Oxidative Addition of Dichloromethane to $[(dppe)Rh]_2(\mu\text{-}Cl)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$). X-ray Structure of $[(dppe)RhCl]_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)$

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Summary: Dichloromethane reacts with the rhodium chloride-bridged dimer $[(dppe)Rh]_2(\mu\text{-}Cl)_2$, where dppe = $Ph_2PCH_2CH_2PPh_2$, to generate the bridging-methylene derivative $[(dppe)RhCl]_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)$.

The utility of metal-phosphine complexes as catalyst precursors is well established.[1] In particular, the combination of rhodium stabilized by ancillary phosphine ligands is probably among the most widely used systems for homogeneous catalysis. This is in part due to the stability of this class of complexes as well as the flexibility in being able to tailor the phosphine ligands; for example, the use of chiral phosphine ligands on rhodium is a standard in asymmetric catalytic reactions.

Recently, we have been investigating rhodium-phosphine-based systems as homogeneous catalysts for the hydrogenation of imines.[2,3] In general, the catalyst precursors are generated in situ by addition of a chelating phosphine to a suitable Rh(I) precursor; the particular bidentate phosphines are $Ph_2PCH_2CH_2PPh_2$ (dppe) and related chiral derivatives such as $Ph_2PCH(R)CH_2PPh_2$ (R = cyclohexyl: cycphos). In attempts to optimize the conditions for catalysis, we had occasion to examine the effect of different solvents on the rate of imine hydrogenation.[3] Dichloromethane (CH_2Cl_2) has been used previously as solvent (sometimes optimally)[4] in the hydrogenation of olefinic substrates using rhodium complexes containing (di)tertiary phosphine ligands,[5,6] as well as for hydroacylation reactions catalyzed by rhodium-phosphine complexes[7] including dppe derivatives.[8] In this paper we describe an unexpected reaction between the solvent dichloromethane and one of the possible catalyst precursors to generate a methylene-bridged rhodium dimer.

Results and Discussion

The chloride-bridged rhodium dimer $[(dppe)Rh]_2(\mu\text{-}Cl)_2$ (1) can be prepared in toluene by displacement of the cyclooctene ligands of $[(\eta^2\text{-}C_8H_{14})_2Rh]_2(\mu\text{-}Cl)_2$.[8] This dppe dimer is only sparingly soluble in most solvents, and the $^{31}P\{^1H\}$ NMR spectrum of this material was reported in CD_2Cl_2.[8] In our hands, this preparation produced the correct material with a small amount (5-7%) of an unknown compound as judged by $^{31}P\{^1H\}$ NMR spectroscopy in C_6D_6. However, we were surprised to find that a solution of $[(dppe)Rh]_2(\mu\text{-}Cl)_2$ in CH_2Cl_2 slowly transformed over a period of hours to a completely new compound. This new material formed essentially in quantitative yield after about 36 h. This transformation could be conveniently followed by $^{31}P\{^1H\}$ NMR spectroscopy; the initial doublet due to 1 at 73.2 ppm ($^1J_{Rh}$ = 198 Hz) slowly transformed ($t_{1/2}$ = approximately 4 h) to a new doublet at 66.7 ppm ($^1J_{Rh}$ = 153 Hz). No other intermediates were observed. The elemental analyses of this new material indicated that it has the empirical formula $[(dppe)Rh]_2(\mu\text{-}Cl)_2\cdot CH_2Cl_2$; that is, one molecule of CH_2Cl_2 added to the starting dimer 1. In fact, the initially isolated material contains more than 1 equiv of CH_2Cl_2 on the basis of ^1H NMR spectroscopy; however, when the crystals are subjected to vacuum all but 1 equiv of CH_2Cl_2 can be readily removed. The ^1H NMR spectrum of this material showed the expected peaks for the dppe ligand and an additional broad, featureless resonance at 4.09 ppm integrating for two hydrogens based on a binuclear structure; this last resonance was absent when the reaction was performed in CD_2Cl_2. To characterize this material unequivocally, its solid-state structure was determined by single-crystal X-ray diffraction.

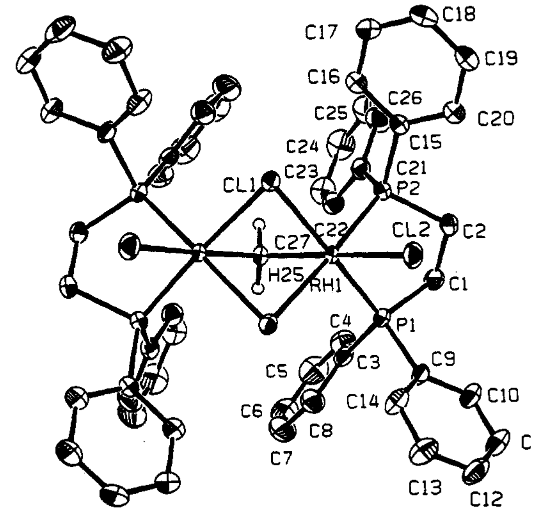

Figure 1. Molecular structure and numbering scheme for $[(dppe)RhCl]_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)$.

The molecular structure, which has 2-fold symmetry, is shown in Figure 1. The binuclear structure is apparent with the two rhodium centers joined by two chloride ligands and a bridging methylene unit; the dppe ligands are bound in a bidentate fashion to each rhodium. Each rhodium center is in a symmetrical, quasi-octahedral environment and formally can be considered as Rh(III). The angle subtended by the methylene, Rh(1)-C(27)-Rh(1)*, is 95.2 (2)°, considerably less than the 107.2 (2)° observed in a pyrazolyl-bridged iridium complex[9] but similar to the

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(1) *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983.

(2) Kang, G.-J.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1466.

(3) Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P.; Kang, G.-J.; Herb, G.; Thorburn, I. S.; Spogliarich, R. *J. Mol. Catal.* **1990**, *62*, 243.

(4) Crabtree, R. H.; Chodosh, D. F.; Quirk, J. M.; Felkin, H.; Fillebeen-Khan, T.; Morris, G. E. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum: New York, 1979; Vol. 3, p 475.

(5) Riley, D. P.; Shumate, R. E. *J. Org. Chem.* **1980**, *45*, 5187.

(6) Suggs, J. W.; Cox, S. D.; Crabtree, R. H.; Quirk, J. M. *Tetrahedron Lett.* **1981**, *22*, 303.

(7) Larcock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*, 190.

(8) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936, 946.

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Table I. Crystallographic Data[a]

compd	$[(dppe)RhCl]_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)$
formula	$C_{53}H_{50}Cl_4P_4Rh_2$
fw	1158.50
cryst system	orthorhombic
space group	*Pbcn*
a, Å	21.432 (2)
b, Å	9.379 (1)
c, Å	24.212 (2)
V, Å^3	4867 (1)
Z	4
D_c, g/cm^3	1.581
$F(000)$	2344
μ(Cu Kα), cm^{-1}	92.40
cryst dimens, mm	0.12 × 0.32 × 0.40
scan type	ω–2θ
scan range, deg in ω	$0.94 + 0.20 \tan \theta$
scan speed, deg/min	32
data collcd	$+h,-k,+l$
$2\theta_{max}$, deg	155
cryst decay	negligible
tot. no. of unique reflcns	5759
no. of reflcns with $I \geq 3\sigma(I)$	3949
no. of variables	290
R	0.029
R_w	0.039
gof	1.96
max Δ/σ (final cycle)	0.002
resid density, e/Å^3	−0.42 to +0.42

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Cu radiation (λ = 1.541 78 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [C + B + (0.02F^2)^2]/Lp^2$ (C = scan count, B = normalized background count), function minimized $\sum w(|F_0| - |F_c|)^2$, where $w = 4F_o/\sigma^2(F^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

98.7 (3)° reported for a thiolato-bridged iridium derivative.[10] In contrast, a binuclear, bridging-methylene rhodium complex having bridging-dppm ligands has a much wider angle of 114.5 (5)°.[11] It would appear that this angle is rather flexible and is determined by the other bridging ligands in the particular complex. The rhodium–carbon bond length is 2.057 (3) Å for the bridging methylene and is similar to that found in the already mentioned related systems.

Table II. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2)[a]

atom	x	y	z	B_{eq}
Rh(1)	0.070823 (9)	0.02659 (2)	0.252312 (8)	2.12 (1)
Cl(1)	−0.00215 (3)	−0.0865 (1)	0.31691 (3)	2.88 (3)
Cl(2)	0.14562 (4)	−0.1789 (1)	0.25275 (4)	3.67 (4)
P(1)	0.13630 (4)	0.1432 (1)	0.19485 (3)	2.65 (3)
P(2)	0.12985 (4)	0.1197 (1)	0.31957 (3)	2.73 (3)
C(1)	0.1998 (2)	0.2233 (5)	0.2360 (1)	3.7 (2)
C(2)	0.2079 (2)	0.1393 (4)	0.2896 (1)	3.5 (2)
C(3)	0.1038 (2)	0.2895 (4)	0.1542 (1)	3.1 (1)
C(4)	0.1102 (2)	0.4333 (5)	0.1684 (2)	4.5 (2)
C(5)	0.0822 (3)	0.5382 (5)	0.1367 (2)	5.8 (3)
C(6)	0.0483 (3)	0.5027 (6)	0.0914 (2)	6.1 (3)
C(7)	0.0408 (2)	0.3628 (6)	0.0769 (2)	5.6 (2)
C(8)	0.0686 (2)	0.2564 (5)	0.1083 (2)	4.3 (2)
C(9)	0.1742 (2)	0.0350 (4)	0.1415 (1)	3.1 (1)
C(10)	0.2339 (2)	0.0663 (5)	0.1229 (2)	4.6 (2)
C(11)	0.2595 (2)	−0.0101 (6)	0.0798 (2)	5.6 (2)
C(12)	0.2272 (2)	−0.1161 (5)	0.0547 (2)	5.2 (2)
C(13)	0.1679 (2)	−0.1478 (5)	0.0721 (2)	5.0 (2)
C(14)	0.1421 (2)	−0.0748 (5)	0.1162 (2)	4.2 (2)
C(15)	0.1380 (2)	0.0130 (4)	0.3816 (1)	3.1 (1)
C(16)	0.0891 (2)	0.0081 (5)	0.4194 (2)	3.8 (2)
C(17)	0.0948 (2)	−0.0704 (5)	0.4675 (2)	4.5 (2)
C(18)	0.1488 (2)	−0.1431 (5)	0.4786 (2)	4.8 (2)
C(19)	0.1972 (2)	−0.1394 (6)	0.4415 (2)	5.1 (2)
C(20)	0.1922 (2)	−0.0612 (5)	0.3932 (2)	4.0 (2)
C(21)	0.1146 (2)	0.2979 (4)	0.3462 (1)	3.3 (2)
C(22)	0.0895 (2)	0.4018 (4)	0.3118 (2)	3.8 (2)
C(23)	0.0845 (2)	0.5427 (5)	0.3281 (2)	5.0 (2)
C(24)	0.1049 (3)	0.5806 (6)	0.3801 (3)	6.3 (3)
C(25)	0.1295 (3)	0.4796 (6)	0.4151 (2)	6.2 (3)
C(26)	0.1342 (2)	0.3390 (5)	0.3988 (2)	4.7 (2)
C(27)	0	0.1744 (5)	$^1/_4$	2.4 (2)

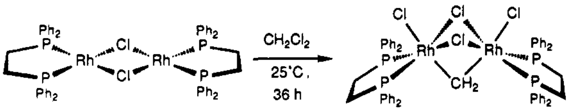
[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i{}^*a_j{}^*(a_ia_j)$.

Table III. Bond Lengths (Å) with Estimated Standard Deviations[a]

Rh(1)–Cl(1)	2.4531 (7)	C(9)–C(10)	1.387 (5)
Rh(1)–Cl(1)*	2.4700 (8)	C(9)–C(14)	1.383 (5)
Rh(1)–Cl(2)	2.5071 (9)	C(10)–C(11)	1.379 (6)
Rh(1)–P(1)	2.2587 (8)	C(11)–C(12)	1.357 (7)
Rh(1)–P(2)	2.2394 (8)	C(12)–C(13)	1.372 (6)
Rh(1)–C(27)	2.057 (3)	C(13)–C(14)	1.383 (5)
P(1)–C(1)	1.845 (4)	C(15)–C(16)	1.392 (5)
P(1)–C(3)	1.826 (4)	C(15)–C(20)	1.384 (5)
P(1)–C(9)	1.833 (3)	C(16)–C(17)	1.383 (5)
P(2)–C(2)	1.833 (3)	C(17)–C(18)	1.371 (6)
P(2)–C(15)	1.812 (4)	C(18)–C(19)	1.371 (6)
P(2)–C(21)	1.821 (4)	C(19)–C(20)	1.385 (5)
C(1)–C(2)	1.529 (5)	C(21)–C(22)	1.390 (5)
C(3)–C(4)	1.400 (5)	C(21)–C(26)	1.397 (5)
C(3)–C(8)	1.378 (5)	C(22)–C(23)	1.383 (6)
C(4)–C(5)	1.386 (6)	C(23)–C(24)	1.381 (7)
C(5)–C(6)	1.356 (8)	C(24)–C(25)	1.375 (8)
C(6)–C(7)	1.368 (7)	C(25)–C(26)	1.380 (6)
C(7)–C(8)	1.388 (6)		

[a] Here and elsewhere an asterisk refers to symmetry operation $-x, y, {}^1/_2 - z$.

Oxidative addition of CH_2Cl_2 to the dppe dimer 1 to generate the observed bridging-methylene compound (eq 1) is somewhat surprising. Normally, more reactive *gem*-dihalides are employed for this type of transformation; for example, CH_2I_2 and CH_2Br_2 are required to produce bridging-methylene complexes of Ir[9,10] and Pd,[12] in some cases with no interference from the solvent CH_2Cl_2.[12] Oxidative addition of CH_2Cl_2 to rhodium(I) is observed when the metal contains very basic ligands such as PMe_3 or dmpe.[13] Very recently, oxidative addition of CH_2Cl_2 has been observed in rhodium(I)–acac complexes containing chelating phosphines including dppe.[14]



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(1)

In light of this reaction with the solvent, some of our earlier results on the effect of solvent of the hydrogenation of imines may now be rationalized. Our attempts to use CH_2Cl_2 always gave much lower conversions as compared to MeOH/benzene mixtures,[3] presumably due to some interference by the solvent. Caution should be exercised

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[9] Brost, R. D.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 498.

[10] Amane, M. E.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* **1985**, *4*, 773.

[11] McKeer, I. R.; Cowie, M. *Inorg. Chim. Acta* **1982**, *65*, L107. dppm = bis(diphenylphosphino)methane.

[12] Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

[13] Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1543.

[14] Fennis, P. J.; Budzelaar, P. H. M.; Frijns, J. H. G.; Orpen, A. G. *J. Organomet. Chem.* **1990**, *393*, 287.

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Table IV. Bond Angles (deg) with Estimated Standard Deviations

Cl(1)–Rh(1)–Cl(1)*	82.35 (3)	C(4)–C(3)–C(8)	118.0 (4)
Cl(1)–Rh(1)–Cl(2)	94.15 (3)	C(3)–C(4)–C(5)	120.4 (4)
Cl(1)–Rh(1)–P(1)	176.65 (3)	C(4)–C(5)–C(6)	120.4 (5)
Cl(1)–Rh(1)–P(2)	93.74 (3)	C(5)–C(6)–C(7)	120.4 (5)
Cl(1)–Rh(1)–C(27)	80.70 (7)	C(6)–C(7)–C(8)	119.9 (5)
Cl(1)*–Rh(1)–Cl(2)	93.07 (3)	C(3)–C(8)–C(7)	121.0 (4)
Cl(1)*–Rh(1)–P(1)	99.23 (3)	P(1)–C(9)–C(10)	121.4 (3)
Cl(1)*–Rh(1)–P(2)	175.99 (3)	P(1)–C(9)–C(14)	120.3 (3)
Cl(1)*–Rh(1)–C(27)	80.29 (7)	C(10)–C(9)–C(14)	118.2 (3)
Cl(2)–Rh(1)–P(1)	88.72 (3)	C(9)–C(10)–C(11)	120.2 (4)
Cl(2)–Rh(1)–P(2)	86.30 (3)	C(10)–C(11)–C(12)	121.1 (4)
Cl(2)–Rh(1)–C(27)	172.0 (1)	C(11)–C(12)–C(13)	119.6 (4)
P(1)–Rh(1)–P(2)	84.72 (3)	C(12)–C(13)–C(14)	120.1 (4)
P(1)–Rh(1)–C(27)	96.62 (8)	C(9)–C(14)–C(13)	120.8 (4)
P(2)–Rh(1)–C(27)	100.02 (7)	P(2)–C(15)–C(16)	119.4 (3)]
Rh(1)–Cl(1)–Rh(1)*	76.20 (2)	P(2)–C(15)–C(20)	121.8 (3)
Rh(1)–P(1)–C(1)	108.8 (1)	C(16)–C(15)–C(20)	118.7 (3)
Rh(1)–P(1)–C(3)	117.3 (1)	C(15)–C(16)–C(17)	120.4 (4)
Rh(1)–P(1)–C(9)	116.2 (1)	C(16)–C(17)–C(18)	120.2 (4)
C(1)–P(1)–C(3)	105.4 (2)	C(17)–C(18)–C(19)	119.8 (4)
C(1)–P(1)–C(9)	106.2 (2)	C(18)–C(19)–C(20)	120.6 (4)
C(3)–P(1)–C(9)	101.8 (2)	C(15)–C(20)–C(19)	120.2 (4)
Rh(1)–P(2)–C(2)	105.5 (1)	P(2)–C(21)–C(22)	120.0 (3)
Rh(1)–P(2)–C(15)	116.2 (1)	P(2)–C(21)–C(26)	121.5 (3)
Rh(1)–P(2)–C(21)	120.9 (1)	C(22)–C(21)–C(26)	118.0 (4)
C(2)–P(2)–C(15)	107.2 (2)	C(21)–C(22)–C(23)	121.9 (4)
C(2)–P(2)–C(21)	102.2 (2)	C(22)–C(23)–C(24)	118.8 (5)
C(15)–P(2)–C(21)	103.4 (2)	C(23)–C(24)–C(25)	120.4 (5)
P(1)–C(1)–C(2)	109.4 (2)	C(24)–C(25)–C(26)	120.7 (5)
P(2)–C(2)–C(1)	106.4 (2)	C(21)–C(26)–C(25)	120.2 (5)
P(1)–C(3)–C(4)	123.6 (3)	Rh(1)–C(27)–Rh(1)*	95.2 (2)
P(1)–C(3)–C(8)	118.3 (3)		

when CH_2Cl_2 is used as a solvent for catalytic reactions involving rhodium and chelating-phosphine systems.

Experimental Section

All synthetic reactions were performed under nitrogen in standard Schlenk-type glassware. CH_2Cl_2 was dried over CaH_2 under nitrogen and vacuum degassed immediately prior to use. The NMR spectra were recorded in CD_2Cl_2 on a Bruker AMX-500 or a Bruker AC-200 spectrometer. The ^1H NMR spectra were referenced to the residual solvent proton at 5.32 ppm, and the $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4 set at 0.00 ppm. $[(dppe)Rh]_2(\mu\text{-}Cl)_2$ (1) was prepared according to the literature procedure;[8] the $^{31}P\{^1H\}$ NMR spectrum of 1 in C_6D_6 showed a doublet at 73.5 ppm ($^1J_{Rh}$ = 199 Hz) with a doublet due to a minor component (5–7%) at 77.5 ppm ($^1J_{Rh}$ = 200 Hz).

$[(dppe)RhCl]_2(\mu\text{-}Cl)(\mu\text{-}CH_2)$. $[(dppe)Rh]_2(\mu\text{-}Cl)_2$ (219 mg, 0.204 mmol) was dissolved in CH_2Cl_2 (5 mL), and the solution was allowed to stand for 24 h. The solvent volume was slowly reduced over a period of 24 h to ≈1.5 mL, during which time large yellow-orange crystals separated. After the mixture was cooled to −15 °C for 1 h, the crystals were filtered off and washed with cold CH_2Cl_2 (0.5 mL). Drying in vacuo (18 h) caused the crystals to rapidly become opaque due to loss of solvated CH_2Cl_2. Yield: 120 mg (51%). Anal. Calcd for $C_{53}H_{50}Cl_4P_4Rh_2$: C, 54.95; H, 4.35. Found: C, 54.68; H, 4.39. ^1H NMR (ppm, CD_2Cl_2, 500 MHz): $P(C_6H_5)_2$, 7.98 (m, 8 H), 7.49 (m, 4 H), 7.43 (m, 8 H), 7.17 (m, 12 H), 7.03 (m, 8 H); $\mu\text{-}CH_2$, 4.09 (br, 2 H); PCH_2CH_2P, 2.92 (m, 4 H), 2.23 (m, 4 H). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2, 81 MHz): 66.7 (d, $^1J_{Rh}$ = 153 Hz). FAB Mass Spectrum: *m/e* 1159, $(M + 1)^+$.

X-ray-quality crystals were grown by diffusion of a near-saturated solution of the complex in CH_2Cl_2 into diethyl ether; crystals were sealed in glass capillaries under N_2.

X-ray Crystallographic Analysis of $[(dppe)RhCl]_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)$. Crystallographic data appear in Table I. The final unit-cell parameters were obtained by least-squares methods on the setting angles for 25 reflections with 2θ = 76.5–91.4°. The intensities of three standard reflections, measured every 150 reflections throughout the data collection, showed only small random variations. The data were processed and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for three reflections).[15]

The structure was solved by conventional heavy-atom methods, the coordinates of the Rh atom being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent difference Fourier synthesis. The molecule has crystallographically imposed C_2 symmetry, the 2-fold axis passing through the bridging methylene carbon atom. All non-hydrogen atoms were refined with anisotropic thermal parameters. The crystallographically unique hydrogen atom of the $\mu\text{-}CH_2$ group was refined with an isotropic thermal parameter, and the remaining hydrogen atoms were fixed in calculated positions (C–H = 0.98 Å, B_H = 1.2*B*(bonded atom)). Neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 16. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables II–IV, respectively. Hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure factor amplitudes are included as supplementary material.

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Registry No. 1, 53204-14-1; CH_2Cl_2, 75-09-2; $[(dppe)RhCl]_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)$, 136060-75-8.

Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes (13 pages); a table of measured and calculated structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

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(15) TEXSAN/TEXRAY structure analysis package, which includes versions of the following: MITHRIL, integrated direct methods, by C. J. Gilmore; DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy: ORTEP II, illustrations, by C. K. Johnson.

(16) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

Photodimerization of 1-Phenyl-2-(trimethylsilyl)ethyne

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Summary: Room-temperature photolysis at 254 nm of 1-phenyl-2-(trimethylsilyl)ethyne (**1**) produces two cyclooctatetraenes, **2** and **3**, for which structures **2a** and **3a** are suggested from ^1H NMR spectra.

Several years ago, while studying some photochemical reactions involving 1-phenyl-2-(trimethylsilyl)ethyne (1), we noticed the formation of yellow products when 1 was irradiated. Mass spectrometry showed that the products were dimers of 1, but their structure was unknown until recently. We now present evidence that the photolysis of 1 leads, via intermolecular dimerization, to cyclo-

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