Reactions of Low-Valent Dirhodium Complexes with Alkynes. Synthesis and Reactivity of Alkyne and Vinylidene Complexes

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Treatment of the low-valent binuclear complex $Rh_2(CO)_3(dppm)_2$ (1, dppm = bis(diphenylphosphino)methane) with excess phenylacetylene in benzene yields the A-frame bridging vinylidene complex $Rh_2(CO)_2(dppm)_2(C=CHPh)$ (2), while treatment of 1 with a stoichiometric amount of phenylacetylene in refluxing acetone produces the non-A-frame bridging acetylene complex $Rh_2(CO)_2(dppm)_2(PhC\equiv CH)$ (3). The bridging diphenylacetylene complex $Rh_2(CO)_2(dppm)_2(PhC\equiv CPh)$ (4) has also been prepared. At 80 °C, solutions of 2 catalyze the disproportionation of $PhC\equiv CH$ to 1,4-diphenylbutadiyne and styrene. Compound 2 also catalyzes the hydrogenation of $PhC\equiv CH$ to styrene. Deuterium labeling studies indicate that the vinylidene species is involved in the catalysis, resulting primarily in a novel "geminal" hydrogenation of $PhC\equiv CH$ to $PhCH=CD_2$. The molecular structures of 2 and 4 have been determined by single-crystal X-ray diffraction. (2: $P\bar{1}$, a = 14.684 (4) Å, b = 14.818 (4) Å, c = 13.527 (2) Å, α = 102.56 (2)°, β = 101.56 (2)°, γ = 73.13 (2)°, Z = 2, R = 0.048, R_w = 0.069. 4: $P2_1/c$, a = 12.602 (2) Å, b = 21.093 (2) Å, c = 27.119 (5) Å, β = 90.77 (1)°, Z = 4, R = 0.051, R_w = 0.058.) The A-frame structure of 2 shows distorted square-planar coordination including trans P donors at each Rh and a Rh···Rh separation of 3.011 (1) Å. The structure of 4 reveals that the PhCCPh moiety bridges the two Rh atoms in the perpendicular or μ,η^2 mode with each Rh possessing a distorted tetrahedral geometry. The Rh–Rh bond length in 4 is 2.644 (1) Å.

Introduction

Terminal alkynes react with transition-metal complexes by several different routes. The organometallic products of such reactions include π-complexes,[2,3] σ-bonded acetylide complexes,[4–9] and terminal or bridging vinylidene complexes.[10–15] In large part, this variety stems from the bifunctionality offered by terminal alkynes, with metal–alkyne interactions occurring at either the C≡C bond or the acetylenic C–H bond. Subsequent reaction with additional alkyne can also reflect the dual modes of reactivity, leading to a variety of organic products including new alkynes,[16] linear dimers,[17–23] cyclic oligomers,[24–27] and polyacetylenes.[28,29]

We have recently shown that this bifunctionality plays a major role in the reactions of the low-valent binuclear complex $Rh_2(CO)_3(dppm)_2$ (1, dppm = bis(diphenylphosphino)methane) with terminal alkynes.[30] In particular, the reaction of 1 with phenylacetylene in benzene produces a kinetic distribution of the A-frame vinylidene complex $Rh_2(CO)_2(dppm)_2(C=CHPh)$ (2) and the bridging acetylene complex $Rh_2(CO)_2(dppm)_2(PhC\equiv CH)$ (3), the former being the thermodynamically preferred isomer. On the basis of kinetic studies and the selective inhibition of the formation of 3 by carbon monoxide, it was proposed that 2 forms by an associative process, while 3 is produced only through alkyne coordination to an intermediate Rh(0) dimer, $Rh_2(CO)_2(dppm)_2$ (A), generated by reversible CO dissociation from 1 (Scheme I). Thus in this system, the reactions of the alkyne triple bond and the acetylenic C–H bond are competitive, allowing the isolation of isomeric products arising from fundamentally different interactions at the metal centers.

In the present report we describe in detail the preparation and characterization of these and related complexes and their role in novel catalytic alkyne hydrogenation and disproportionation reactions.

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Scheme I
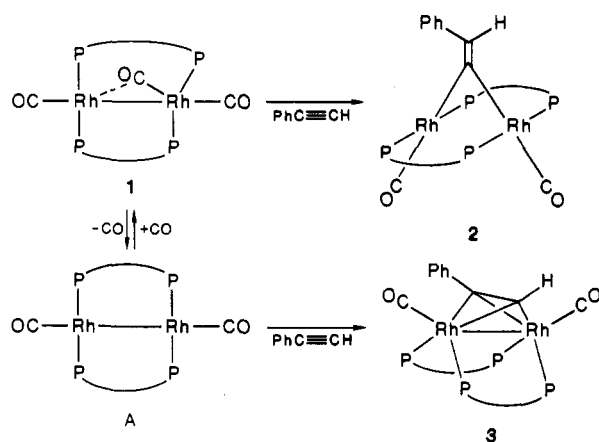
Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dry nitrogen by using a Vacuum Atmosphere's glovebox and/or Schlenk techniques. Toluene, benzene, and diethyl ether were distilled from sodium/benzophenone. Acetone was dried over 4A molecular sieves and freeze–pump–thawed. Diphenylacetylene and 1,4-diphenyl-butadiyne (Aldrich) were used as received. (*E*)-1,4-Diphenyl-butenyne was prepared from phenylacetylene and RhCl(PPh$_3$)$_3$.[17] Phenylacetylene was twice distilled and freeze–pump–thawed. Rh$_2$(CO)$_3$(dppm)$_2$[31a] and Rh$_2$(CO)$_2$(dppm)$_2$(H)$_2$[31b] were prepared as described previously. Hydrogen, deuterium, and carbon monoxide (Matheson) were used as received. Elemental analyses were performed by MicAnal Co., Tucson, AZ.

^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in benzene-d_6 on a Brucker WH-400 or a GE QE-300 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 467 infrared spectrophotometer.

Procedures. Rh$_2$(CO)$_2$(dppm)$_2$(μ-C=CHPh) (2). A solution of 1 (180 mg, 0.17 mmol) and PhC≡CH (400 μL, 3.65 mmol) in 10 mL of toluene was stirred at 25 °C for 6 h, at which time the solvent volume was reduced to 3 mL and 20 mL of diethyl ether was added. Filtration at −20 °C yielded 80 mg (42%) of dark purple crystals. A second crop of 46 mg (24%) was obtained in a similar manner. ^{1}H NMR (C$_6$D$_6$; –CH$_2$– region): δ 3.85 (m, 2 H), 2.25 (m, 2 H). ^{31}P{^{1}H} NMR: δ 31.22 (m, J_{Rh-P} = 167 Hz). IR (Nujol): ν(CO) 1934 (s), 1910 (s) cm^{-1}. Satisfactory elemental analysis of 2 could not be obtained; percentage carbon found was always low and was varied widely even in duplicate analyses on the same preparation. Typical Anal. Calcd for C$_{60}$H$_{50}$O$_2$P$_4$Rh$_2$: C, 63.62; H, 4.45. Found: C, 62.07; H, 4.17. The formulation of 2 was confirmed by a single-crystal X-ray study (vide infra).

Rh$_2$(CO)$_2$(dppm)$_2$(μ,η^2-PhC=CH) (3). A solution of 1 (180 mg, 0.17 mmol) and PhC≡CH (20 μL, 0.18 mmol) in 10 mL of acetone was refluxed for 5 h and allowed to cool to 25 °C. The removal of solvent yielded a yellow solid that was washed with a total of 25 mL of diethyl ether and dried in vacuo, giving 100 mg of product (52%). Anal. Calcd for C$_{60}$H$_{50}$O$_2$P$_4$Rh$_2$: C, 63.62; H, 4.45. Found: C, 63.87; H, 4.38. ^{1}H NMR (C$_6$D$_6$): δ 6.02 (1 H, t, $^2J_{Rh-H}$ = 6.8 Hz, PhCC–H), 4.51 (1 H, q, $J_{P-H} \approx J_{H-H}$ = 11 Hz, CH$_2$), 3.76 (1 H, q, $J_{P-H} \approx J_{H-H}$ = 11 Hz, CH$_2$), 3.53 (1 H, q, $J_{P-H} \approx J_{H-H}$ = 11 Hz, CH$_2$), 3.33 (1 H, q, $J_{P-H} \approx J_{H-H}$ = 11 Hz, CH$_2$). ^{31}P{^{1}H} NMR: δ 22.39 (m), 19.65 (m). IR (Nujol): ν(CO) 1938 (sh), 1923 (s) cm^{-1}; ν(C≡C): 1425 (m) cm^{-1}. High resolution mass spectrum: calcd for [M − 1]$^+$ 1131.079; found 1131.075.

Rh$_2$(CO)$_2$(dppm)$_2$(μ,η^2-PhC≡CPh) (4). A solution of 1 (100 mg, 0.10 mmol) and PhCCPh (20 mg, 0.11 mmol) in 5 mL of benzene was refluxed for 2 days. Cooling of the solution was followed by removal of the solvent under vacuum. Recrystallization from heptane yielded 80 mg (71%) of flaky gold crystals.

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Table I. Summary of Crystal Data and Data Collection and Refinement Parameters[a]

	2	4
formula	Rh$_2$P$_4$O$_2$C$_{60}$H$_{50}$	Rh$_2$P$_4$O$_2$C$_{84}$H$_{72}$
fw	1132.77	1443.22
space group	P1̄	P2$_1$/c
a, A	14.684 (4)	12.602 (2)
b, A	14.818 (4)	21.093 (2)
c, A	13.527 (2)	27.119 (5)
α, deg	102.56 (2)	90.00
β, deg	101.56 (2)	90.77 (1)
γ, deg	73.13 (2)	90.00
V, A^3	2719	7208
Z	2	4
d_{calcd}, g/cm^3	1.38	1.33
cryst size, mm	0.3 × 0.3 × 0.2	0.5 × 0.3 × 0.3
radiatn (Mo Kα), Å	0.710 73	0.710 73
scan type	ω–2θ	ω–2θ
scan width, deg	0.7 + 0.35 tan θ	0.7 + 0.35 tan θ
scan rate, deg/min	1.2–20	1.2–20
2θ range, deg	4 < 2θ < 44	4 < 2θ < 40
octants collected	+h,±k,±l	+h,+k,±l
no. of unique data collected	7082	6690
no. of obsd data	4562	4191
absorptn coeff, cm^{-1}	7.49	5.82
data omissn	I > 3σ	I > 2σ
no. of parameters varied	631	529
data/parameter	7.2	7.9
R	0.048	0.051
R_w	0.069	0.058
goodness of fit	1.93	1.51

^{a} Calculations were carried out on the Molecular Structure Corp. Texray 230 computer system using the Enraf-Nonius CAD4 and SDP-Plus programs. For a description of the crystallographic computing package see: Frenz, B. A. In *Computing in Crystallography*; Shenk, H., Olthof-Hazekamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. See also: *CAD4 Operations Manual*; Enraf-Nonius: Delft, Holland, 1982; and *Structure Determination Package–User's Guide*; B. A. Frenz and Associates: College Station, TX, and Enraf-Nonius: Delft, Holland, 1982. The intensity data were not corrected for absorption. The function minimized in the least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)^2$. Anomalous dispersion was included in the calculated structure factors. The residuals are defined as $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The goodness of fit or the error in an observation of unit weight is defined as $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variables.

^{1}H NMR (C$_6$D$_6$): δ 3.75 (m, 2 H), 3.58 (m, 2 H). ^{31}P{^{1}H} NMR: δ 21.35 (m). IR (Nujol): ν(CO) 1941, 1926 cm^{-1}; ν(C≡C) 1425 (m) cm^{-1}. Satisfactory elemental analysis of 4 could not be obtained; percentage carbon found was always low and was varied widely even in duplicate analyses on a single preparation. Typical Anal. Calcd for C$_{66}$H$_{54}$O$_2$P$_4$Rh$_2$: C, 65.58; H, 4.50. Found: C, 64.49; H, 4.69. The formulation of 4 was confirmed by a single-crystal X-ray structural study (vide infra).

Reaction of 2 with ^{13}CO. Compound 2 (5 mg) in toluene-d_8 was sealed in a NMR tube under 200 torr of 99% ^{13}CO. ^{1}H NMR (−CH$_2$– region): (a) 28.5 °C, δ 3.62, 2.195; (b) −36 °C, δ 3.40, 2.00. ^{13}C NMR (CO region, −36 °C): δ 217 (br), 210 (d of t, $^1J_{Rh-C}$ = 66, $^2J_{P-C}$ = 15 Hz), 206 (d of t, $^1J_{Rh-C}$ = 66, $^2J_{P-C}$ = 15 Hz), 184 (s, ^{13}CO).

Isomerization of 3 to 2. Compound 3 (5 mg) in benzene-d_6 was sealed in a NMR tube under nitrogen and heated to 80 °C. Conversion to 2 was monitored by ^{1}H NMR spectroscopy over a period of days.

Catalytic Disproportionation of PhC≡CH. In a typical run, compound 2 (5 mg, 4 μmol) and PhC≡CH (50 μL, 0.456 mmol) in 0.5 mL of benzene-d_6 were sealed under nitrogen and heated to 80 °C. The reaction was monitored by ^{1}H NMR spectroscopy for several days, then the tube was opened, ca. 5 mg Cr(acac)$_3$ was added, and ^{13}C NMR spectra were measured. Finally, the

Table II. Refined Positional and Isotropic Thermal Parameters and Their Estimated Standard Deviations for
Rh$_2$(PhCCPh)(CO)$_2$(dppm)$_2$ (4)^a

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Rh1	0.56287 (7)	0.17066 (4)	0.60818 (3)	2.73 (2)	C39	1.011 (1)	0.1258 (6)	0.5391 (5)	6.0 (3)*
Rh2	0.70542 (7)	0.25731 (4)	0.63312 (3)	2.89 (2)	C40	1.061 (1)	0.1435 (6)	0.4975 (4)	5.6 (3)*
P1	0.6089 (2)	0.1630 (1)	0.52461 (9)	2.79 (6)	C41	1.0301 (9)	0.1963 (6)	0.4732 (4)	5.2 (3)*
P2	0.7794 (2)	0.2610 (1)	0.5543 (1)	2.96 (6)	C42	0.9470 (8)	0.2332 (5)	0.4898 (4)	4.0 (2)*
P3	0.6308 (2)	0.0935 (1)	0.6621 (1)	3.29 (7)	C43	0.7259 (8)	0.0310 (5)	0.6485 (4)	3.2 (2)*
P4	0.7921 (2)	0.1956 (1)	0.6940 (1)	3.33 (7)	C44	0.7854 (9)	0.0340 (5)	0.6065 (4)	4.2 (3)*
O1	0.3327 (6)	0.1333 (4)	0.6010 (3)	6.5 (2)	C45	0.8635 (9)	−0.0110 (6)	0.5966 (4)	5.2 (3)*
O2	0.7544 (7)	0.3893 (4)	0.6689 (3)	6.7 (2)	C46	0.881 (1)	−0.0601 (6)	0.6311 (4)	5.5 (3)*
C1	0.4218 (8)	0.1434 (5)	0.6029 (4)	3.9 (3)	C47	0.8220 (9)	−0.0634 (6)	0.6720 (4)	5.3 (3)*
C2	0.7410 (8)	0.3393 (5)	0.6553 (4)	3.9 (3)	C48	0.7443 (9)	−0.0197 (5)	0.6816 (4)	4.3 (3)*
C3	0.5492 (8)	0.2702 (4)	0.6124 (3)	2.9 (2)	C49	0.5277 (8)	0.0469 (5)	0.6915 (4)	3.6 (2)*
C4	0.5498 (7)	0.2444 (5)	0.6571 (3)	3.0 (2)	C50	0.4632 (9)	0.0115 (5)	0.6614 (4)	4.7 (3)*
C5	0.6791 (8)	0.2366 (5)	0.5073 (3)	3.0 (2)	C51	0.379 (1)	−0.0240 (6)	0.6794 (5)	6.4 (3)*
C6	0.7002 (8)	0.1333 (5)	0.7154 (4)	3.8 (3)	C52	0.363 (1)	−0.0242 (6)	0.7294 (5)	6.2 (3)*
C7	0.4826 (8)	0.3182 (5)	0.5885 (4)	3.8 (2)*	C53	0.425 (1)	0.0094 (6)	0.7600 (5)	6.7 (3)*
C8	0.372 (1)	0.3132 (6)	0.5904 (5)	5.8 (3)*	C54	0.509 (1)	0.0454 (6)	0.7417 (4)	5.4 (3)*
C9	0.310 (1)	0.3582 (7)	0.5643 (5)	8.0 (4)*	C55	0.8151 (8)	0.2358 (5)	0.7537 (4)	3.9 (2)*
C10	0.356 (1)	0.4035 (7)	0.5393 (5)	8.2 (4)*	C56	0.7435 (9)	0.2795 (6)	0.7694 (4)	5.1 (3)*
C11	0.461 (1)	0.4130 (7)	0.5381 (5)	7.6 (4)*	C57	0.755 (1)	0.3114 (6)	0.8156 (5)	6.7 (3)*
C12	0.5256 (9)	0.3680 (6)	0.5631 (4)	5.0 (3)*	C58	0.845 (1)	0.2995 (8)	0.8414 (6)	9.1 (4)*
C13	0.4908 (8)	0.2576 (5)	0.7034 (4)	3.5 (2)*	C59	0.920 (1)	0.2594 (8)	0.8283 (6)	10.0 (5)*
C14	0.4897 (9)	0.3193 (6)	0.7222 (4)	5.5 (3)*	C60	0.906 (1)	0.2254 (7)	0.7812 (5)	7.5 (4)*
C15	0.437 (1)	0.3322 (7)	0.7658 (5)	7.6 (4)*	C61	0.9204 (8)	0.1560 (5)	0.6873 (4)	3.3 (2)*
C16	0.384 (1)	0.2859 (8)	0.7874 (6)	9.3 (5)*	C62	1.0001 (9)	0.1930 (5)	0.6684 (4)	4.9 (3)*
C17	0.379 (1)	0.2258 (8)	0.7703 (6)	9.5 (5)*	C63	1.104 (1)	0.1697 (6)	0.6646 (5)	6.0 (3)*
C18	0.4343 (9)	0.2112 (6)	0.7262 (4)	5.4 (3)*	C64	1.126 (1)	0.1094 (6)	0.6784 (5)	6.4 (3)*
C19	0.6809 (7)	0.0979 (4)	0.4963 (3)	2.7 (2)*	C65	1.048 (1)	0.0721 (6)	0.6960 (5)	6.6 (3)*
C20	0.7626 (8)	0.1040 (5)	0.4643 (4)	3.9 (2)*	C66	0.9454 (9)	0.0961 (5)	0.7016 (4)	4.9 (3)*
C21	0.8053 (9)	0.0509 (5)	0.4409 (4)	4.4 (3)*	C101	0.332 (1)	0.647 (1)	0.6419 (5)	12.4 (6)
C22	0.7656 (9)	−0.0075 (5)	0.4505 (4)	4.7 (3)*	C102	0.333 (2)	0.582 (1)	0.6440 (7)	15.9 (7)
C23	0.6860 (9)	−0.0156 (5)	0.4825 (4)	4.6 (3)*	C103	0.420 (2)	0.553 (1)	0.6212 (6)	14.2 (7)
C24	0.6431 (8)	0.0374 (5)	0.5062 (4)	3.3 (2)*	C104	0.497 (2)	0.586 (1)	0.5988 (8)	15.5 (8)
C25	0.4963 (7)	0.1667 (4)	0.4813 (3)	2.7 (2)*	C105	0.497 (2)	0.651 (1)	0.5966 (7)	15.0 (8)
C26	0.4860 (8)	0.1295 (5)	0.4394 (4)	3.9 (2)*	C106	0.414 (2)	0.6842 (9)	0.6205 (6)	12.7 (6)
C27	0.3945 (9)	0.1337 (6)	0.4103 (4)	5.4 (3)*	C107	0.987 (1)	0.6264 (9)	0.2829 (6)	11.5 (6)
C28	0.3159 (9)	0.1743 (6)	0.4210 (4)	5.2 (3)*	C108	0.986 (2)	0.567 (1)	0.3049 (8)	13.7 (7)
C29	0.3246 (9)	0.2124 (6)	0.4618 (5)	5.6 (3)*	C109	0.892 (2)	0.545 (1)	0.3242 (9)	16.8 (9)
C30	0.4137 (9)	0.2075 (5)	0.4919 (4)	4.3 (3)*	C110	0.811 (2)	0.584 (2)	0.3241 (8)	20 (1)
C31	0.8141 (8)	0.3409 (5)	0.5340 (4)	3.3 (2)*	C111	0.798 (2)	0.634 (1)	0.3020 (6)	16.2 (8)
C32	0.8910 (9)	0.3718 (6)	0.5618 (4)	5.1 (3)*	C112	0.892 (2)	0.6621 (8)	0.2822 (7)	13.8 (6)
C33	0.918 (1)	0.4350 (6)	0.5511 (5)	6.3 (3)*	C113	0.184 (2)	0.370 (1)	0.4123 (7)	16.2 (8)
C34	0.869 (1)	0.4630 (6)	0.5125 (5)	6.7 (3)*	C114	0.090 (2)	0.3712 (9)	0.4291 (7)	14.5 (7)
C35	0.797 (1)	0.4345 (6)	0.4830 (4)	5.6 (3)*	C115	0.015 (2)	0.389 (1)	0.3878 (9)	16.2 (8)
C36	0.7686 (9)	0.3720 (5)	0.4952 (4)	4.5 (3)*	C116	0.070 (2)	0.398 (1)	0.3369 (8)	19.8 (9)
C37	0.8948 (7)	0.2168 (4)	0.5320 (3)	2.7 (2)*	C117	0.160 (2)	0.392 (2)	0.334 (1)	30 (1)
C38	0.9263 (8)	0.1630 (5)	0.5573 (4)	4.1 (2)*	C118	0.213 (1)	0.381 (2)	0.3685 (9)	27 (1)

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

mixture was analyzed by gas chromatography. Products described in the text were confirmed by comparison with authentic samples.[32]

Catalytic Hydrogenation of PhC≡CH. Compound 2 (5 mg, 4 μmol) and PhC≡CH (40 μL, 0.365 mmol) in 0.5 mL of benzene-d_6 were sealed under hydrogen (1.6 atm at 25 °C) and heated to 80 °C. The reaction was monitored by ^{1}H NMR. The reaction under deuterium was carried out similarly, except with a deuterium pressure of 0.55 atm at 25 °C. In this case the tube was opened and mass spectral data were obtained.

Structure Determinations. Crystal Structure Determination of Rh$_2$(CO)$_2$(dppm)$_2$(μ,η^2-PhC≡CPh)·3C$_6$H$_6$ (4). A crystal measuring 0.5 × 0.3 × 0.3 mm, grown by slow evaporation of a benzene solution, was found to be monoclinic with cell dimensions a = 12.602 (2) Å, b = 21.093 (2) Å, c = 27.119 (5) Å, and β = 90.77 (1)°, space group P2$_1$/c. Data were collected as

summarized in Table I. Direct methods (Multan) were employed to locate the two rhodium and four phosphorus atoms. Subsequent cycles of least-squares refinements and difference Fourier maps located the remaining non-hydrogen atoms including three molecules of benzene of crystallization. In the final model all non-hydrogen atoms were described with anisotropic thermal parameters except for the dppm phenyl carbons. Hydrogen atoms were placed at calculated positions around the phenyl rings. Table II contains the final refined positional and isotropic thermal parameters for the structure. Supplementary material contains the final anisotropic thermal parameters, the calculated hydrogen positional parameters, complete tabulations of bond distances and angles, and a listing of observed and calculated structure factor amplitudes for the structure. See paragraph regarding supplementary material at the end of the paper.

Crystal Structure Determination of Rh$_2$(CO)$_2$(dppm)$_2$-(μ-C≡CHPh) (2). A crystal measuring 0.3 × 0.3 × 0.2 mm, grown from toluene/diethyl ether, was found to be triclinic with cell dimensions a = 14.684 (4) Å, b = 14.818 (4) Å, c = 13.527 (2) Å, α = 102.56 (2)°, β = 101.56 (2)°, and γ = 73.13 (2)°. Data were collected as summarized in Table I. Direct methods (Multan) were employed to locate the two rhodium and four phosphorus atoms. Subsequent cycles of least-squares refinements and difference Fourier maps located the remaining non-hydrogen atoms.

(32) ^{1}H NMR data used to identify the products are as follows: styrene (vinylic protons), δ 5.06 (J = 10.8 Hz), 5.59 (J = 17.0 Hz), 6.57 (J = 17.0 10.8 Hz); (E)-1,4-diphenylbutadiene (vinylic protons), δ 6.29 (J = 16.2 Hz), the other vinylic H resonance was obscured; (Z)-1,4-diphenylbutadiene (vinylic protons), δ 5.79 (J = 11.8 Hz), 6.41 (J = 11.8 Hz); 1,4-diphenylbutadiyne ortho H, δ 7.34 (d, J = 7.9 Hz). ^{13}C NMR data for 1,4-diphenylbutadiyne (acetylenic carbons): δ 74.9, 82.2.

Table III. Refined Positional and Isotropic Thermal Parameters and Their Estimated Standard Deviations for Rh₂(μ-CCHPh)(CO)₂(dppm)₂ (2)

atom	x	y	z	B, Å²
Rh1	0.36010 (5)	0.17161 (5)	0.69292 (5)	3.02 (2)
Rh2	0.24461 (5)	0.27003 (5)	0.86464 (5)	2.98 (2)
P1	0.2228 (2)	0.1365 (2)	0.5996 (2)	3.16 (6)
P2	0.1018 (2)	0.2604 (2)	0.7628 (2)	3.47 (6)
P3	0.3580 (2)	0.3502 (2)	0.9446 (2)	3.07 (6)
P4	0.4863 (2)	0.2284 (2)	0.7866 (2)	2.91 (6)
O1	0.4756 (6)	−0.0287 (6)	0.6229 (7)	7.7 (3)
O2	0.1984 (7)	0.2315 (6)	1.0539 (6)	8.9 (3)
C1	0.4333 (7)	0.0467 (7)	0.6526 (8)	4.3 (3)
C2	0.2184 (7)	0.2393 (7)	0.9804 (7)	4.6 (3)
C3	0.2752 (6)	0.3063 (6)	0.7393 (6)	3.0 (2)
C4	0.2505 (6)	0.3898 (6)	0.7070 (7)	3.5 (2)
C5	0.1082 (6)	0.2244 (7)	0.6219 (7)	3.7 (2)
C6	0.4548 (6)	0.3447 (6)	0.8721 (7)	3.2 (2)
C7	0.2904 (7)	0.4130 (7)	0.6253 (8)	4.7 (3)
C8	0.280 (1)	0.5081 (9)	0.620 (1)	8.6 (4)
C9	0.320 (1)	0.5294 (9)	0.549 (1)	13.1 (4)
C10	0.366 (1)	0.468 (1)	0.479 (1)	13.4 (5)
C11	0.379 (1)	0.375 (1)	0.484 (1)	12.7 (5)
C12	0.3409 (9)	0.346 (1)	0.5540 (9)	8.2 (4)
C13	0.2190 (8)	0.1285 (7)	0.4640 (7)	4.3 (3)
C14	0.2718 (9)	0.055 (1)	0.4077 (9)	7.6 (4)
C15	0.2818 (9)	0.052 (1)	0.3074 (9)	7.9 (4)
C16	0.236 (1)	0.116 (1)	0.2593 (9)	12.3 (6)
C17	0.237 (3)	0.187 (3)	0.316 (2)	10 (1)
C17A	0.139 (2)	0.188 (2)	0.304 (2)	10.8 (9)
C18	0.207 (3)	0.207 (3)	0.428 (2)	8 (1)
C18A	0.126 (2)	0.188 (2)	0.405 (2)	10.9 (9)
C19	0.2018 (7)	0.0242 (7)	0.6096 (7)	3.7 (2)
C20	0.1389 (7)	−0.0196 (8)	0.5429 (9)	5.2 (3)
C21	0.1232 (9)	−0.1019 (8)	0.557 (1)	6.6 (4)
C22	0.170 (1)	−0.1434 (8)	0.634 (1)	7.0 (4)
C23	0.2368 (9)	−0.1052 (8)	0.706 (1)	6.6 (4)
C24	0.2540 (8)	−0.0231 (7)	0.6954 (8)	5.2 (3)
C25	0.0336 (6)	0.1812 (7)	0.7836 (8)	4.5 (3)
C26	−0.0652 (8)	0.1932 (9)	0.7427 (9)	6.4 (3)
C27	−0.1126 (8)	0.1311 (9)	0.756 (1)	7.5 (4)
C28	−0.061 (1)	0.0565 (9)	0.809 (1)	9.1 (5)
C29	0.0308 (9)	0.048 (1)	0.853 (2)	12.9 (5)
C30	0.0748 (9)	0.1145 (9)	0.841 (1)	10.1 (4)
C31	0.0130 (7)	0.3762 (7)	0.7639 (8)	4.7 (3)
C32	−0.0648 (8)	0.3986 (9)	0.690 (1)	7.3 (4)
C33	−0.1276 (9)	0.488 (1)	0.703 (1)	8.4 (5)
C34	−0.1135 (9)	0.5563 (8)	0.783 (1)	7.5 (4)
C35	−0.0369 (8)	0.5400 (8)	0.858 (1)	5.9 (3)
C36	0.0295 (8)	0.4514 (7)	0.8541 (9)	5.8 (3)
C37	0.2982 (6)	0.4786 (7)	0.9699 (7)	3.6 (2)
C38	0.2335 (7)	0.5086 (8)	1.0407 (9)	5.8 (3)
C39	0.1798 (8)	0.6015 (8)	1.057 (1)	7.1 (3)
C40	0.1871 (9)	0.6666 (8)	1.004 (1)	7.6 (4)
C41	0.254 (1)	0.6406 (9)	0.933 (1)	7.3 (4)
C42	0.3073 (8)	0.5464 (7)	0.9205 (8)	4.9 (3)
C43	0.4235 (7)	0.3311 (7)	1.0700 (7)	3.8 (2)
C44	0.4376 (9)	0.2476 (8)	1.1031 (9)	6.0 (3)
C45	0.491 (1)	0.2313 (9)	1.2011 (9)	7.4 (4)
C46	0.5304 (9)	0.302 (1)	1.2599 (9)	8.0 (4)
C47	0.518 (1)	0.389 (1)	1.2294 (8)	7.5 (4)
C48	0.468 (1)	0.4030 (8)	1.1359 (9)	6.5 (4)
C49	0.5414 (8)	0.0782 (7)	0.8952 (8)	4.9 (3)
C50	0.5709 (6)	0.1497 (6)	0.8748 (7)	3.4 (2)
C51	0.6617 (7)	0.1620 (7)	0.9160 (8)	5.0 (3)
C52	0.7209 (9)	0.1082 (9)	0.981 (1)	6.9 (4)
C53	0.6958 (9)	0.0332 (9)	1.0032 (9)	6.1 (4)
C54	0.6067 (9)	0.0160 (8)	0.9627 (8)	6.0 (3)
C55	0.5652 (6)	0.2504 (6)	0.7118 (7)	3.5 (2)
C56	0.6156 (7)	0.3220 (8)	0.7464 (8)	5.2 (3)
C57	0.6743 (8)	0.3365 (8)	0.684 (1)	6.8 (3)
C58	0.6846 (8)	0.2771 (8)	0.5896 (9)	6.2 (3)
C59	0.6381 (7)	0.2068 (8)	0.5544 (8)	5.1 (3)
C60	0.5757 (7)	0.1933 (7)	0.6163 (7)	4.6 (3)

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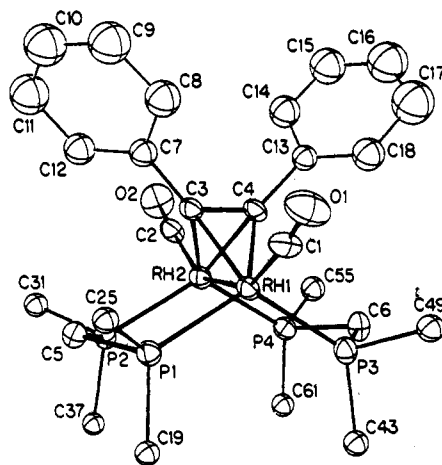

Figure 1. A perspective drawing of the molecular structure of Rh₂(μ,η²-PhCCPh)(CO)₂(dppm)₂ (4). The dppm phenyl carbon atoms are omitted for clarity. The phenyl carbon atoms are numbered consecutively beginning with the ipso carbons.

One phenyl ring on P1 was found to be disordered with respect to slight rocking along the P1–C13 axis. Analysis of difference Fourier maps parallel to the ring produced a model in which C17 (meta) and C18 (ortho) are each divided between two positions (0.65 and 0.35 occupancies). While the other meta and ortho carbons (C15 and C14) exhibit thermal ellipsoids that are elongated along the direction of the rocking, separate positions could not be refined. In the final model all heavy atoms were refined anisotropically with hydrogen atoms placed at calculated positions around all the phenyls except for the disordered ring. Successful refinement confirmed the choice of the centric space group P1̄. Table III contains the final refined positional and isotropic thermal parameters for the structure. Supplementary material contains the final anisotropic thermal parameters, the calculated hydrogen positional parameters, and a listing of observed and calculated structure factor amplitudes for the structure. See paragraph regarding supplementary material at the end of the paper.

Results and Discussion

Synthesis and Structure of Alkyne-Bridged Complexes. For internal alkynes, complexes of the general formula Rh₂(RCCR′)(CO)₂(dppm)₂ are readily prepared by heating benzene solutions of 1 and the alkyne at 80 °C for 1–2 days as shown in eq 1 for PhC≡CPh. Crystals of 4 suitable for X-ray diffraction study were obtained as the tribenzene solvate.
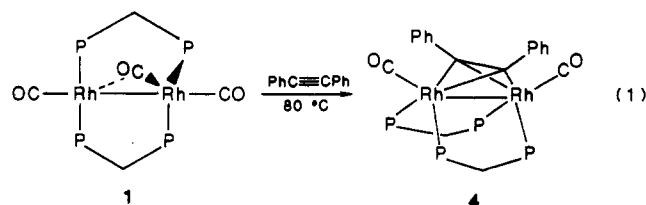
The molecular structure of Rh₂(μ,η²-PhCCPh)(CO)₂(dppm)₂ (4) as determined by crystal structure analysis is shown in Figure 1. In the structure, diphenylacetylene bridges two Rh atoms connected by a Rh–Rh single bond of length 2.644 (1) Å. The alkyne bridge is oriented in the "perpendicular" or μ,η² mode, as shown in Figure 2, and formally serves as a four-electron donor to the two Rh centers. The alkyne C–C bond length of 1.329 (11) Å is longer than that found in uncoordinated acetylenes (1.20 Å) and is comparable with 31 literature values tabulated for the perpendicular bridging mode of alkyne coordination in a recent article on alkyne complexes.[2]
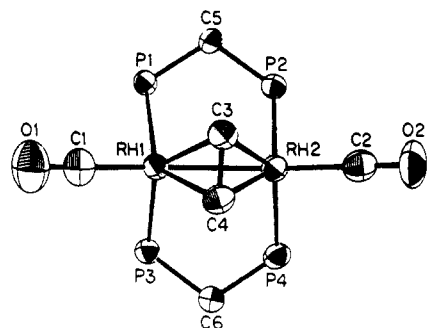
Figure 2. A perspective view of the inner coordination geometry of Rh$_2$(μ,η^2-PhCCPh)(CO)$_2$(dppm)$_2$ (4) showing the μ,η^2 or perpendicular mode of PhC≡CPh coordination.

Table IV. Selected Bond Distances (Å) for Rh$_2$(PhCCPh)(CO)$_2$(dppm)$_2$ (4)

atom 1	atom 2	dist	atom 1	atom 2	dist
Rh1	Rh2	2.644 (1)[a]	P2	C5	1.858 (8)
Rh1	P1	2.352 (2)	P2	C31	1.823 (9)
Rh1	P3	2.343 (3)	P2	C37	1.837 (8)
Rh1	C1	1.864 (11)	P3	C6	1.875 (9)
Rh1	C3	2.107 (8)	P3	C43	1.818 (9)
Rh1	C4	2.052 (8)	P3	C49	1.819 (9)
Rh2	P2	2.344 (2)	P4	C6	1.851 (9)
Rh2	P4	2.359 (3)	P4	C55	1.845 (9)
Rh2	C2	1.891 (11)	P4	C61	1.828 (9)
Rh2	C3	2.062 (8)	O1	C1	1.145 (10)
Rh2	C4	2.094 (8)	O2	C2	1.123 (10)
P1	C5	1.851 (8)	C3	C4	1.329 (11)
P1	C19	1.821 (8)	C3	C7	1.454 (12)
P1	C25	1.834 (8)	C4	C13	1.494 (11)

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

In the structure of **4** the dppm ligands do not occupy mutually trans positions at the metal centers as is found in A-frame complexes. The P–Rh–P bond angles are 117.46 (9)° and 118.07 (9)°, with the dppm ligands bent away from the bridging alkyne. Selected bond distances and angles for **4** are tabulated in Tables IV and V while complete listings of these parameters are provided in the supplementary material. The coordination geometry about each Rh is essentially distorted tetrahedral if the stereochemical influence of the Rh–Rh bond is ignored and the alkyne is assumed to occupy a single coordination site of each metal. The structure is thus analogous to a number of μ,η^2-alkyne-bridged complexes containing d^9 metals including the well-studied Co$_2$(μ-RCCR)(CO)$_6$ systems.[3] Perhaps more interesting from an electronic structural viewpoint is the fact that the geometry of **4** contrasts with stoichiometrically similar dppm-bridged complexes of Pd and Rh which contain alkynes bridging in the "parallel" rather than the perpendicular mode (in the parallel mode, designated as μ,η^1, the alkyne C–C and the M–M vectors are parallel). These complexes include M$_2$(μ,η^1-CF$_3$CCCF$_3$)Cl$_2$(dppm)$_2$, where M = Pd[33a] and Rh,[33b] and Rh$_2$(μ-CO)(μ,η^1-(MeOOC)CC(COOMe))Cl$_2$(dppm)$_2$.[34] A theoretical treatment of bridging alkyne structural preferences has been presented.[2]

In solution **4** exhibits spectroscopic properties consistent with those of the structure observed in the solid. In the ^{1}H NMR spectrum, two multiplets are observed at δ 3.75 and 3.58 corresponding to pairs of endo and exo dppm methylene protons. A single non-first-order multiplet is found at δ 21.35 in the ^{31}P {^{1}H} NMR spectrum. The alkyne C≡C bond of **4** exhibits a stretch at 1425 cm^{-1} in the infrared spectrum which is close to the $\nu_{C≡C}$ value of 1402 cm^{-1} reported for the structurally similar complex Co$_2$(CO)$_6$(HCCH).[35] Two carbonyl bands for **4** are found at 1941 and 1926 cm^{-1}.

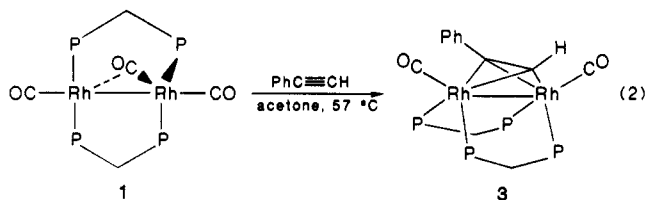The synthesis of the μ,η^2-alkyne adduct **3** from PhC≡CH and **1** requires somewhat greater care, as a result of competing formation of the vinylidene complex **2** (vide infra), as well as subsequent isomerization of **3** to **2** under the reaction conditions. Compound **3** is prepared by refluxing a 1:1 mixture of **1** and PhC≡CH in acetone for 5 h, (eq 2), but prolonged heating should be avoided, as this results in isomerization. Small amounts of **2** can be removed from the yellow product by recrystallization or

(33) (a) Balch, A. L.; Lee, C. L.; Lindsay, C. H.; Olmstead, M. M. *J. Organomet. Chem.* **1979**, *18*, 2996–3003. (b) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682–2688.

(34) Cowie, M.; Southern, T. G. *J. Organomet. Chem.* **1980**, *193*, C46–C50.

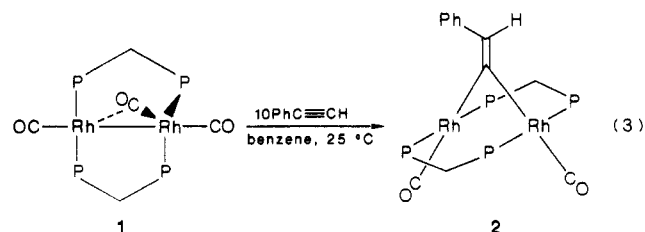(35) Iwashita, Y.; Tamura, F.; Nakamura. A. *Inorg. Chem.* **1969**, *8*, 1179–1183.

repeated washing with diethyl ether. Compound **3** is moderately air-stable in solution and the solid state, although crystals of **3** suitable for X-ray diffraction studies could not be obtained.

The spectroscopic properties of complex **3** reflect the lower symmetry imposed by the monosubstituted alkyne. The four dppm methylene protons are inequivalent and appear as four near quartets owing to an accidental degeneracy of P–H and geminal H–H coupling constants, as confirmed by homonuclear decoupling experiments. The acetylenic proton appears as a triplet at δ 6.01 ($^2J_{Rh-H}$ = 6.8 Hz), coupled to the two rhodium nuclei. Two multiplets at δ 22.39 and 19.65 are present in the ^{31}P NMR spectrum, reflecting the inequivalence of the dppm ligands. In addition to ν_{CO} bands at 1938 and 1923 cm^{-1}, the infrared spectrum of **3** exhibits a C≡C stretch at 1425 cm^{-1}.

Two other alkyne complexes containing the Rh$_2$(CO)$_2$(dppm)$_2$ moiety have been prepared and analyzed by ^{1}H NMR spectroscopy in situ as means of identifying possible byproducts in the catalytic reactions described below. These complexes are the μ,η^2 analogues containing PhC≡C—C≡CPh and (E)-PhC≡C—CH=CHPh. The ^{1}H NMR spectra of these complexes are very similar to that of **3**, with the dppm methylene protons appearing as four approximate quartets having chemical shifts nearly coincident with to those of **3**. It is believed that the alkyne is coordinated in the perpendicular or μ,η^2 fashion in these compounds.

Synthesis and Structure of the Vinylidene Complex 2. The synthesis of **2** is accomplished by the reaction of **1** with a tenfold excess of PhC≡CH in benzene at room temperature as in eq 3. Under these reaction conditions,

Table V. Selected Bond Angles (deg) for Rh$_2$(PhCCPh)(CO)$_2$(dppm)$_2$ (4)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Rh2	Rh1	P1	96.78 (6)[a]	Rh2	P2	C5	109.9 (3)
Rh2	Rh1	P3	94.56 (6)	Rh2	P2	C31	113.8 (3)
Rh2	Rh1	C1	150.9 (3)	Rh2	P2	C37	127.5 (3)
Rh2	Rh1	C3	49.9 (2)	C5	P2	C31	102.3 (4)
Rh2	Rh1	C4	51.1 (2)	C5	P2	C37	99.8 (4)
P1	Rh1	P3	117.46 (9)	C31	P2	C37	100.2 (4)
P1	Rh1	C1	98.5 (3)	Rh1	P3	C6	109.5 (3)
P1	Rh1	C3	98.1 (2)	Rh1	P3	C43	127.7 (3)
P1	Rh1	C4	134.2 (3)	Rh1	P3	C49	113.0 (3)
P3	Rh1	C1	100.1 (3)	C6	P3	C43	100.3 (4)
P3	Rh1	C3	133.5 (3)	C6	P3	C49	103.5 (4)
P3	Rh1	C4	99.0 (3)	C43	P3	C49	99.9 (4)
C1	Rh1	C3	103.3 (4)	Rh2	P4	C6	109.0 (3)
C1	Rh1	C4	101.5 (4)	Rh2	P4	C55	115.3 (3)
C3	Rh1	C4	37.3 (3)	Rh2	P4	C61	125.6 (3)
Rh1	Rh2	P2	93.85 (6)	C6	P4	C55	98.3 (4)
Rh1	Rh2	P4	96.01 (7)	C6	P4	C61	105.3 (4)
Rh1	Rh2	C2	151.2 (3)	C55	P4	C61	99.6 (4)
Rh1	Rh2	C3	51.4 (2)	Rh1	C1	O1	172.5 (9)
Rh1	Rh2	C4	49.7 (2)	Rh2	C2	O2	174.4 (9)
P2	Rh2	P4	118.07 (9)	Rh1	C3	Rh2	78.7 (3)
P2	Rh2	C2	99.2 (3)	Rh1	C3	C4	69.1 (5)
P2	Rh2	C3	97.8 (3)	Rh1	C3	C7	135.7 (6)
P2	Rh2	C4	132.3 (2)	Rh2	C3	C4	72.7 (5)
P4	Rh2	C2	100.2 (3)	Rh2	C3	C7	138.9 (6)
P4	Rh2	C3	134.1 (3)	C4	C3	C7	133.0 (8)
P4	Rh2	C4	98.0 (3)	Rh1	C4	Rh2	79.2 (3)
C2	Rh2	C3	101.1 (4)	Rh1	C4	C3	73.6 (5)
C2	Rh2	C4	104.2 (4)	Rh1	C4	C13	136.9 (6)
C3	Rh2	C4	37.3 (3)	Rh2	C4	C3	70.0 (5)
Rh1	P1	C5	108.2 (3)	Rh2	C4	C13	135.5 (6)
Rh1	P1	C19	125.9 (3)	C3	C4	C13	134.2 (8)
Rh1	P1	C25	114.4 (3)	P1	C5	P2	112.3 (4)
C5	P1	C19	106.5 (4)	P3	C6	P4	111.4 (4)
C5	P1	C25	99.8 (4)				
C19	P1	C25	98.7 (4)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.
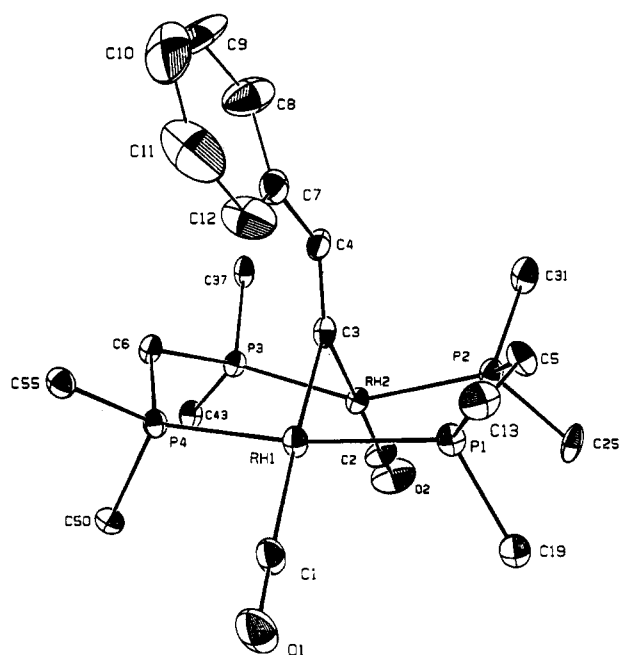
Figure 3. A perspective drawing of the vinylidene A-frame complex Rh$_2$(CO)$_2$(dppm)$_2$(μ-C=CHPh) (2). Only the ipso-carbon atoms of the dppm phenyl groups are shown for clarity. The phenyl carbon atoms of each ring are numbered consecutively beginning with the ipso carbon.

formation of **3** is limited to less than 5% of reaction products, in keeping with kinetic studies indicating that **2** is formed via an associative process, while **3** is not.[29] Compound **2** is air-sensitive in solution and the solid state.

The preparation of vinylidene complex **2** has also been reported by Grundy and co-workers following a different synthetic route involving treatment of the cationic acetylide complex [Rh$_2$(CO)$_2$(dppm)$_2$(C≡CPh)]$^+$ with LiBEt$_3$H.[4]

The solid-state structure of Rh$_2$(CO)$_2$(dppm)$_2$(μ-C=CHPh) (**2**) is shown in Figure 3. The complex possesses an "A-frame" geometry with no formal Rh–Rh bond (3.011 (1) Å) and roughly square-planar coordination about the metal centers. The two dppm ligands are mutually trans at each Rh center although some distortion from planarity is noted at Rh2 with a P2–Rh2–P3 angle of 152.44 (8)°. The vinylidene proton was not located on electron density maps but is assumed to complete a normal sp^2 geometry about the α-vinylidene carbon atom C4 which shows a bond angle of 126.2 (7)° for C3–C4–C7. The C3–C4 bond length of 1.329 (11) Å indicates double-bond character and is typical for bridging vinylidene complexes.[10] Selected bond distances and angles for **2** are given in Tables VI and VII while complete tabulations are presented in the supplementary material.

The ^{1}H NMR spectrum of **2** in benzene-d_6 solution exhibits two multiplets at δ 3.85 (2 H) and 2.25 (2 H) arising from the equivalent sets of endo and exo dppm methylene protons. This is consistent with the A-frame structure and a plane of symmetry containing the vinylidene group and the Rh atoms as found in the solid state. The spectrum in toluene-d_8 is invariant from +50 to –65 °C. The vinylic proton resonance is not observed and is presumed to be obscured by the phenyl protons. Two carbonyl stretches are observed at 1934 and 1910 cm^{-1}.

Solutions of the vinylidene complex **2** are an intense purple color, exhibiting an absorbance at 570 nm in the

Table VI. Selected Bond Distances (Å) for Rh$_2$(μ-CCHPh)(CO)$_2$(dppm)$_2$ (2)

atom 1	atom 2	dist	atom 1	atom 2	dist
Rh1	Rh2	3.011 (1)^a	P3	C37	1.836 (7)
Rh1	P1	2.288 (2)	P3	C43	1.811 (8)
Rh1	P4	2.291 (2)	P4	C6	1.845 (7)
Rh1	C1	1.876 (8)	P4	C50	1.869 (7)
Rh1	C3	2.063 (7)	P4	C55	1.819 (7)
Rh2	P2	2.290 (2)	O1	C1	1.138 (8)
Rh2	P3	2.285 (2)	O2	C2	1.130 (9)
Rh2	C2	1.859 (8)	C3	C4	1.329 (9)
Rh2	C3	2.051 (7)	C4	C7	1.491 (10)
P1	C5	1.838 (7)	C7	C8	1.390 (13)
P1	C13	1.802 (8)	C7	C12	1.382 (12)
P1	C19	1.814 (8)	C8	C9	1.36 (2)
P2	C5	1.877 (7)	C9	C10	1.30 (3)
P2	C25	1.843 (8)	C10	C11	1.35 (3)
P2	C31	1.829 (8)	C11	C12	1.38 (2)
P3	C6	1.856 (7)			

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.

visible spectrum, with rough measurements indicating an extinction coefficient in excess of 10 000 M^{-1} cm^{-1}.

Observation of a Carbon Monoxide Adduct of 2. Like many A-frame complexes, 2 rapidly and reversibly forms an adduct with carbon monoxide as shown in eq 4.[36-38] In the presence of ^{13}CO at ambient temperature


2
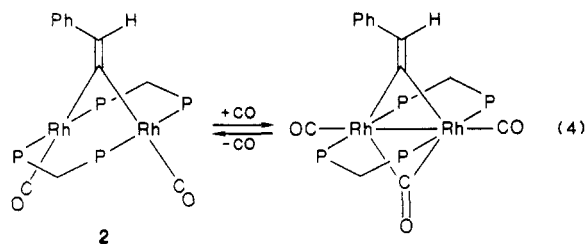
the dppm methylene resonances in the ^{1}H NMR spectrum of 2 shift upfield, and the color becomes noticeably redder. The observation of a single set of resonances in the ^{1}H NMR spectrum, shifted upfield from those of 2, indicates that 2 and the CO adduct are in rapid exchange on the NMR time scale. Cooling the sample to −36 °C shifts the equilibrium in favor of the CO adduct, as evidenced by a color change to pale yellow. Warming the sample to 80 °C produces the intense purple color of pure 2. While no ^{13}C NMR resonances are observed in the carbonyl region at ambient temperatures, at −36 °C the spectrum reveals resonances at δ 217 (br), 210 (d of t), 206 (d of t), and 184 (s), the last due to uncomplexed ^{13}CO. The chemical shift and coupling pattern of the δ 210 and 206 resonances are consistent with two terminal carbonyl ligands, syn and anti with respect to the vinylidene phenyl ring. Coupling to the rhodium ($^1J_{Rh-C}$ = 66 Hz) and the two adjacent cis phosphorus nuclei ($^2J_{P-C}$ = 15 Hz) leads to the observed patterns. The downfield shift of the δ 217 resonance is consistent with a bridging carbonyl ligand. Unresolved coupling to four phosphorus and two rhodium nuclei results in the broad lineshape.

Alkyne Disproportionation Catalyzed by 2. The term "alkyne disproportionation" has been used in recent times synonymously with "alkyne metathesis" in reference to a process in which alkyne bond scission and reconsti-

tution leads to a distribution of new alkyne products (eq 5).[39-41]

$$RC{\equiv}CR + R'C{\equiv}CR' \xrightarrow[\quad]{[cat.]} 2RC{\equiv}CR' \quad (5)$$
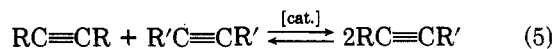
Disproportionation in the more traditional sense refers to a process in which one substance acts as both oxidant and reductant in a particular reaction. This definition describes the observed redistribution of phenylacetylene to styrene and 1,4-diphenylbutadiyne catalyzed by 2 (eq 6), which may thus be labeled as an alkyne dispropor-

$$PhC{\equiv}CH \xrightarrow[2]{80\ °C} PhCH{=}CH_2 + PhC{\equiv}C{-}C{\equiv}CPh$$

$$(6)$$
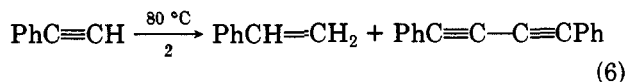
tionation. Sealed NMR tubes containing PhCCH and 2 (ca. 1 mol %) in benzene-d_6 were heated at 85 °C and monitored by ^{1}H NMR. Typically, 50% of the alkyne was consumed after 4 days, with styrene and 1,4-diphenyl-butadiyne accounting for 85–90% of the organic products and (E)- and (Z)-1,4-diphenylbutenyne (1:1) accounting for another 10% of the products.

As the disproportionation proceeds, 2 slowly decomposes to unidentified products. Concurrently, the rate of formation of styrene decreases dramatically, suggesting that 2 takes part in the catalytic cycle. Comparison of ^{1}H NMR spectra of the reaction mixture with those of the μ,η^2-alkyne complexes of PhCCH (3), PhC{≡}CC{≡}CPh, and (E)-PhC{≡}CCH{=}CHPh indicates that these complexes are not present in detectable quantities among the decomposition products.

Several workers have reported studies of the Rh(I)-catalyzed oligomerization of phenylacetylene and other acetylenes.[16-19] Kern observed that neat PhC{≡}CH treated with RhCl(PPh$_3$)$_3$ produces a syrup of oligomers, from which a 50% yield of (E)-1,4-diphenylbutenyne crystallizes.[17] Closer examination by Carlton and Read showed that both the linear ((E)-1,4-diphenyl) and branched (1,3-diphenyl) butenynes are initially formed but that the latter is thermally unstable, decomposing to higher oligomers.[20] 1,4-Diphenylbutadiyne and (Z)-1,4-diphenyl-butenyne are not produced from PhC{≡}CH with mononuclear rhodium catalysts.[19,20,45]

The reaction in eq 6, however, is superficially similar to the Cu(I)-catalyzed oxidative coupling of alkynes shown in eq 7, commonly called the Glaser coupling. The Glaser

$$RC{\equiv}CH \xrightarrow[O_2]{Cu(I)} PhC{\equiv}C{-}C{\equiv}CPh + H_2O \quad (7)$$
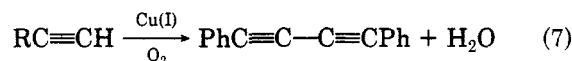
coupling produces diyne and water from alkynes with oxygen as the oxidant.[23,42-44] In the disproportionation reaction (6), one molecule of PhC{≡}CH acts as the oxidant and hydrogen atom acceptor, while two other diphenyl-acetylene molecules undergo the coupling reaction. Complex 2 decomposes rapidly in solutions exposed to air, precluding attempts to use oxygen as an oxidant in this

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(44) Nish, W. G. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S.; Ed.; Academic: New York, 1973; Part B, p 1.

(45) However, the (Z)-butenyne is produced in the anaerobic Cu(I)-catalyzed (Straus) coupling of PhC{≡}CH.[22]

Table VII. Selected Bond Angles (deg) for Rh₂(μ-CCHPh)(CO)₂(dppm)₂ (2)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Rh2	Rh1	P1	87.48 (5)[a]	C5	P2	C31	100.1 (4)
Rh2	Rh1	P4	88.83 (5)	C25	P2	C31	103.4 (4)
Rh2	Rh1	C1	135.1 (3)	Rh2	P3	C6	117.4 (2)
Rh2	Rh1	C3	42.8 (2)	Rh2	P3	C37	108.4 (2)
P1	Rh1	P4	172.12 (7)	Rh2	P3	C43	121.3 (3)
P1	Rh1	C1	91.5 (2)	C6	P3	C37	103.4 (3)
P1	Rh1	C3	86.8 (2)	C6	P3	C43	102.7 (3)
P4	Rh1	C1	96.0 (2)	C37	P3	C43	101.2 (4)
P4	Rh1	C3	85.7 (2)	Rh1	P4	C6	116.3 (2)
C1	Rh1	C3	177.3 (3)	Rh1	P4	C50	115.6 (3)
Rh1	Rh2	P2	92.87 (5)	Rh1	P4	C55	115.2 (3)
Rh1	Rh2	P3	91.60 (5)	C6	P4	C50	102.7 (3)
Rh1	Rh2	C2	137.5 (3)	C6	P4	C55	101.6 (3)
Rh1	Rh2	C3	43.1 (2)	C50	P4	C55	103.4 (3)
P2	Rh2	P3	152.44 (8)	Rh1	C1	O1	176.3 (8)
P2	Rh2	C2	97.1 (3)	Rh2	C2	O2	172.2 (8)
P2	Rh2	C3	84.0 (2)	Rh1	C3	Rh2	94.1 (3)
P3	Rh2	C2	97.8 (3)	Rh1	C3	C4	135.2 (5)
P3	Rh2	C3	80.9 (2)	Rh2	C3	C4	130.5 (5)
C2	Rh2	C3	178.6 (3)	C3	C4	C7	126.2 (7)
Rh1	P1	C5	117.1 (2)	P1	C5	P2	110.4 (4)
Rh1	P1	C13	112.4 (3)	P3	C6	P4	111.3 (4)
Rh1	P1	C19	116.8 (3)	C4	C7	C8	119.4 (9)
C5	P1	C13	101.6 (4)	C4	C7	C12	124.6 (8)
C5	P1	C19	103.5 (3)	C8	C7	C12	116.0 (9)
C13	P1	C19	103.6 (4)	C7	C8	C9	120.0 (1)
Rh2	P2	C5	115.2 (2)	C8	C9	C10	126.0 (2)
Rh2	P2	C25	120.4 (3)	C9	C10	C11	116.0 (1)
Rh2	P2	C31	113.0 (3)	C10	C11	C12	123.0 (2)
C5	P2	C25	102.1 (3)	C7	C12	C11	120.0 (1)

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

Scheme II
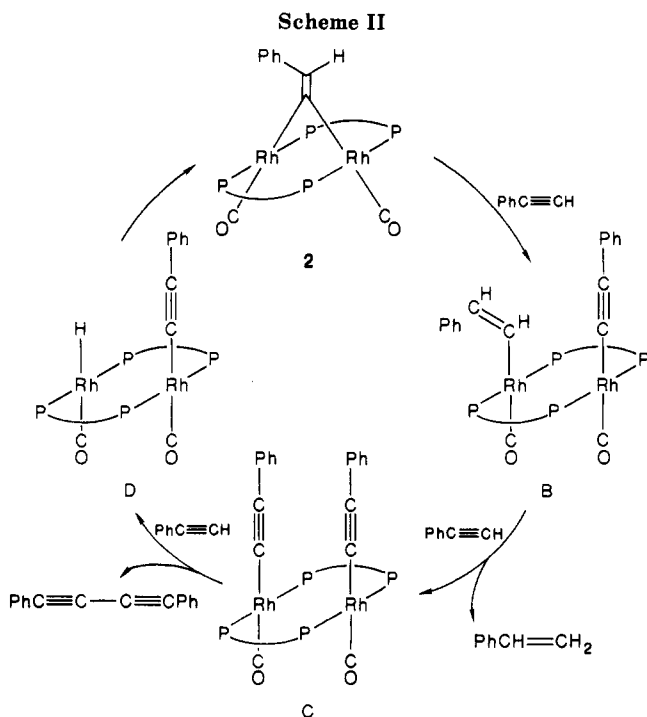
case. RhCl(PPh₃)₃, however, shows no tendency to catalyze formation of diyne under the aerobic conditions of the oligomerization reactions.[18-20]

While detailed study of the mechanism of the disproportionation reaction (6) has not been carried out, the selectivity for diyne vs. enyne formation may result from the binuclear nature of the vinylidene complex. A possible mechanism based on simple addition and elimination steps which can account for the observed organic products is shown in Scheme II. In this catalysis, key proposed intermediates in addition to the vinylidene complex 2 include the styrenyl–acetylide intermediate B, the diacetylide complex C, and the acetylide–hydride complex D. For each of the intermediates, both metal centers may play a role in binding substrate moieties, although the actual addition and elimination steps may proceed at a single metal center. Grundy and co-workers have advocated the intermediacy of a species similar to D in their preparation of 2,[4] and the alkyne-to-vinylidene rearrangement has frequently been proposed in both mononuclear and polynuclear complexes.[10-12,15] A specific recent report is that of Lukehart involving platinum hydride addition across an acetylide ligand on a second platinum center to yield a bridging vinylidene complex.[46]

Alkyne Hydrogenation. In the disproportionation reaction (6), PhC≡CH is both reduced to styrene and oxidatively coupled to diphenylbutadiyne. The formation of styrene led us to investigate catalysis of PhC≡CH hydrogenation by the vinylidene complex 2. Indeed, when PhC≡CH is placed in a benzene solution of 2 under H₂, catalytic hydrogenation occurs leading to styrene (eq 8).

$$\text{PhC} \equiv \text{CH} + \text{H}_2 \xrightarrow[\;\;2\;\;]{80\ °C} \text{PhCH}{=}\text{CH}_2 \qquad (8)$$
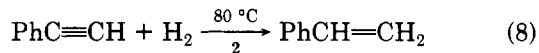
Sealed NMR tubes containing PhCCH, hydrogen (ca. 1.6 atm), and 2 (ca. 1 mol %) in benzene-d_6 were heated at 85 °C and monitored by ¹H NMR spectroscopy. Typically, 20% of the alkyne was consumed after 16 h. Significantly, during the first several turnovers the concentration of the μ,η^2-alkyne-bridged complex 3 rises from ca. 0 to a constant 44%, with a corresponding decrease in 2.
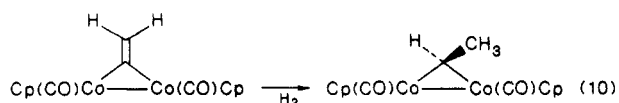
The implications of a vinylidene complex in a hydrogenation scheme and the presence of the acetylene complex 3 in the catalytic mixture raise several questions concerning this process. The hydrogenation of alkynes catalyzed by transition metals generally proceeds with cis stereochem-

(46) Afzal, D.; Lenhert, P. G.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 3050–3052.

istry,[47,48] although in a few instances trans addition has been observed.[49] If **3** is the catalyst in the present case, *cis* hydrogenation would be expected, based on precedented binuclear systems.[43,47,50] If, however, **2** is the active catalyst, the hydrogenation could be envisioned as occurring with a completely different stereochemical result.

As an initial probe of the hydrogenation mechanism, a solution of **2** was heated under D_2 in the absence of added PhC≡CH. After 5 h at 80 °C, decomposition of the vinylidene complex is >90% complete. The ^1H NMR spectrum indicates that the styrene and ethylbenzene liberated contain a proton in the α-position only (eq 9).

$$PhCH{=\!\!=}CD_2 \ + \ PhCHD{-\!\!-}CD_3 \quad (9)$$
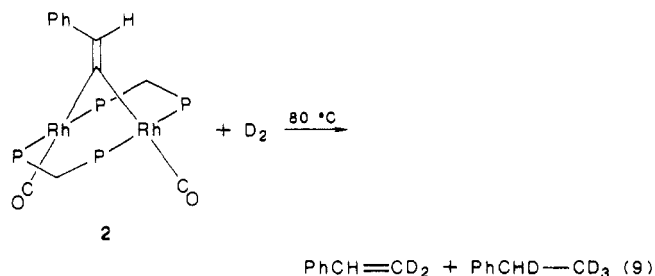
Thus both rhodium–vinylidene bonds are hydrogenated without significant exchange at the α-position. Ethylbenzene is presumably formed by subsequent addition of D_2 to styrene, catalyzed by rhodium decomposition products, although addition across the vinylidene double bond prior to metal–carbon bond cleavage is precedented. Specifically, Jacobsen and Bergman have reported the addition of hydrogen across the olefinic bond in the dicobalt vinylidene complex $Cp_2Co_2(CO)_2(\mu\text{-}C{=\!\!=}CH_2)$ to produce the bridging ethylidene complex shown in eq 10 in moderate yield.[51,52] Subsequent reaction of the ethy-

lidene complex with hydrogen reportedly leads to decomposition and a mixture of ethane and ethylene. Formation of the analogous μ-alkylidene from **2** and H_2 does not appear to be important in the present catalytic hydrogenation, as ethylbenzene is not produced in the presence of added phenylacetylene.[53]

The rise in concentration of the bridging alkyne complex **3** to a constant value during the hydrogenation is somewhat surprising, since at 80 °C **3** will slowly convert to the more stable vinylidene complex **2** as in eq 11.[30] We have previously shown that the formation of **2** and **3** from PhC≡CH and the tricarbonyl complex $Rh_2(CO)_3(dppm)_2$
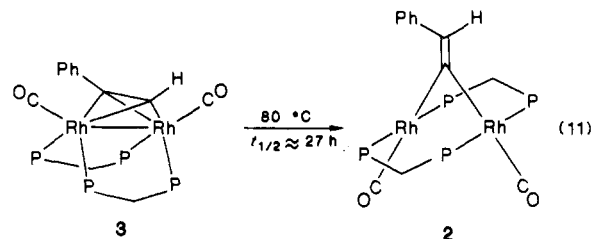
(**1**) are competitive and follow different reaction channels as in Scheme I. The pathway leading to **3** involves generation of the highly unsaturated 16e–16e complex Rh_2-$(CO)_2(dppm)_2$ (**A**) by CO dissociation from **1** and rapid reaction with phenylacetylene. While **3** can isomerize to **2**, it does not react directly with H_2. This can be demonstrated by heating a solution of **3** under D_2. After 5 h at 80 °C, the only observable reaction is isomerization to **2** (eq 11), which has occurred to the extent of ca. 10% of starting complex. Only trace amounts of styrene were detected, presumably due to (9).

While **3** is produced during the hydrogenation at a rate sufficient to offset isomerization back to **2**, **3** cannot be part of the primary catalytic cycle for alkyne hydrogenation. Styrene formation in (8) proceeds to the extent of 18 turnovers in 16 h at 80 °C, whereas the isomerization reaction (11) is on the order of 50 times slower. Formation of **3** followed by conversion to **2** during the catalytic cycle would require a turnover rate no faster than that of isomerization.[54] The appearance of **3** during the hydrogenation therefore results from a different reaction pathway.

If PhC≡CH is converted into a vinylidene species such as **2** prior to hydrogenation, the original acetylenic proton should end up in the α-position of the resultant styrene. This notion is somewhat supported by experiment. When a large excess of PhC≡CH is heated at 80 °C with **2** under a D_2 atmosphere, the distribution (in percent) of styrene products at 45% conversion as determined by ^1H NMR spectroscopy and mass spectrometry is as follows: PhCH=CD$_2$, 57 (2); PhCH=CH$_2$, 12 (2); *cis*-PhCH= CHD, 10 (2); *trans*-PhCH=CHD, 10 (2); and PhCD=CD$_2$, 4 (2). Upper limits for other possible styrene products are as follows: *cis*-PhCD=CHD (<3%), *trans*-PhCD=CHD (<3%), and PhCD=CH$_2$ (<5%). The coupled product PhC≡CC≡CPh is also formed in significant relative amounts (in percent) during this experiment (~20 (5)). Numbers in parentheses are estimated standard deviations.

While more than half of the styrene product is the expected styrene-β,β-d_2, in support of the role of **2** as the catalyst, the significant quantities of styrene-d_0 and 1,4-diphenylbutadiyne indicate that the alkyne disproportionation process, eq 6, occurs competitively. In addition to the products mentioned above, analysis shows a large degree of deuterium incorporation into the acetylenic position of the unreacted alkyne. This suggests that exchange with free alkyne also occurs at some point in the cycle. The observed isotopic enrichment is consistent with the expected thermodynamic distributions of H and D between rhodium hydride and acetylenic positions.[55]

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(48) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.

(49) Murakami, M.; Suzuki, K.; Kang, J. *J. Chem. Soc. Jpn.* **1963**, *84*, 669. Murakami, M.; Suzuki, K.; Itatani, H.; Kyo, M.; Senoh, S. Jap. Pat. 21974, 1965; *Chem. Abstr.* **1966**, *64*, 4945.

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(51) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023–2032.

(52) Jacobsen, E. N.; Bergman, R. G. *Organometallics* **1984**, *3*, 329–331.

(53) It is also possible that phenylacetylene inhibits addition of hydrogen across the vinylidene ligand, although it seems more likely that the ethylbenzene results from styrene hydrogenation and that the alkylidene is not involved.

(54) Although it is possible that the isomerization of **3** to **2** is accelerated under the conditions of the hydrogenation, the rate of isomerization is qualitatively unchanged in separate experiments under D_2 and PhC≡CH.

(55) The thermodynamic preference for D in the acetylenic position arises from the higher C–H(D) stretching frequency relative to the Rh–H(D) bond and the resulting relative differences in zero-point energies. Additionally, a kinetic preference in the addition of PhC≡CH is expected on the basis of the related reaction of PhC≡CH with **1** to produce **2**, for which a k_H/k_D of 2.6 was observed.[30]

Another species potentially active in the catalytic hydrogenation is the dihydride complex $Rh_2H_2(CO)_2$-$(dppm)_2^{31}$ which could form by oxidative addition of H_2 to A. However, independently prepared samples of the dideuteride form of this complex react with phenylacetylene to produce primarily *cis*-PhCD=CHD. The reaction is also accompanied by an unusual CIDNP effect which will be reported separately.[56] In the present study, the small amounts of α,β-dideuteriostyrene and the large amounts of styrene with no deuterium in the α-position (vide supra) indicate that $Rh_2H_2(CO)_2(dppm)_2$ does not participate in the catalysis of eq 8.

The hydrogenation reaction (8) represents a new and mechanistically interesting process which involves a vinylidene intermediate in alkyne hydrogenation. Similarly, the disproportionation reaction (6) catalyzed by the vinylidene complex 2 also gives results which differ from those found for mononuclear systems. The unusual re-

activity patterns and reaction pathways which can emerge when two metal centers are maintained in close proximity as in A-frame complexes exemplified by 2 are the focus of ongoing studies.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen positional parameters, and complete bond distances and angles of $Rh_2(CO)_2(dppm)_2$-$(\mu,\eta^2$-PhC≡CPh)·3C_6H_6 (4) and $Rh_2(CO)_2(dppm)_2(\mu$-C=CHPh) (2) (12 pages); listings of observed and calculated structure factors for 2 and 4 (88 pages). Ordering information is given on any current masthead page.

(56) Hommeltoft, S. I.; Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* 1986, *108*, 5345.

Communications

Carbon Dioxide Chemistry of a Binuclear Iridium(0) Complex: Oxygen Atom Transfer to a Coordinated Aryl Isocyanide Ligand and the Structure of $[Ir_2(\mu$-CO)(μ-H)(C(O)NHR)$_2$(CNR)$_2$-(Me$_2$PCH$_2$PMe$_2$)$_2$]Cl (R = 2,6-Me$_2$C$_6$H$_3$)

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Summary: The reaction of the Ir^0 species Ir$_2(\mu$-CNR)$_2$-(CNR)$_2$(Me$_2$PCH$_2$PMe$_2$)$_2$ (1, R = 2,6-Me$_2$C$_6$H$_3$) with carbon dioxide leads to the formation of a carbon dioxide adduct, Ir$_2$(CN(CO$_2$)R)$_2$(CNR)$_2$(Me$_2$PCH$_2$PMe$_2$)$_2$ (3, R = 2,6-Me$_2$C$_6$H$_3$). Complex 3 is labile and loses 2 equiv of carbon dioxide upon heating. In methylene chloride solvent, 3 decomposes cleanly to a carbamoyl complex, [Ir$_2(\mu$-CO)(μ-H)(C(O)NHR)$_2$(CNR)$_2$(Me$_2$PCH$_2$PMe$_2$)$_2$]Cl (4, R = 2,6-Me$_2$C$_6$H$_3$). Labeling studies with ^{13}CO$_2$ show that the bridging carbonyl ligand of complex 4 is derived from carbon dioxide. The formation of complex 4 is the result of oxygen atom transfers from carbon dioxide to two coordinated isocyanide ligands. The crystal structure of complex 4 has been determined. Complex 4 crystallized in the monoclinic space group *P*2$_1$/*n* with a = 12.887 (5) Å, b = 22.078 (5) Å, c = 22.652 (5) Å, V = 6403.0 (6) Å^3, and Z = 4. The structure was refined to R and R$_w$ of 0.047 and 0.066, respectively, for 5252 observations in the range of 4° ≤ 2θ ≤ 45° with I ≥ 3σ(I) and Mo Kα radiation.

The activation of carbon dioxide by transition-metal complexes has received much attention in recent years as a possible means of incorporating carbon dioxide into organic molecules.[1–7] The deoxygenation of carbon dioxide has also been reported,[5b] however, it is not clear whether an oxygen atom can be generally transferred from carbon dioxide to organic molecules. A formal CO$_2$ oxygen atom transfer to isocyanides to give isocyanates, and CO has been reported, but not mechanistically established.[7] We recently reported the mechanism of oxygen atom transfer from CO$_2$ to the methyl isocyanide ligand of a binuclear Ni(0) complex, which follows the isotopic course shown in eq 1.[2] We now report another oxygen atom transfer

$$O=C^*=O + C≡NR \rightleftharpoons C≡O + O=C^*=NR \quad (1)$$
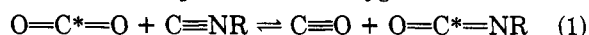
pathway for the CO$_2$ molecule in the reaction of carbon dioxide with a binuclear iridium(0) isocyanide complex. We also report the solid-state structure of the resulting carbamoyl diiridium complex. A ^{13}CO$_2$-labeling study

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