]^2$ where $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + (P(F_o)^2)^2]Lp^2$, where S^2 is the scan rate squared, C is the total integrated peak count, R^2 is the ratio (squared) of scan time to background counting time, B is the total background count, and Lp is the Lorentz–polarization factor. For **3** unit weights were employed.

1. The space group was uniquely determined by systematic absences to be $P2_1/c$. The crystals were generally of poor quality due mainly to their solvent dependence, and no significant data were obtained beyond 2θ = 35°. The crystal finally chosen for data collection deteriorated by 25%, so an anisotropic decay correction was applied. There are two severely disordered molecules of hexane present in the unit cell. Eight carbon atoms of these groups were located and refined with isotropic thermal parameters (C27–C36). Hydrogen atoms were not located.

2. The space group was uniquely determined by systematic absences to be $Pbcn$. Hydrogen atoms were not located, and the structure refined smoothly to give R = 0.0502 and R_w = 0.0554. The highest peak in the final difference Fourier was 0.6 e Å^{-3} and was not chemically significant.

3. Systematic absences indicated possible space groups of $I2$, Im, or $I2/m$. $I2/m$ was chosen as the correct space group on the basis of successful refinement. The $23\bar{3}$ reflection had a very large degree of error associated with it, and it was excluded in the least-squares refinement. Agreement factors for equivalent reflections were 0.021 (intensity) and 0.012 (F_o). The final difference Fourier revealed two peaks greater than 0.5 e Å^{-3}; one was 0.835 Å from Rh (0.746 e Å^{-3}) and the other was 0.743 Å from As (0.741 e Å^{-3}). Hydrogen atoms were not located. The final full-matrix, least-squares refinement with anisotropic thermal parameters for all atoms gave final values of R = 0.0333 and R_w = 0.0403 ($R = \sum|F_o| - |F_c|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$.

Atomic thermal parameters and structure factors for **1** and **3** and complete tables of bond lengths and angles, temperature factors, and structure factors for **2** are available as supplementary material.[26]

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Registry No. **1**, 104114-32-1; **2**, 104114-33-2; **3**, 94645-33-7; **4**, 94645-32-6; **5**, 104114-34-3; $Rh_4(CO)_{12}$, 19584-30-6; $[Rh(COD)Cl]_2$, 12092-47-6; $[Rh(CO)_2Cl]_2$, 14523-22-9; Rh, 7440-16-6.

Supplementary Material Available: Tables of general temperature factors for **1**–**3**, complete tables of bond lengths and angles and least-squares planes for **2**, and a labeled ORTEP diagram of the second independent molecule for **2** (16 pages); tables of structure factors for **1**–**3** (88 pages). Ordering information is given on any current masthead page.

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Synthesis, Properties, and Structural Characterization of the Bis(dimethylphosphino)methane Complex $Mo_2(\mu\text{-dmpm})_2Cl_4$

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The new quadruply bonded dimolybdenum(II) compound $Mo_2(\mu\text{-dmpm})_2Cl_4$ (dmpm = bis(dimethylphosphino)methane) has been prepared by reaction of $Mo_2(O_2CCH_3)_4$ with dmpm in toluene and by reaction of $K_4Mo_2Cl_8$ with dmpm in toluene/methanol mixtures. Crystals grown from methanol are monoclinic, space group $P2_1/n$, with $a = 8.643$ (1) Å, $b = 8.893$ (1) Å, $c = 14.705$ (2) Å, $\beta = 100.02$ (1)°, $V = 1113.0$ (2) Å^3, and $Z = 2$. The crystal structure was solved and refined to residuals of $R = 0.0328$, $R_w = 0.0615$, and quality of fit 1.492. When crystals are grown by diffusion of hexane into a dichloromethane solution of $Mo_2(\mu\text{-dmpm})_2Cl_4$, a tetragonal modification is obtained, with $a = 9.063$ (15) Å, $c = 8.039$ (3) Å, $V = 660$ (3) Å^3, and $Z = 1$. This structure was solved and refined in space group $P4/mmm$, with final residuals of $R = 0.0599$, $R_w = 0.0698$, and quality of fit 1.32. The quadruple-bond distances are 2.1253 (4) and 2.134 (4) Å, respectively, in the monoclinic and tetragonal modifications. The tetragonal structure is disordered, while the monoclinic structure is not. The $^{31}P\{^1H\}$ NMR spectrum of the complex (in CH_2Cl_2) has one resonance ($\delta = -0.77$), verifying the equivalence of the four phosphorus nuclei. Electrochemical studies (by cyclic voltammetry in 0.1 M $TBAH/CH_2Cl_2$) reveal a reversible process at +0.49 V, an irreversible oxidation with $E_{p,a} = +1.25$ V, and an irreversible reduction with $E_{p,c} = -1.75$ V (all vs. Ag/AgCl).

Introduction

While several studies have been conducted on dinuclear compounds of the type $M_2X_4(LL)_2$ (X = halide, LL = bidentate phosphine) which contain multiple bonds between the metal atoms,[2–6] little work has yet been carried out when LL is the bis(dimethylphosphino)methane (dmpm) ligand. Recently, we found that the reactions of this ligand with $[Re_2Cl_8]^{2-}$ and with $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ give the novel compound $Re_2(\mu\text{-dmpm})_3Cl_4$, which contains a $Re{\equiv}Re$ bond and three bridging dmpm ligands.[7] This reactivity is quite different from that encountered with either dppm (dppm = $Ph_2PCH_2PPh_2$) or dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$), which gave the complexes $Re_2(\mu\text{-dppm})_2Cl_4$ and $\alpha\text{-}Re_2Cl_4(dmpe)_2$, respectively.[8]

In view of this difference in reactivity between dmpm and dppm, we have investigated the reactions of dmpm with dimolybdenum(II) species. In these instances the new quadruply bonded dimolybdenum(II) compound $Mo_2(\mu\text{-dmpm})_2Cl_4$ is formed as dark blue crystals. The synthesis, characterization, and crystal structure are reported and contrasted with those of the previously reported complex $Mo_2(\mu\text{-dppm})_2Cl_4$.[4,9,10]

Experimental Section

Starting Materials. Samples of $Mo_2(O_2CCH_3)_4$[11] and $K_4Mo_2Cl_8$[12] were prepared by using procedures similar to those described in the literature. The $Me_2PCH_2PMe_2$ (dmpm) ligand was purchased from Strem Chemicals, diluted to 1.2 M in toluene, and stored under an atmosphere of dry nitrogen. Chlorotrimethylsilane was purchased from Aldrich Chemical Co. and used without further purification. Solvents used in the preparation and workup of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry nitrogen with use of standard procedures.

Preparation of $Mo_2(\mu\text{-dmpm})_2Cl_4$. Method 1. A 25-mL three-neck flask was charged with 0.201 g (0.47 mmol) of $Mo_2(O_2CCH_3)_4$, 0.30 mL (2.36 mmol) of Me_3SiCl, 0.80 mL (0.96 mmol) of dmpm (1.2 M in toluene), and 15 mL of toluene. The suspension was refluxed for 1 h and then stirred for a further 4 h while it was still warm. The reaction mixture was cooled to room temperature and the blue product filtered off, washed with toluene followed by pentane, and finally vacuum-dried; yield 0.277 g (98%). Anal. Calcd for $C_{10}H_{28}Cl_4Mo_2P_4$: C, 19.82; H, 4.67; Cl, 23.40. Found: C, 20.03; H, 4.81; Cl, 23.45.

Method 2. $K_4Mo_2Cl_8$ (0.32 g, 0.50 mmol) was placed in a flask equipped with a stirring bar. A solution of 1.0 g of dmpm in 9.0 mL of toluene was prepared in a Schlenk tube, and 2.0 mL of this solution (ca. 1.5 mmol of dmpm) was added to the flask. Methanol (25 mL) was then added and, upon stirring, the mixture soon turned blue. After the mixture had been stirred for 6 h, a blue precipitate settled out of a purple solution. The blue solid was filtered off, washed with hexane, and dried in vacuo. This product was contaminated with potassium chloride; it was purified by dissolving it in CH_2Cl_2, filtering the resulting blue solution, and precipitating the solid by slow addition of hexane; yield 0.22 g (73%).

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