

Head to Head Acetylene Coupling at a Heterobimetallic Center To Give a Rhodacyclopentadiene-Iron Unit. Syntheses and X-ray Crystal Structures of $(t\text{-Bu}_2\text{PH})(\text{CO})_2\text{Fe}(\mu\text{-CO})(\mu\text{-}t\text{-Bu}_2\text{P})\text{Rh}(\text{COD})(\text{Fe-Rh})$, $(\text{CO})_2\text{Fe}(\mu\text{-}t\text{-Bu}_2\text{P})(\mu\text{-}\eta^4\text{-C}_4\text{H}_2(\text{Ph})_2)\text{Rh}(\text{HCCPh})(\text{Fe-Rh})$, and $\text{Rh}_2\text{Fe}(\text{CO})_3(t\text{-Bu}_2\text{PH})(\mu\text{-CO})_2(\mu\text{-}t\text{-Bu}_2\text{P})_2$

Atta M. Arif, Don J. Chandler, and Richard A. Jones*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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Reaction of $\text{Fe}(\text{CO})_3(t\text{-Bu}_2\text{PH})(t\text{-Bu}_2\text{PLi})$, generated in situ from $\text{Fe}(\text{CO})_3(t\text{-Bu}_2\text{PH})_2$ and $n\text{-BuLi}$, with $[\text{Rh}(\text{COD})\text{Cl}]_2$ (COD = 1,5 cyclooctadiene) gives the heterobimetallic, di-*tert*-butylphosphido-bridged complex $(t\text{-Bu}_2\text{PH})(\text{CO})_2\text{Fe}(\mu\text{-CO})(\mu\text{-}t\text{-Bu}_2\text{P})\text{Rh}(\text{COD})(\text{Fe-Rh})$ (1) (30%). The molecular structure of 1 contains a single Fe-Rh bond that is bridged by a di-*tert*-butylphosphido unit. The coordination geometry about Fe is roughly trigonal bipyramidal with one CO ligand occupying a semibridging site to the Rh atom. The *t*-Bu₂PH ligand is trans to the *t*-Bu₂P⁻ unit. The coordination geometry about Rh is roughly square-planar. 1 reacts with phenylacetylene (2.5 equiv) in THF under reflux (2 h) to give dark red $(\text{CO})_2\text{Fe}(\mu\text{-}t\text{-Bu}_2\text{P})(\mu\text{-}\eta^4\text{-C}_4\text{H}_2\text{Ph}_2)\text{Rh}(\text{HCCPh})(\text{Fe-Rh})$ (2) in 70% yield. The C₄H₂Ph₂ unit is formed from the head to head coupling of two acetylene units and straddles the Fe-Rh bond so that the RhC₄ unit is virtually planar and equivalent to a metallacyclopentadiene group in its bonding to Fe. The Fe atom bears two terminal CO ligands and, including its bonding to the P atom of the *μ*-*t*-Bu₂P⁻ group, has a three-legged piano stool coordination geometry. The Rh atom also bears an η^2 -phenylacetylene unit. Heating 1 under reflux in acetonitrile produces $\text{Rh}_2\text{Fe}(\text{CO})_3(t\text{-Bu}_2\text{PH})(\mu\text{-CO})_2(\mu\text{-}t\text{-Bu}_2\text{P})_2$ (3) (22%) in addition to minor amounts of $[\text{Rh}(\text{CO})(t\text{-Bu}_2\text{PH})]_2(\mu\text{-H})(\mu\text{-}t\text{-Bu}_2\text{P})$ (ca. 5%) and $(\text{CO})(t\text{-Bu}_2\text{PH})\text{Rh}(\mu\text{-}t\text{-Bu}_2\text{P})\text{Fe}(\text{CO})_4$ (ca. 5%). The molecular geometry of 3 consists of a Rh₂Fe triangle in which two *t*-Bu₂P units bridge an Fe-Rh and the Rh-Rh bond. Two CO groups bridge the remaining Fe-Rh bond. One Rh atom bears a *t*-Bu₂PH group and the other a terminal CO ligand. The Fe atom bears two terminal CO ligands. Crystal data for 1: C₂₇H₄₆FeO₃P₂Rh; M_r 639.37; monoclinic; Cc (No. 9); a = 8.735 (2) Å, b = 22.720 (3) Å, c = 30.485 (4) Å, β = 98.28 (2)°; V = 5987.2 (5) Å³; D_{calcd} = 1.419 g cm⁻³; Z = 8; μ(Mo Kα) = 11.57 cm⁻¹. Refinement of 2863 reflections (I > 3σ(I)) out of 5122 unique observed reflections (2° < 2θ < 48°) gave R and R_w values of 0.0667 and 0.0730, respectively. Data/parameter ratio = 8.47, hydrogen atoms not located. Crystal data for 2: C₃₄H₃₆FeO₂PRh; M_r 666.39; triclinic; P1 (No. 2); a = 10.073 (2) Å, b = 12.785 (3) Å, c = 12.955 (3) Å, α = 97.715 (2)°, β = 105.69 (2)°, γ = 101.800 (2)°; V = 1540.2 (5) Å³; D_{calcd} = 1.437 g cm⁻³; Z = 2; μ(Mo Kα) = 10.764 cm⁻¹. Refinement of 3073 reflections (I > 3σ(I)) out of 4829 unique observed (3° < 2θ < 48°) gave R and R_w values of 0.0560 and 0.0654, respectively. Data/parameter ratio = 6.402. Crystal data for 3: C₂₉H₅₅FeO₅P₃Rh₂; M_r 838.34; monoclinic; P2₁/n (No. 1014); a = 13.222 (4) Å, b = 17.940 (4) Å, c = 16.299 (6) Å, β = 104.76 (3)°; V = 3738.6 (5) Å³; Z = 4; D_{calcd} = 1.489 g cm⁻³; μ(Mo Kα) = 14.002 cm⁻¹. Refinement of 2061 reflections (I > 3σ(I)) out of 3956 unique observed (3° < 2θ < 48°) gave R and R_w values of 0.0820 and 0.0885, respectively. Common to all three structures: radiation (Mo Kα) 0.71073 Å (graphite monochromator). Methods: MULTAN; difference Fourier; full-matrix least squares.

Introduction

The coupling of acetylene molecules across a dimetal center is a process of potential relevance to a number of catalytic processes such as the Reppe cyclization of acetylene to form cyclooctatetraene and benzene.¹⁻³ Well-documented examples of two acetylenes coupling across a homobimetallic center were first reported by Knox and co-workers.⁴ For example, heating $[\text{Cr}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$ with RC₂R (R = H, CO₂Me, or Ph) in heptane produces black, crystalline $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})]_2(\text{RC}_2\text{R})_2$ in good yields. Since this report a number of other examples of two acetylene couplings at dimetallic centers have been reported. For example, Chisholm and co-workers have re-

ported the reaction of W₂(O-*t*-Bu)₆ and W₂(OR)₆(py)₂ (R = *i*-Pr, CH₂-*t*-Bu) with C₂H₂ to give W₂(O-*t*-Bu)₆(μ-C₄H₄) and W₂(OR)₆(μ-C₄H₄)(C₂H₂), respectively.⁵

As part of our general studies of the reactivity patterns of heterobimetallic phosphido-bridged complexes with small molecules we have investigated the reactions of the Fe-Rh complex $(t\text{-Bu}_2\text{PH})(\text{CO})_2\text{Fe}(\mu\text{-CO})(\mu\text{-}t\text{-Bu}_2\text{P})\text{Rh}(\text{COD})$ (1) with acetylenes and nitriles (RCN). Reaction of 1 with phenylacetylene in THF under reflux gives good yields of $(\text{CO})_2\text{Fe}(\mu\text{-}t\text{-Bu}_2\text{P})(\mu\text{-}\eta^4\text{-C}_4\text{H}_2\text{Ph}_2)\text{Rh}(\text{HCCPh})$ (2), in which two acetylene molecules are coupled head to head and the COD ligand is replaced by a single phenylacetylene (see Scheme I) (COD = 1,5-cyclooctadiene). There are few other examples of this type of heterometallacyclopentadiene,⁶ and these include CpM[C₄H₄Fe(CO)₃] (M = Co, Rh),⁷ CpCoFe(C₄H₄)(CO)₃,⁸ [Me₄C₄Fe(CO)₃](NiC₄H₄),⁹

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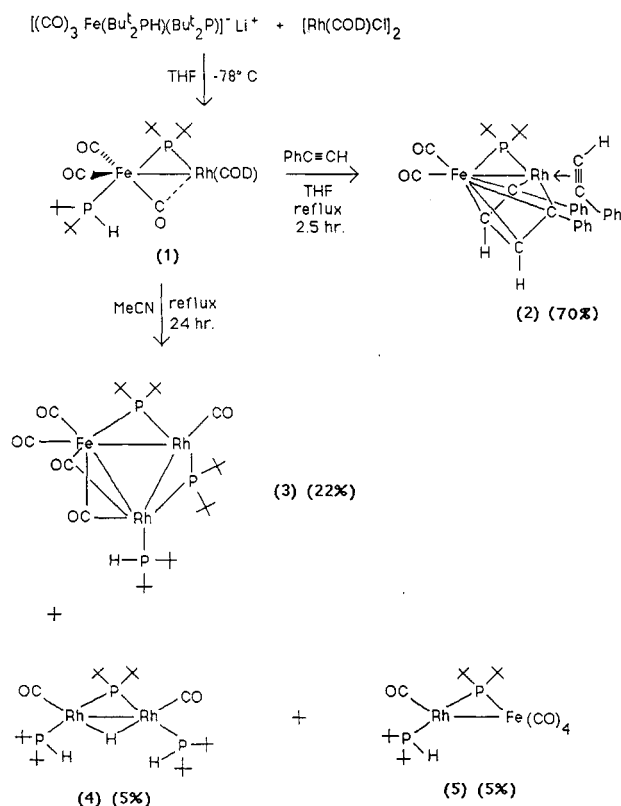
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Scheme I



$[\text{CpMC}_4\text{R}_4(\text{CO})_2]\text{Co}(\text{CO})_2$ ($\text{M} = \text{Mo}, \text{W}$),¹⁰ and $\text{CpFeNi}(\text{C}_4\text{Ph}_4)\text{Cp}$.¹¹ In contrast, reaction of **1** in the nitriles MeCN and PhCN under reflux gives moderate yields of the heterotrimeric cluster $\text{Rh}_2\text{Fe}(\text{CO})_3(\text{t-Bu}_2\text{PH})(\mu\text{-CO})_2(\mu\text{-t-Bu}_2\text{P})_2$ (**3**) (22%) as well as low yields of $[\text{Rh}(\text{CO})(\text{t-Bu}_2\text{PH})]_2(\mu\text{-H})(\mu\text{-t-Bu}_2\text{P})$ (**4**) (5%) and $(\text{CO})(\text{t-Bu}_2\text{PH})\text{Rh}(\mu\text{-t-Bu}_2\text{P})\text{Fe}(\text{CO})_4$ (**5**) (5%) (Scheme I). We describe here the syntheses, structures, and bonding in **1**, **2**, and **3**. Complexes **4** and **5** will be described elsewhere.^{12,13}

Results and Discussion

Reaction of the lithiated phosphine complex $\text{Fe}(\text{CO})_3(\text{t-Bu}_2\text{PH})(\text{t-Bu}_2\text{PLi})$, generated in situ, with $[\text{Rh}(\text{COD})\text{Cl}]_2$ in THF at -78°C gives yellow-brown, crystalline, hexane-soluble $(\text{t-Bu}_2\text{PH})(\text{CO})_2\text{Fe}(\mu\text{-CO})(\mu\text{-t-Bu}_2\text{P})\text{Rh}(\text{COD})$ (**1**) in moderate yield (30%) (Scheme I). We have previously used the general route of salt elimination from the reaction of a coordinated lithiated phosphine with a metal halide moiety to prepare a range of heterobimetallic phosphido-bridged complexes.^{14,15} There are a number of related Fe-Rh diphenylphosphido-bridged heteronuclear

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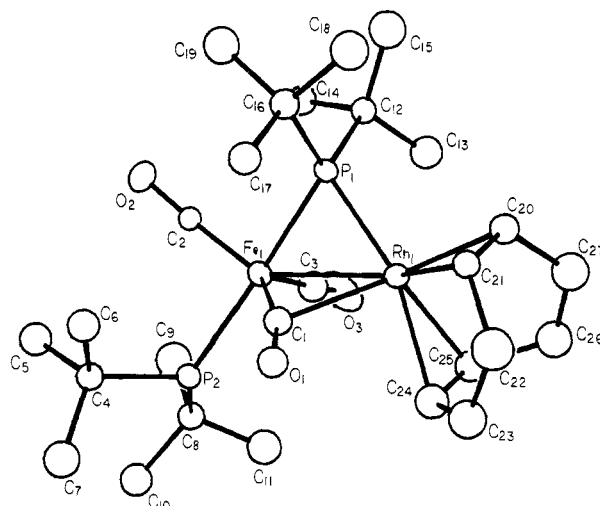


Figure 1. ORTEP view of **1**. The atoms are shown at the 50% probability level.

complexes known. For example, $(\text{CO})_4\text{Fe}(\mu\text{-PPH}_2)\text{Rh}(\text{CO})(\text{PET}_3)$ was recently reported by Geoffroy and co-workers.¹⁶

Spectroscopic data for **1** is in accord with the structure as determined by a single-crystal X-ray diffraction study. Thus the IR spectrum shows the presence of both terminal and bridging CO ligands ($\nu_{\text{CO}} = 1938$ (s), 1877 (s), 1845 (s) cm^{-1}) as well as P-H ($\nu_{\text{P-H}} = 2300$ (w) cm^{-1}). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicates the presence of a phosphido group bridging a metal-metal bond⁹ (δ 186.59 (dd, $^1J_{\text{Rh-P}} = 137.13$ Hz, $^2J_{\text{P-P}} = 24.05$ Hz) as well as the $\text{t-Bu}_2\text{PH}$ group bound to Fe (δ 101.54 (d, $^2J_{\text{P-P}} = 23.49$ Hz)).

X-ray Crystal Structure of 1. Complex **1** crystallizes in the monoclinic space group Cc with two independent molecules in the asymmetric unit (eight in the unit cell). A general view of one molecule of **1** is shown in Figure 1. The bonding parameters of both molecules are quite similar. In the following discussion, values in square brackets are those for the second molecule of **1**. Crystallographic data are collected in Table I, and positional parameters are given in Table II.

The overall molecular geometry contains a single Fe-Rh bond (Fe-Rh = 2.634 (2) Å [2.638 (2) Å]), which is bridged by a $\text{t-Bu}_2\text{P}^-$ group, and a semibridging CO ligand (C(1)-O(1)). The coordination geometry about Fe, ignoring the Fe-Rh bond, is roughly trigonal-bipyrimidal. The $\text{t-Bu}_2\text{PH}$ ligand bonded to Fe lies trans to the bridging $\text{t-Bu}_2\text{P}^-$ unit (P(1)-Fe-P(2) = 167.5 (2)° [166.2 (2)°]). The three CO ligands bonded to Fe are virtually coplanar with the two normal terminal groups C(2)-O(2) and C(3)-O(3) bent back slightly away from the side of the molecule that contains the Rh moiety. Thus C(2)-Fe-C(3) = 109.2 (8)° [110.4 (8)°], and the sum of the angles subtended about Fe = 359.9° [359.9°].

The Fe-C(1)-O(1) angle of 162 (1)° [159 (1)°] and the Fe-C(1) distance of 1.86 (2) Å [1.88 (2) Å] indicate only a slight degree of bonding to the Rh atom. Thus the C(1)-Rh distance is relatively long (2.29 (2) Å [2.27 (2) Å]). The Fe-P(1) and Rh-P(1) distances are normal (Fe-P(1) = 2.291 (4) Å [2.289 (4) Å], Rh-P(1) = 2.260 (4) Å [2.266 (4) Å]) and can be compared to those found in similar complexes. For example Fe-P = 2.274 (4) Å in $(\text{CO})_3(\text{PMe}_3)\text{Fe}(\mu\text{-t-Bu}_2\text{P})\text{Co}(\text{CO})_2(\text{PMe}_3)$ ¹⁵ and Rh-P = 2.296

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Table I. Crystal Structure Parameters for 1, 2, and 3

	1	2	3
description			
color	yellow-brown	dark red	dark green
habit	plate	brick	plate
max dimens, mm	0.25 × 0.22 × 0.20	0.22 × 0.20 × 0.15	0.25 × 0.20 × 0.13
unit cell			
cryst system	monoclinic	triclinic	monoclinic
space group	<i>Cc</i>	<i>P</i> $\bar{1}$	<i>P</i> $2_1/n$ (No. 1014)
unit-cell parameters			
<i>a</i> , Å	8.735 (2)	10.073 (2)	13.222 (4)
<i>b</i> , Å	22.720 (2)	12.785 (3)	17.940 (4)
<i>c</i> , Å	30.485 (4)	12.955 (3)	16.299 (6)
α , deg	90	97.715 (2)	90
β , deg	98.28 (2)	105.69 (2)	104.76 (3)
γ , deg	90	101.800 (2)	90
<i>U</i> , Å ³	5987.2 (5)	1540.2 (5)	3738.6 (5)
<i>Z</i>	8	2	4
formula	C ₂₇ H ₄₆ FeO ₃ P ₂ Rh	C ₃₄ H ₃₆ FeO ₂ PRh	C ₂₉ H ₅₅ FeO ₅ P ₃ Rh ₂
<i>M</i> _r	639.37	666.39	838.34
<i>D</i> _{calcd} , g cm ⁻³	1.419	1.437	1.489
μ _{calcd} , cm ⁻¹	11.57	10.76	14.00
radiatn, Å	Mo K α (0.710 73)	Mo K α (0.710 73)	Mo K α (0.710 73)
scan technique	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan width, deg	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
range/indices (<i>hkl</i>)	0–10, 0–26, –32 to +32	–11 to +11, –14 to +14, 0–14	0–15, 0–20, –18 to +18
2 θ range deg	2–48	3–48	3–48
no. of reflctns measd	5122	4829	3956
std reflctns			
intensity	4,2,8, 4,2,12	$\bar{5}$,2,2, 3, $\bar{3}$,4	4,5,3, $\bar{1}$, $\bar{9}$,2
orientatn	2,12,1, 4,4,10	2,2,4, 2, $\bar{3}$,5	0,2,9 $\bar{5}$,4,7
decay of std, %	2.0	0.6	<1
min % transmissn	87.6	91.0	83.6
max % transmissn	99.6	99.8	99.7
av % transmissn	95.8	96.5	93.0
agreement factor for averaged reflctns			
<i>F</i> _o	0.042	0.062	0.029
<i>I</i>	0.027	0.036	0.028
structure determination			
no. of reflctns used (<i>I</i> > 3 σ (<i>I</i>))	2863	3073	2061
no. of parameters varied	338	480	199
data/parameter ratio	8.470	6.402	10.357
shift to error ratio	0.114	1.757	0.459
esd of an observn of unit wt	3.63	3.92	4.68
<i>R</i>	0.0667	0.0560	0.0820
<i>R</i> _w	0.0730	0.0654	0.0885

(1) Å in (CO)₄(PMe₃)Cr(μ -*t*-Bu₂P)Rh(CO)(PMe₃).¹⁴

The Rh atom of 1 has a roughly square-planar coordination geometry consisting of P(1), C(1), and the midpoints of the two double bonds of the COD ligand.¹⁷ The COD ligand is bound in the expected boat or tub conformation as found in many other transition-metal-COD complexes.¹⁸

Synthesis of (CO)₂Fe(μ -*t*-Bu₂P)(μ - η^4 -C₄H₂Ph₂)Rh(HCCPh)(Fe–Rh) (2). Complex 1 reacts with a variety of acetylenes in THF under reflux to give dark red solutions. In the case of phenylacetylene we were able to isolate and characterize the major product (CO)₂Fe(μ -*t*-Bu₂P)(μ - η^4 -C₄H₂Ph₂)Rh(HCCPh) (2), which is formed in good yield (70% based on 1). In 2 the *t*-Bu₂PH, COD, and one CO ligand of 1 have been replaced by two coupled acetylenes that bridge the Fe–Rh bond and with a terminal acetylene group bonded to Rh. The spectroscopic prop-

(17) Deviations (Å) from the least-squares plane where the midpoints of C(20)–C(21) and C(24)–C(25) are C(200) and C(240): molecule 1, Rh(1) 0.620 (1), P(1) –0.100 (6), C(1) –0.79 (3), C(200) 0.12 (1), C(240) 0.15 (1); molecule 2, Rh(2) 0.442 (1), P(3) –0.149 (5), C(1A) –0.70 (3), C(200A) –0.46 (1), C(240A) 0.86 (1).

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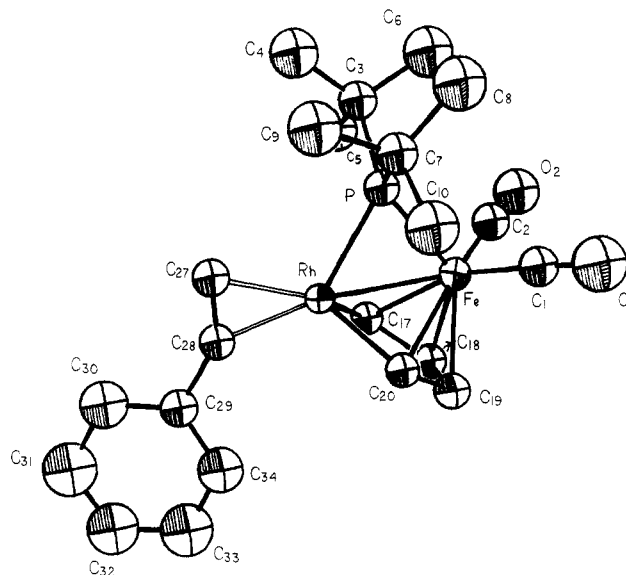


Figure 2. ORTEP view of 2. H atoms and the phenyl groups of the μ - η^4 -C₄H₂Ph₂ group have been omitted for clarity. The atoms are shown at the 50% probability level.

erties of 2 are in accord with the structure determined by an X-ray diffraction study. The IR spectrum indicates only terminal CO ligands (ν_{CO} = 1981 (s), 1925 (s) cm⁻¹),

Table II. Positional Parameters and Estimated Standard Deviations for 1^a

atom	x	y	z	B, Å ²
Rh(1)	0.889	0.01235 (8)	0.023	2.31 (3)
Rh(2)	0.9651 (3)	0.26246 (8)	0.67443 (8)	2.35 (3)
Fe(1)	1.0022 (4)	0.0572 (2)	0.4667 (1)	2.40 (7)
Fe(2)	0.6350 (4)	0.3073 (2)	0.2311 (1)	2.36 (7)
P(1)	0.3811 (8)	0.4689 (3)	0.4502 (2)	2.2 (1)
P(2)	1.0689 (8)	-0.1526 (3)	-0.0187 (2)	2.4 (1)
P(3)	0.5296 (7)	0.2193 (3)	0.2478 (2)	2.2 (1)
P(4)	1.1857 (8)	0.0972 (3)	-0.2830 (2)	2.2 (1)
O(1)	0.743 (2)	-0.1081 (8)	0.0090 (6)	3.3 (4)*
O(2)	1.030 (3)	-0.0688 (9)	-0.1260 (6)	4.9 (5)
O(3)	1.288 (3)	-0.005 (1)	0.009 (1)	7.6 (7)
O(4)	0.833 (2)	0.1417 (7)	-0.3105 (6)	2.7 (4)
O(5)	1.260 (3)	0.1814 (9)	-0.1756 (7)	5.6 (6)
O(6)	1.379 (3)	0.246 (1)	0.6866 (9)	8.2 (7)
C(1A)	0.938 (3)	0.171 (1)	0.7020 (9)	3.1 (5)*
C(1)	0.834 (3)	-0.079 (1)	-0.0057 (9)	3.1 (5)*
C(2)	1.019 (3)	-0.066 (1)	-0.0869 (8)	2.2 (5)*
C(2A)	1.203 (3)	0.187 (1)	0.7887 (8)	2.6 (5)*
C(3A)	1.282 (4)	0.226 (1)	0.702 (1)	5.2 (8)*
C(3)	1.169 (3)	-0.026 (1)	-0.006 (1)	3.9 (6)*
C(4A)	1.132 (3)	0.041 (1)	0.7576 (9)	3.1 (5)*
C(4)	0.977 (3)	-0.210 (1)	-0.0584 (9)	2.9 (5)*
C(5)	1.066 (4)	-0.220 (1)	-0.099 (1)	4.3 (7)*
C(5A)	1.090 (3)	-0.020 (1)	0.7324 (9)	3.8 (6)*
C(6)	0.810 (4)	-0.188 (1)	-0.079 (1)	3.9 (6)*
C(6A)	0.985 (4)	0.062 (1)	0.777 (1)	4.4 (7)*
C(7)	1.453 (4)	0.232 (2)	0.966 (1)	5.1 (7)*
C(7A)	1.262 (4)	0.032 (1)	0.798 (1)	4.5 (7)*
C(8)	1.279 (3)	-0.170 (1)	-0.0005 (9)	3.3 (6)*
C(8A)	1.379 (3)	0.079 (1)	0.7011 (9)	3.4 (6)*
C(9)	1.376 (4)	-0.146 (2)	-0.035 (1)	6.1 (9)*
C(9A)	1.413 (4)	0.012 (2)	0.694 (1)	5.3 (8)*
C(10)	1.319 (4)	-0.240 (1)	0.004 (1)	4.7 (7)*
C(10A)	1.512 (4)	0.109 (1)	0.734 (1)	4.9 (7)*
C(11)	1.327 (4)	-0.143 (2)	0.046 (1)	5.5 (8)*
C(11A)	1.383 (4)	0.106 (1)	0.653 (1)	4.4 (7)*
C(12A)	1.169 (3)	0.345 (1)	0.7632 (9)	3.7 (6)*
C(12)	1.005 (3)	0.097 (1)	-0.0623 (8)	2.8 (5)*
C(13)	1.603 (4)	0.617 (1)	0.982 (1)	4.6 (7)*
C(13A)	1.101 (4)	0.399 (2)	0.782 (1)	5.8 (8)*
C(14A)	1.318 (4)	0.325 (2)	0.793 (1)	5.3 (8)*
C(14)	1.120 (3)	0.076 (1)	-0.0953 (9)	3.5 (6)*
C(15)	1.408 (4)	0.648 (2)	0.914 (1)	5.7 (8)*
C(15A)	1.219 (4)	0.369 (2)	0.716 (1)	5.8 (8)*
C(16)	1.191 (3)	0.531 (1)	0.9100 (9)	3.2 (5)*
C(16A)	0.880 (3)	0.283 (1)	0.7876 (9)	3.8 (6)*
C(17A)	0.955 (3)	0.280 (1)	0.836 (1)	4.0 (6)*
C(17)	1.099 (3)	0.475 (1)	0.9188 (9)	3.7 (6)*
C(18A)	0.763 (4)	0.335 (1)	0.779 (1)	4.5 (7)*
C(18)	1.085 (4)	0.584 (1)	0.916 (1)	5.1 (7)*
C(19)	1.222 (4)	0.530 (1)	0.860 (1)	5.0 (7)*
C(19A)	0.777 (4)	0.224 (2)	0.779 (1)	5.6 (8)*
C(20)	0.780 (3)	0.089 (1)	0.0460 (9)	3.4 (6)*
C(20A)	0.833 (4)	0.340 (1)	0.651 (1)	4.9 (7)*
C(21)	0.675 (3)	0.041 (1)	0.0437 (8)	2.6 (5)*
C(21A)	0.731 (3)	0.292 (1)	0.6524 (9)	3.4 (6)*
C(22A)	0.660 (4)	0.256 (1)	0.613 (1)	4.7 (7)*
C(22)	0.647 (4)	0.008 (2)	0.086 (1)	6.1 (8)*
C(23)	0.763 (4)	-0.034 (1)	0.106 (1)	5.2 (8)*
C(23A)	0.755 (5)	0.213 (2)	0.593 (1)	6.6 (9)*
C(24A)	0.930 (4)	0.215 (1)	0.608 (1)	4.7 (7)*
C(24)	1.419 (4)	0.465 (1)	1.090 (1)	4.4 (7)*
C(25)	1.017 (3)	0.011 (1)	0.0930 (9)	3.8 (6)*
C(25A)	1.019 (4)	0.263 (1)	0.603 (1)	4.8 (7)*
C(26)	0.987 (4)	0.072 (1)	0.116 (1)	5.3 (8)*
C(26A)	0.976 (5)	0.319 (2)	0.583 (1)	6.5 (9)*
C(27)	0.878 (4)	0.110 (2)	0.092 (1)	5.5 (8)*
C(27A)	0.894 (5)	0.361 (2)	0.609 (1)	6.4 (9)*

^a Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\langle \frac{1}{3} [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)] \rangle$.

and the ³¹P{¹H} NMR spectrum consists of a simple doublet to low field (δ 421.51 ($^1J_{\text{Rh-P}} = 82.8$ Hz)), indi-

Table III. Positional Parameters and Estimated Standard Deviations for 2^a

atom	x	y	z	B, Å ²
Rh	0.68180 (8)	0.26572 (7)	0.67640 (6)	2.40 (1)
Fe	0.7614 (1)	0.3034 (1)	0.8830 (1)	2.86 (3)
P	0.5382 (3)	0.2141 (2)	0.7802 (2)	3.06 (6)
O(1)	0.822 (1)	0.1734 (8)	1.0478 (7)	7.3 (3)
O(2)	0.7154 (9)	0.4614 (8)	1.0414 (7)	6.2 (2)
C(1)	0.793 (1)	0.225 (9)	0.9808 (9)	3.7 (3)
C(2)	0.729 (1)	0.3991 (9)	0.9760 (9)	3.7 (3)
C(3)	0.390 (1)	0.2840 (9)	0.7853 (9)	3.7 (3)
C(4)	0.249 (1)	0.229 (1)	0.699 (1)	6.0 (4)
C(5)	0.439 (1)	0.399 (1)	0.774 (1)	4.8 (3)
C(6)	0.373 (1)	0.292 (1)	0.905 (1)	7.6 (4)
C(7)	0.466 (1)	0.0634 (8)	0.7735 (9)	3.6 (2)
C(8)	0.404 (1)	0.036 (1)	0.862 (1)	6.5 (4)
C(9)	0.360 (2)	0.14 (1)	0.662 (1)	7.3 (5)
C(10)	0.588 (1)	0.010 (1)	0.786 (1)	7.0 (4)
C(11)	0.686 (1)	0.5255 (8)	0.6459 (9)	3.6 (3)
C(12)	0.660 (1)	0.625 (1)	0.630 (1)	5.3 (3)
C(13)	0.698 (1)	0.7106 (8)	0.713 (1)	5.2 (3)
C(14)	0.763 (1)	0.6986 (9)	0.816 (1)	5.8 (4)
C(15)	0.793 (1)	0.6048 (9)	0.838 (1)	4.7 (3)
C(16)	0.753 (1)	0.5135 (9)	0.7519 (8)	3.4 (2)
C(17)	0.7948 (9)	0.4114 (7)	0.7683 (8)	2.8 (2)
C(18)	0.923 (1)	0.4184 (8)	0.8510 (8)	3.1 (2)
C(19)	0.956 (1)	0.3166 (9)	0.8492 (8)	3.6 (3)
C(20)	0.8542 (9)	0.2304 (8)	0.7655 (8)	2.8 (2)
C(21)	0.890 (1)	0.1234 (8)	0.7434 (9)	3.5 (2)
C(22)	0.859 (1)	0.069 (1)	0.639 (1)	4.7 (3)
C(23)	0.900 (1)	-0.027 (1)	0.616 (1)	5.6 (3)
C(24)	0.969 (1)	-0.071 (1)	0.700 (1)	5.9 (4)
C(25)	0.999 (1)	-0.016 (1)	0.800 (1)	6.5 (4)
C(26)	0.961 (1)	0.081 (1)	0.826 (1)	4.9 (3)
C(27)	0.549 (1)	0.2110 (9)	0.5211 (8)	3.5 (2)
C(28)	0.668 (1)	0.2597 (8)	0.5190 (7)	2.9 (2)
C(29)	0.759 (1)	0.2975 (9)	0.4543 (8)	3.5 (2)
C(30)	0.694 (1)	0.304 (1)	0.348 (1)	5.7 (4)
C(31)	0.783 (2)	0.340 (1)	0.282 (1)	8.5 (5)
C(32)	0.931 (2)	0.367 (1)	0.332 (1)	8.4 (4)
C(33)	0.989 (1)	0.363 (2)	0.438 (1)	8.1 (5)
C(34)	0.905 (1)	0.327 (1)	0.498 (1)	5.9 (4)

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

cative of a phosphido group bridging a metal-metal bond.¹⁰ Unfortunately, the complex is not sufficiently soluble in the common deuterated solvents for reliable ¹³C NMR data to be obtained.

X-ray Crystal Structure of 2. The complex crystallizes in the triclinic space group $P\bar{1}$ and a view of the molecule with the atom numbering scheme is shown in Figure 2. Crystallographic data for 2 are collected in Table I, and positional parameters are given in Table III. As can be seen in Figure 2 the central phosphido-bridged Fe-Rh framework remains intact and the coupled acetylene unit straddles the Fe-Rh bond opposite to the μ -*t*-Bu₂P group. The geometry of the *t*-Bu₂P-Rh-Fe moiety is similar to that in 1 with Rh-Fe = 2.525 (1) Å, Rh-P = 2.288 (1) Å, and Fe-P = 2.249 (2) Å.

The bonding of the coupled acetylene unit to the Fe-Rh bond is of interest. Although the precise mechanism of formation of 2 is not known, it is interesting to note that the two acetylene molecules couple in a "head to head" fashion. In other cases of two acetylene molecules coupling across two metals "head to tail" coupling has been observed,⁶⁻¹⁰ and for CpFeNiC₄Ph₂H₂(Cp)¹¹ a mixture of the possible isomers is formed. It seems likely that the "head to head" coupling observed here is favored on steric grounds.

All four of the previously acetylenic carbon atoms, C(17), C(18) C(19), and C(20), are bonded to Fe while only C(17)

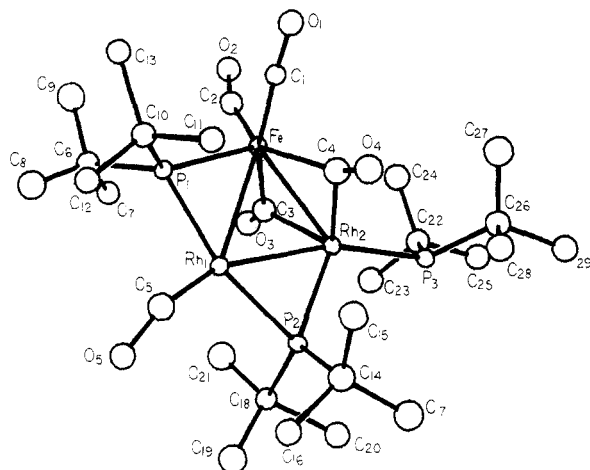


Figure 3. ORTEP view of **3**. The atoms are shown at the 50% probability level.

and C(20) are bonded to Rh. The C–C distances involved are similar (C(17)–C(18) = 1.414 (7) Å, C(18)–C(19) = 1.408 (8) Å, and C(19)–C(20) = 1.435 (8) Å). The Rh atom is virtually coplanar with these carbon atoms,²⁰ thus one view of the bonding is that of a “rhodacyclopentadiene–iron” as shown in the scheme. The acetylene group is bonded to Rh so that the phenyl group lies on the opposite side of the molecule to the *t*-Bu₂P unit, again presumable for steric reasons.

Synthesis of Rh₂Fe(CO)₃(*t*-Bu₂PH)(μ-CO)₂(μ-*t*-Bu₂P)₂ (3**).** Since phenylacetylene was found to couple across the dinuclear Fe–Rh framework of **1** to give **2**, we explored the possibility of coupling reactions with other triply bonded organic species.²¹ In the case of the nitriles MeCN and PhCN disintegration of the molecular framework of **1** occurs, and several products are formed in relatively low yields (see scheme I). We have successfully isolated and characterized one of the products as the heteronuclear cluster Rh₂Fe(CO)₃(*t*-Bu₂PH)(μ-CO)₂(μ-*t*-Bu₂P)₂ (**3**), which can be isolated from the reaction mixture by crystallization from hexene as black, moderately air-stable crystals. Also formed in low yields in these reactions are [Rh(CO)(*t*-Bu₂PH)]₂(μ-H)(μ-*t*-Bu₂P) (**4**) (5%) and (CO)(*t*-Bu₂PH)Rh(μ-*t*-Bu₂P)Fe(CO)₄ (**5**) (5%), which were identified by ³¹P NMR spectroscopy of the reaction mixtures.

The structure of **3** consists of a closed Rh₂Fe triangle in which the Rh–Rh bond and one Fe–Rh bond are bridged by *t*-Bu₂P[−] units. The remaining Fe–Rh bond is bridged by two μ-CO ligands. One Rh atom bears a single terminal CO group while the other has a *t*-Bu₂PH ligand attached. The Fe atom bears two terminal CO ligands. Clearly a major disintegration of **1** occurs to permit the formation of **3** and the minor products **4** and **5**. It is interesting to note that use of a nitrile (MeCN or PhCN) is required for the formation of **3**. Thus, heating **1** in toluene at 70 °C for 12 h produces only **4** and **5** in low yield. Of related interest is the recent observation by Geoffroy and co-workers of the facile reversible cleavage of the Rh–Co bond in (PET₃)₂(CO)Rh–Co(CO)₄ in acetonitrile solutions.²²

As for **1** and **2** spectroscopic data for **3** are not completely structurally diagnostic although they are in accord

Table IV. Positional Parameters and Estimated Standard Deviations for **3**^a

atom	x	y	z	B, Å ²
Rh(1)	0.5338 (2)	0.0969 (2)	0.7447 (2)	3.40 (6)
Rh(2)	0.3319 (2)	0.0963 (2)	0.7481 (2)	3.75 (7)
Fe(1)	0.4282 (4)	0.2250 (3)	0.7609 (3)	2.5 (1)
P(1)	0.5956 (8)	0.2143 (6)	0.7605 (8)	4.5 (3)
P(2)	0.4293 (8)	−0.0062 (6)	0.7276 (6)	3.6 (2)
P(3)	0.1633 (8)	0.0616 (6)	0.7536 (7)	4.0 (3)
O(1)	0.370 (3)	0.349 (2)	0.645 (2)	8 (1)*
O(2)	0.420 (4)	0.329 (3)	0.887 (3)	14 (2)*
O(3)	0.427 (3)	0.141 (3)	0.919 (2)	11 (2)*
O(4)	0.298 (4)	0.173 (3)	0.596 (2)	13 (2)*
O(5)	0.719 (4)	0.019 (2)	0.734 (7)	13 (4)*
C(1)	0.396 (3)	0.298 (2)	0.690 (2)	4.3 (9)*
C(2)	0.440 (5)	0.284 (4)	0.836 (4)	12 (2)*
C(3)	0.412 (4)	0.152 (3)	0.848 (3)	6 (1)*
C(4)	0.329 (4)	0.179 (3)	0.666 (3)	7 (1)*
C(5)	0.642 (6)	0.064 (5)	0.737 (5)	14 (3)*
C(6)	0.701 (3)	0.240 (3)	0.861 (3)	6 (1)*
C(7)	0.665 (3)	0.204 (3)	0.932 (3)	6 (1)*
C(8)	0.801 (4)	0.225 (3)	0.860 (3)	9 (2)*
C(9)	0.707 (5)	0.320 (4)	0.879 (4)	12 (2)*
C(10)	0.637 (4)	0.251 (3)	0.667 (3)	7 (1)*
C(11)	0.549 (3)	0.230 (3)	0.588 (3)	6 (1)*
C(12)	0.739 (4)	0.211 (3)	0.655 (3)	8 (1)*
C(13)	0.652 (3)	0.344 (3)	0.670 (3)	6 (1)*
C(14)	0.401 (5)	−0.045 (4)	0.610 (4)	10 (2)*
C(15)	0.379 (6)	0.020 (4)	0.561 (4)	13 (2)*
C(16)	0.501 (8)	−0.090 (6)	0.614 (6)	10 (4)*
C(17)	0.302 (6)	−0.101 (5)	0.600 (5)	16 (3)*
C(18)	0.469 (3)	−0.070 (2)	0.844 (3)	5 (1)*
C(19)	0.551 (6)	−0.128 (4)	0.820 (4)	13 (2)*
C(20)	0.362 (6)	−0.128 (5)	0.812 (5)	14 (3)*
C(21)	0.519 (7)	−0.013 (5)	0.910 (6)	9 (3)*
C(22)	0.129 (4)	0.081 (3)	0.859 (3)	7 (1)*
C(23)	0.209 (4)	0.042 (3)	0.925 (3)	8 (1)*
C(24)	0.141 (5)	0.165 (4)	0.877 (4)	11 (2)*
C(25)	0.020 (5)	0.048 (4)	0.851 (4)	11 (2)*
C(26)	0.054 (4)	0.088 (4)	0.668 (4)	9 (2)*
C(27)	0.038 (5)	0.171 (4)	0.649 (4)	10 (2)*
C(28)	0.099 (4)	0.063 (3)	0.581 (3)	8 (1)*
C(29)	−0.054 (6)	0.044 (5)	0.645 (5)	14 (3)*

^a Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

with the X-ray structure (see below). Thus the IR spectrum indicates the presence of the *t*-Bu₂PH ligand ($\nu_{\text{P-H}} = 2300$ (w) cm^{−1}) and terminal and bridging CO ligands ($\nu_{\text{CO}} = 2020$ (w), 1981 (s), 1948 (s), 1792 (m), 1751 (m) cm^{−1}). The ³¹P{¹H} NMR spectrum consists of two multiplets, shifted well downfield (δ 384.73 and 368.42, assigned to the two bridging phosphido groups and an upfield doublet (δ 54.06) assigned to the unique *t*-Bu₂PH group bound to Rh.

X-ray Crystal Structure of **3.** Complex **3** crystallizes in the monoclinic space group *P*2₁/*n* with four molecules in the unit cell. A view of the molecule is shown in Figure 3. Crystallographic data are collected in Table I, and positional parameters are given in Table IV.

A number of other heterotrinary Fe–Rh clusters are known, and the bonding parameters of **3** are similar to those in these related complexes. Thus the Rh–Rh distance (2.683 (4) Å) and Rh–Fe distances (Rh(1)–Fe = 2.735 (6) Å and Rh(2)–Fe = 2.618 (6) Å) may be compared to those found in Fe₂Rh(μ-PPh₂)₃(CO)₆(PR₃)₂²³ (Fe–Rh = 2.690 (1) Å and 2.986 (1) Å) and Fe₂Rh₂(μ-PPh₂)₄(μ-CO)₂(CO)₆²⁴ (Fe–Rh = 2.623 (2) Å and Rh–Rh = 2.723 (2) Å). It is interesting that the phosphide-bridged Fe–Rh(1)

(20) Deviations (Å) from the least-squares plane are as follows: Rh −0.033 (1), C(17) 0.04 (1), C(18) −0.02 (1), C(19), −0.02 (1), C(20) 0.04 (1).
(21) See, for example: Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* 1984, 106, 6815.

(22) Roberts, D. A.; Mercer, W. C.; Zahurak, S. M.; Geoffroy, G. L.; DeBrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* 1982, 104, 910.

(23) Breen, M. J.; Geoffroy, G. L. *Organometallics* 1982, 1, 1437.

(24) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Chem. Soc., Dalton Trans.* 1983, 1607.

bond is longer than the Rh–Rh bond, probably the result of both rhodium atoms having a formal electron count of 16 and therefore being electron deficient. The Fe–Rh (2) bond is shorter than either of the other metal–metal bonds and this is associated with the presence of two bridging carbonyls. The three metals and the three phosphorus atoms are essentially planar,²⁵ and the two bridging carbonyls are located above and below this plane.

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. RhCl(PMe₃)₃,²⁶ [Rh(COD)Cl]₂,²⁷ and *t*-Bu₂PH₂²⁸ were prepared by the literature procedures. 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 (³¹P, 32.384 MHz), Bruker WM-90 (³¹P, 36.43 MHz), Nicolet NT-200 (¹H and ³¹P). IR spectra were as Nujol mulls (KBr plates) or in solution (matched KBr or CaF₂ cells). NMR spectra were recorded in C₆D₆ at ambient temperature (unless otherwise stated) and are referenced to Me₄Si (δ 0.0, ¹H) and 85% H₃PO₄(aq) (δ 0.0, ³¹P, downfield is positive).

Preparation of Bis(di-*tert*-butylphosphine)tricarbonyliron(0), Fe(CO)₃(*t*-Bu₂PH)₂. Iron pentacarbonyl (7.15 g, 36.5 mmol) was added to a solution of di-*tert*-butylphosphine (10.66 g, 73.0 mmol) in hexane (60 mL) in a quartz Schlenk flask. The solution was irradiated (20 h) with light from a 550-W Hanovia mercury vapor lamp at room temperature. The solution was then filtered and cooled (–20 °C). Yellow prisms formed after 3 h. They were collected and dried under vacuum: yield 7.1 g (45%); mp 163–164 °C dec. NMR: ¹H (C₆D₆), δ 4.82 (d, ¹J_{P–H} = 332 Hz, 1 H, PH), 1.21 (d, ¹J_{P–H} = 15 Hz, 18 H, *t*-Bu₂P); ³¹P{¹H} (C₆D₆) δ 85.46 (s), in the ³¹P spectrum (proton coupled), a broad doublet is observed (¹J_{P–H} = 345.98 Hz). IR (hexane solution, KBr cell): 2302 (m), 1967 (m), 1980 (s), 1870 (s) cm^{–1}. Microanal. Calcd for C₁₉H₃₈FeO₃P₂: C, 52.80; H, 8.80; P, 14.36. Found: C, 52.51; H, 9.01; P, 14.18.

Preparation of (CO)₂(*t*-Bu₂PH)Fe(μ-CO)(μ-*t*-Bu₂P)Rh(COD) (1) (COD = 1,5-Cyclooctadiene). A solution of *n*-BuLi (0.37 mL of 2.41 M in hexane, 0.89 mmol) was added to a solution of Fe(CO)₃(*t*-Bu₂PH)₂ (0.38 g, 0.89 mmol) in THF (40 mL) at –78 °C. The solution was allowed to warm to 10 °C and then recooled to –78 °C. It was then added to a solution of [Rh(COD)Cl]₂ (0.22 g, 0.45 mmol) in THF (40 mL) at –78 °C. The yellow-brown solution was allowed to warm to room temperature (2 h), and then volatile materials were removed under vacuum. The residue was extracted with hexane (2 × 25 mL) and the solution filtered. The volume of the filtrate was reduced to ca. 20 mL under vacuum and cooled (–20 °C). After 24 h, yellow crystals of 1 were obtained. They were collected and dried under vacuum: yield 0.19 g (30%); mp 124–126 °C dec; ¹H NMR δ 5.52, 4.97 (br s, 4 H, COD), 4.40 (d, ¹J_{P–H} = 331 Hz, 1 H, *t*-Bu₂PH), 2.03 (br s, 8 H, COD), 1.53 (d, ³J_{P–H} = 12 Hz, 18 H, *t*-Bu₂P), 1.24 (d, ³J_{P–H} = 14 Hz, 18 H, *t*-Bu₂P); ³¹P{¹H} NMR δ 186.59 (dd, ¹J_{Rh–P} = 137.13 Hz, ²J_{P–P} = 24.05 Hz, μ-*t*-Bu₂P), 101.54 (d, ²J_{P–P} = 23.49 Hz, *t*-Bu₂PH). In the ³¹P NMR, the signal at δ 101.54 becomes a broad doublet (¹J_{P–H} = 368.86 Hz). IR: (hexane solution): 2300 (w), 1938 (s), 1877 (s), 1845 (s), 1603 (w) cm^{–1}. Microanal. Calcd for C₂₇H₄₆FeO₃P₂Rh: C, 50.72; H, 7.25; P, 9.69. Found: C, 50.91; H, 7.31; P, 9.47.

Preparation of (CO)₂Fe(μ-*t*-Bu₂P)(μ-η⁴-C₄H₂Ph₂)Rh(HCCPh) (2). Phenylacetylene (1.97 mL of a 0.828 M solution in toluene, 1.63 mmol) was added to a solution of 1 (0.48 g, 0.65

mmol) in THF (50 mL) and the mixture heated under reflux (2 h) during which time the color changed from yellow-brown to red-brown. The mixture was allowed to cool to room temperature, and volatile materials were removed under vacuum. The residue was extracted into hexane (2 × 30 mL) and the solution filtered and reduced in volume (ca. 15 mL). Cooling (–20 °C) for 12 h gave dark red crystals of 2. They were collected and dried under vacuum: yield 0.30 g (70%); mp 153–155 °C dec. NMR ¹H (C₆D₆), δ 9.39 (dd, 1 H, ¹J_{Rh–H} = 36.0 Hz, ²J_{P–H} = 3.1 Hz, PhC ≡ CH), 7.91 (m, 2 H), 7.2 (m, 13 H, phenyl groups), 5.83 (d, 2 H, ¹J_{P–H} = 3.0 Hz, η⁴-C₄H₂Ph₂), 1.00, (d, 18 H, ¹J_{P–H} = 13.0 Hz, *t*-Bu₂P), ³¹P{¹H} (in THF), δ 421.51 (d, ¹J_{Rh–P} = 82.8 Hz). IR (KBr disk): 2900 (br), 1981 (s), 1925 (s), 1700 (w), 1480 (m), 1430 (br), 1390 (br), 1365 (br), 1160 (m), 1020 (br), 930 (br), 800 (w), 758 (s), 690 (s), 600 (br w) cm^{–1}. Microanal. Calcd for C₃₄H₃₆FeO₂PRh: C, 61.28; H, 5.45. Found: C, 61.17; H, 5.37.

Preparation of Rh₂Fe(CO)₃(*t*-Bu₂PH)(μ-CO)₂(μ-*t*-Bu₂P)₂ (3). A solution of 1 (0.53 g, 0.72 mmol) in acetonitrile (80 mL) was heated under reflux (12 h) during which time the color changed to dark green. Volatile materials were removed under vacuum, and the residue was extracted into hexane (3 × 40 mL). The resulting dark green solution was filtered and the volume reduced (ca. 50 mL) under vacuum. Cooling (–20 °C, 12 h) gave dark green, almost black, crystals of 3 that were collected and dried under vacuum. The supernatant liquid contains small amounts of [Rh(CO)(*t*-Bu₂PH)]₂(μ-H)(μ-*t*-Bu₂P) (4)¹² (5%) and (CO)(*t*-Bu₂PH)Rh(μ-*t*-Bu₂P)Fe(CO)₄ (5)¹³ (5%) by ³¹P NMR. 3: yield 0.13 g (22%); mp 200–203 °C dec; IR (Nujol mull, KBr plates) 2300 (w), 2020 (w), 1981 (s), 1948 (s), 1792 (m), 1751 (m), 1357 (m), 1168 (w), 1018 (w), 835 (w), 800 (w) cm^{–1}; ¹H NMR (25 °C, in C₆D₆) δ 4.96 (dd, ¹J_{P–H} = 315 Hz, ²J_{Rh–H} = 9 Hz, *t*-Bu₂PH), 1.40 (d, 18 H, ²J_{P–H} = 13.8 Hz, *t*-Bu₂P), 1.35 (d, 18 H, ²J_{P–H} = 13.2 Hz, *t*-Bu₂P), 1.23 (d, 18 H, ²J_{P–H} = 15.0 Hz, *t*-Bu₂P); ³¹P{¹H} NMR (at 146.198 MHz in THF, 25 °C) δ 384.73 (ddd, ¹J_{Rh–P} = 155.53 Hz, ¹J_{Rh–P} = 177.98 Hz, ¹J_{P–P} = 103.21 Hz, μ-*t*-Bu₂P(Rh–Rh)), 368.42 (dd, ¹J_{Rh–P} = 175.62 Hz, ²J_{P–P} = 102.71 Hz, μ-*t*-Bu₂P(Fe–Rh)), 54.06 (d, ¹J_{Rh–P} = 207.44 Hz, *t*-Bu₂PH); in the proton-decoupled spectrum, a broad doublet is observed for the latter resonance (¹J_{P–H} = 306.8 Hz). Microanal. Calcd for C₂₉H₅₅FeO₃P₃PO₃Rh₂: C, 41.55; H, 6.61. Found: C, 41.39; H, 6.52.

X-ray Experimental Section

General Data. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo K α radiation. Data were collected by the $\omega/2\theta$ scan technique at 23 ± 2 °C. Details of the standard data collection methods were similar to those outlined in ref 29. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package "SDP PLUS".³⁰

Crystals of 1, 2, and 3 were grown from hexane solution at –20 °C and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by careful centering 25 reflections having 2θ values between 22.0° and 24.0° for 1, 22.0° and 26.0° for 2, and 22.0° and 24.0° for 3. Details of crystal data parameters and other relevant information are collected in Table I. For all three structures the data were corrected for Lorentz and polarization effects and also for absorption by using an empirical ψ scan method (program EAC). Anisotropic decay corrections were also applied. All three structures were solved by direct methods (MULTAN)³¹ followed by successive cycles of difference Fourier maps followed by least-squares refinement. A non-Poisson contribution weighting scheme with an experimental instability factor, P , was used in the final stages of each refinement ($P = 0.05$ (1); 0.05 (2), 0.07 (3)).³²

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(25) Deviations (Å) from the least squares plane are as follows: Rh(1) –0.038 (3), Rh(2) 0.021 (3), Fe 0.067 (4), P(1) –0.05 (1), P(2) 0.05 (1), P(3) –0.05 (1).

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For 1: systematic absences indicated a choice of Cc or $C2/c$ space groups (hkl , $h + k = 2n + 1$; $h0l$, $l = 2n + 1$). Cc was chosen on the basis of successful refinement. Data were collected in the $+h, +k, \pm l$ quadrant. Due to the large number of atoms in the asymmetric unit (two independent molecules) only O(1) and the Rh, Fe, and P atoms were refined anisotropically. The carbon atoms were refined isotropically, and the hydrogen atoms were not located. The maximum peak in the final difference Fourier map had a height of $0.83 \text{ e } \text{\AA}^{-3}$ and was located 0.78 \AA from Rh (1).

For 2: the structure was successfully solved in $P\bar{1}$. Data were collected in the $\pm h, \pm k, \pm l$ hemisphere. All 36 hydrogen atoms were either located or placed in idealized positions and refined with isotropic thermal parameters. All other non-hydrogen atoms were refined anisotropically. The largest peak in the final difference Fourier map was $0.79 \text{ e } \text{\AA}^{-3}$ and was not chemically significant.

For 3: the monoclinic space group $P2_1/n$ (No. 1014) was uniquely determined by systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). Data were collected in the $+h, +k, \pm l$ quadrant. Due to a combination of poor crystal quality and large number of atoms in the structure only the Rh, Fe, and P atoms were refined anisotropically. The O and C atoms were refined iso-

tropically, and the H atoms were not located. The highest peak in the final difference Fourier map was $1.00 \text{ e } \text{\AA}^{-3}$ and was located 1.26 \AA from C(16). Scattering factors were taken from ref 33. Supplementary material is available.³⁴

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Supplementary Material Available: Tables of bond lengths and angles and thermal parameters for 1-3 and H-atom positions and a complete ORTEP drawing for 2 (19 pages); listings of observed and calculated structure factors for 1-3 (81 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Cobalt Dimers of the Type $\text{Co}_2(\text{CO})_3(\text{L-L})_2\text{I}_2$. Crystal Structure of $[\text{Co}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-I})(\text{Me}_2\text{PCH}_2\text{PMe}_2)(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]\text{I}$

Edward C. Lisic and Brian E. Hanson*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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The cobalt dimers $\text{Co}_2(\text{CO})_3(\text{L-L})_2$, $\text{L-L} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) and $\text{Me}_2\text{PCH}_2\text{PMe}_2$ (dmpm), are oxidized by iodine in the presence of bis(diphenylphosphino)methane to yield the ionic complexes $[\text{Co}_2(\text{CO})_3(\text{L-L})(\text{L-L})\text{I}]\text{I}$. In a similar fashion, $\text{Co}_2(\text{CO})_6(\text{dppm})$ reacts with elemental sulfur to yield $\text{Co}_2(\text{CO})_3(\text{dppm})_2\text{S}$. The complex $[\text{Co}_2(\text{CO})_3(\text{dmpm})(\text{dppm})\text{I}]\text{I}$ crystallizes in the $P2_1/n$ space group with dimensions $a = 10.956$ (3) \AA , $b = 15.881$ (6) \AA , $c = 21.393$ (5) \AA , and $\beta = 97.20$ (2) $^\circ$ with four molecules per unit cell. Of a total of 4796 unique reflections collected, 2965 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used to refine the structure. The structure converged at $R = 0.051$ and $R_w = 0.065$. The geometry around the cobalt atoms is very similar to that reported for $[\text{Rh}_2(\text{CO})_3(\text{dppm})_2\text{Cl}]^+$, $[\text{Rh}_2(\text{CO})_3(\text{dppm})_2\text{H}]^+$, and $\text{Ir}_2(\text{CO})_3(\text{dppm})_2\text{S}$. The molecule may be described as an A-frame structure with a neutral ligand, CO, occupying the additional bridging site. The observed Co-Co bond distance is 2.555 (2) \AA consistent with a single bond between the metal atoms. Reduction of the ionic complex with zinc yields a pyrophoric green solid that analyzes approximately for $\text{Co}_2(\text{CO})_3(\text{dppm})_2$.

Transition-metal dimers linked by two or more bridging diphosphine ligands represent a large and important class of molecules. These include multiply bonded dimers such as $\text{Re}_2\text{Cl}_4(\text{dppm})_2^1$ and $\text{Mo}_2\text{Cl}_4(\text{dppm})_2^2$ dimers containing a single bond between metals such as $\text{Co}_2(\text{CO})_6(\text{dppm})^3$, $\text{Fe}_2(\text{CO})_7(\text{dppm})^4$ "A-frame" dimers containing the $\text{M}_2(\mu\text{-X})\text{L}_2$ moiety (structures I and II below) such as $\text{Rh}(\text{CO})_2(\text{dppm})_2\text{S}^5$, $[\text{Rh}_2(\text{CO})_2(\text{dppm})_2\text{Cl}]^+$,⁶ and $[\text{Pd}_2$ -

$(\text{dppm})_2\text{Me}_2\text{Cl}]^+$,⁷ and dimers of gold and silver with and without a formal metal-metal bond.⁸

Bis(diphenylphosphino)methane has played an important role in the development of this chemistry. It is readily available commercially or by a simple synthetic procedure⁹ and is air-stable; thus it is an ideal ligand for exploratory syntheses. Many other bridging bidentate ligands have been used to advantage in investigating the chemistry of metal dimers including 2-hydroxypyridine derivatives,^{2b,10} carboxylates,^{2b,11} and phosphorus ylides.¹² However, none

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