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atomic coordinates (Table II), bond distances and angles (Table III), anisotropic thermal parameters (Table IV), and fractional atomic coordinates for H atoms (Table V) (9 pages); a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

Three-Fragment Oxidative Addition of Dichloromethane to a Mononuclear Rhodium(I) Complex with Concomitant Formation of a Metal-Phosphoranide Bond

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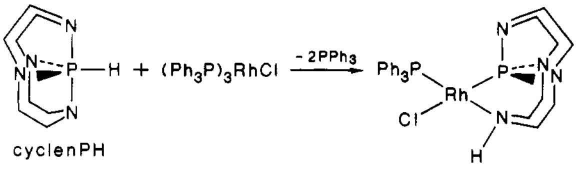
Summary: Cyclenphosphorane reacts with $ClRh(PPh_3)_3$ to initially yield a four-coordinate complex where two PPh_3 groups have been displaced by the phosphorus and one nitrogen atom of the open form of cyclenphosphorane. This species undergoes a three-fragment oxidative addition of dichloromethane to yield a compound with a phosphoranide-metal bond and a novel P-N-C-Rh metallacycle.

Oxidative addition of dihalomethanes to low-valent transition metals is well-documented.[1] In general, these reactions lead to halomethyl[1a-f] (CH_2X-M-X, $CH_2X-M^+X^-$) and methylene-bridged[1g-j] ($X-M-CH_2-M-X$) derivatives.[2] We herein report the synthesis of a new Rh(I) species which undergoes a three-fragment oxidative addition of CH_2Cl_2. The addition is accompanied by an intramolecular ligand rearrangement to yield a covalent phosphoranide-rhodium(III) complex (R_4P-Rh) with a P-N-C-Rh four-membered ring. To our knowledge, this is the first reported example of a three-fragment oxidative addition of CH_2X_2 to a single metal center, as well as the first rhodium complex with a phosphoranide ($R_4P:^-$) ligand.

Wilkinson's catalyst reacts with cyclenphosphorane (cyclenPH)[3] according to eq 1. Compound 1 was synthesized by treating 1.12 g (1.21 mmol) of $ClRh(PPh_3)_3$ with 0.243 g (1.21 mmol) of cyclenPH at -50 °C in THF. The stirred mixture was allowed to warm to ambient temperature over 1 h and stirring continued for another 3 h. After filtration, the precipitated solid was washed with THF and pumped dry to yield 0.570 g of 1[4] (78%) as a highly oxygen-sensitive yellow solid. The $^{31}P\{^1H\}$ NMR spectrum of 1 (CD_2Cl_2) shows an ABX pattern with δ 157 (dd, PN, $^1J_{RhP}$ = 227 Hz), 53 (dd, PC, $^1J_{RhP}$ = 198 Hz), and $^2J_{PP}$ = 52 Hz. The large downfield shift of the nitrogen-bound phosphorus compared to cyclenPH (δ -55) is indicative of P-N bond cleavage. Similar reactivity and chemical shifts have been reported for the related molecule cyclamPH with other transition-metal compounds.[5] The cis arrangement of phosphorus atoms is suggested by the relatively small $^2J_{PP}$ value,[6] and the presence of the N-H bond is confirmed by the observation of a broad, low-in-



(1)

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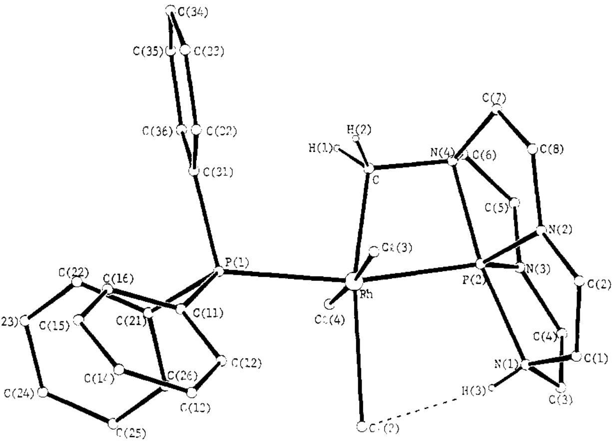

Figure 1. Geometry of the Rh(III) complex 2. Atoms are represented as circles of arbitrary radii. All H atoms excluded for clarity except H(1) and H(2) belonging to the bridging CH_2 group and H(3) involved in an intramolecular H bond.

Table I. Selected Bond Distances (Å) and Angles (deg) for 2

	Bond Distances		
Rh-P(1)	2.407 (2)	C-N(4)	1.49 (1)
Rh-Cl(2)	2.549 (2)	P(2)-N(1)	1.931 (7)
Rh-Cl(3)	3.354 (2)	P(2)-N(2)	1.661 (6)
Rh-Cl(4)	2.351 (2)	P(2)-N(3)	1.677 (7)
Rh-P(2)	2.271 (2)	P(2)-N(4)	1.911 (8)
Rh-C	2.032 (6)		
	Bond Angles		
P(1)-Rh-P(2)	168.6 (1)	Rh-P(2)-N(4)	83.8 (2)
Cl(2)-Rh-C	169.6 (2)	P(2)-Rh-C	73.6 (2)
Cl(3)-Rh-Cl(4)	176.7 (1)	N(1)-P(2)-N(4)	170.6 (3)
Rh-C-N(4)	104.4 (4)	N(2)-P(2)-N(3)	112.4 (3)
P(2)-N(4)-C	98.0 (5)		
	H Bond Geometry		
N(1)···Cl(2)	3.138 (7)	N(1)-H(3)-Cl(2)	163 (5)°
H(3)···Cl(2)	2.40 (5)		

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(1) See, for example: (a) Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1981**, 698. (b) Scherer, O. J.; Jungman, H. *J. Organomet. Chem.* **1981**, *208*, 153. (c) Collman, J. P.; Murphy, D. W.; Dolcetti, G. *J. Am. Chem. Soc.* **1973**, *95*, 2687. (d) Werner, H.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C71. (e) Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630. (f) Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Inorg. Chem.* **1980**, *19*, 3236. (g) Murray, H. H.; Fackler, J. P.; Mazany, A. M. *Organometallics* **1984**, *3*, 1310. (h) Amane, M. E.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* **1985**, *4*, 773. (i) Jandik, P.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73. (j) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

(2) Other products have also been observed: (a) Werner, H.; Zolk, R. *Organometallics* **1985**, *4*, 601 (sulfur-metal bridge insertion of CH_2). (b) Scherer, O. J.; Jungman, H.; Hussong, K. *J. Organomet. Chem.* **1983**, *247*, C1 (formation of a carbonato ligand). (c) Klein, H.-F.; Hammer, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 42. (d) Werner, H.; Hofman, L.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C65. (e) Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, S. *J. Organomet. Chem.* **1982**, *228*, C71 (formation of metallo-bonded phosphorus ylides).

(3) (a) Richman, J. E.; Atkins, T. J. *Tetrahedron Lett.* **1978**, 4333. (b) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149.

(4) Anal. Calcd for $C_{28}H_{32}ClN_4P_2Rh$: C, 51.96; H, 5.38; N, 9.33; Cl, 5.90. Found: C, 50.90; H, 5.34; N, 9.16; Cl, 6.05. ^1H NMR data (200 MHz, CD_2Cl_2): δ 2.3-3.0 (comp m, CH_2, 16 H), 5.1 (br, NH, 1 H), 7.31, 7.68 (m, CH, 15 H).

(5) The molecule cyclamPH has alternating $(CH_2)_2$ and $(CH_2)_3$ groups bridging the nitrogen atoms. (a) Dupart, J.-M.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 1167. (b) Dupart, J.-M; Grand, A.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1982**, *104*, 2316.

(6) (a) Verkade, J. G. *Coord. Chem. Rev.* **1972/1973**, *9*, 1. (b) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes" In *NMR, Basic Principles and Progress*; Diehl, P., Flack, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1979.

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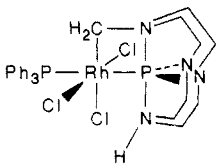
tensity peak in the ^{1}H NMR at 5.1 ppm[4] which disappears immediately upon addition of D_2O. Reaction 1 can be viewed as a simple displacement of two PPh_3 ligands with a phosphine and an amine ligand.

Compound **1** is insoluble in most common solvents and moderately soluble in halogenated solvents. However, **1** also reacts with halogenated solvents. After a few hours in CH_2Cl_2 solution, upfield resonances appear in the ^{31}P NMR spectrum while peaks due to **1** slowly diminish. Within 2 days, all traces of **1** are gone. The product shows an entirely different ABX pattern: δ 13 (dd, PC, $^{1}J_{RhP}$ = 84 Hz), −40 (dd, PN, $^{1}J_{RhP}$ = 132 Hz), $^{2}J_{PP}$ = 872 Hz. The appearance of the upfield resonance at −40 ppm suggests that a pentacoordinate phosphorus is present, and the extremely large $^{2}J_{PP}$ value is indicative of a trans arrangement of P atoms.[6] In addition, a broad singlet in the ^{1}H NMR spectrum at δ 3.19 is observed which is absent when the same reaction is run in CD_2Cl_2, indicating incorporation of a CH_2 group into the product.

The structure of the product **2**[7] was established by X-ray diffraction[8] and is illustrated in Figure 1. Selected bond distances and angles are collected in Table I. The geometry about Rh is distorted octahedral, while the geometry about P(2) is approximately trigonal-bipyramidal, as is usually observed in derivatives of cyclenP.[9] An intramolecular hydrogen bond is found between H(3) and Cl(2).



2

The formation of **2** may involve initial oxidative addition of CH_2Cl_2 to Rh to form a CH_2Cl–Rh–Cl species,[1] followed by rearrangement of the cyclenP group (from tetra- to pentacoordinate) and attack of nitrogen on carbon to displace Cl^-. Although nitrogen atoms bound to phosphorus are usually not very nucleophilic,[6a,10] such is not the case in cyclenP derivatives where the high nucleophilicity of the axial nitrogens is well-known.[9a–c] This may be due to the ring structure of the cyclenP group which holds the axial nitrogens in a more pyramidal geometry compared to the equatorial nitrogens.[9c,d,11] Another factor could be the hypervalent three-center, four-electron bond which places significantly more electron density at the axial positions in a trigonal bipyramid.[12]

The bonding in the Rh–C–N linkage can be viewed in a number of ways. One way is to consider the C–N(4) bond as an ylide, H_2C^-–N^+R_3, with the carbon donating a lone pair of electrons to rhodium. Indeed, *ionic* N, P, As, and S ylide–metal complexes have been isolated, and similar intermediates (i.e., CH_2X–M) have been proposed for their formation.[1a,2d,e,13] Alternatively, the carbon could be considered a neutral carbene, H_2C:, donating a lone pair to rhodium, with the nitrogen donating a lone pair into the vacant p orbital on carbon.[14]

We are currently investigating the scope of the addition reaction as well as the reactions of **2**. Preliminary ^{31}P{^{1}H} NMR evidence suggests that a compound similar to **2** is formed immediately when **1** is dissolved in $CDCl_3$ (with a Rh–CDCl–N linkage): δ 9 (PC, dd, $^{1}J_{RhP}$ = 81 Hz), −37 (PN, dd, $^{1}J_{RhP}$ = 132 Hz), $^{2}J_{PP}$ = 856 Hz.

Acknowledgment. We wish to thank the Robert A. Welch Foundation (M.L. and S.S.C.C.) and the Research Corp. (M.L.) for generous financial support.

Registry No. 1, 104600-81-9; 2, 104619-50-3; 2·CH_2Cl_2, 104712-81-4; cyclenPH, 64317-97-1; $(Ph_3P)_3RhCl$, 14694-95-2.

Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles (4 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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[7] The Rh(III) species **2** was isolated as follows: 1.1 g (1.8 mmol) of **1** was dissolved in 50 mL of CH_2Cl_2 and stirred for 2 days at ambient temperature. The CH_2Cl_2 was then removed and the residue washed with THF. The remaining solid was washed with CH_2Cl_2. Removal of the volatiles from the CH_2Cl_2 washings yielded 0.91 g of **2** as a yellow solid (79%). The ^{1}H NMR spectrum indicated the presence of free CH_2Cl_2 after overnight pumping (see ref 8). Analytically pure samples were obtained by recrystallization from CH_2Cl_2. Anal. Calcd for $C_{27}H_{34}Cl_3N_4P_2Rh \cdot CH_2Cl_2$: C, 43.63; H, 4.71; N, 7.27; Cl, 23.00. Found: C, 43.62; H, 4.71; N, 7.30; Cl, 22.32. ^{1}H NMR data (200 MHz, $CDCl_3$): δ 2.6–3.8 (comp m, CH_2CH_2) 3.19 (s br, $RhCH_2$) [18 H total], 7.26, 7.92 (m, CH, 15 H), 9.3 (br, NH, 1 H).

[8] Crystals of **2** were grown from CH_2Cl_2 solution. One molecule of CH_2Cl_2 crystallizes per molecule of **2**. *Crystal data*: $C_{27}H_{34}N_4Cl_3P_2$-$Rh \cdot CH_2Cl_2$, orthorhombic, space group *Pbca*, a = 18.649 (4) Å, b = 18.857 (3) Å, c = 17.984 (2) Å, V = 6325 (2) Å^3, D_{calcd} (Z = 8) = 1.644 g/cm^3, μ(Mo Kα) = 10.85 cm^{-1}. A crystal (0.64 × 0.30 × 0.06 mm) was used to collect the data on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. A total of 4165 independent reflections were measured in the range $3 < 2\theta < 45°$ using the $\theta/2\theta$ scan technique. Three standard reflections remeasured after every 100 reflections did not show any significant change in intensity during data collection. The data were corrected for Lorentz–polarization effects and for absorption. Only the 2607 observed reflections with $I > 3\sigma(I)$ were used subsequently. The structure was solved by standard Patterson and difference Fourier methods. All non-H atoms were refined anisotropically. All H atoms were located and refined isotropically except for the 16 H atoms on the methylene carbons of the cyclen ring. Owing to the large thermal motion of the cyclen C atoms, C(1)–C(8), the H atoms attached to them were calculated and included in the least-squares calculation with U's set at 0.15 Å^2 but not refined. Full-matrix least squares were carried out by using SHELX76 (Sheldrick, G. M., 1976, program for crystal structure determination, University of Cambridge, England), the function minimized being $\sum w(|F_o| - |F_c|)^2$. The final refinement converged $[(\Delta/\sigma)_{max} = 0.16]$ to R = 0.039 and R_w = 0.038, the weight used being $w^{-1} = \sigma_F^2 + 0.000415F^2$. $\Delta\rho_{max}$ = 0.42 e/Å^3 at 1.1 Å from Rh.

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[11] A few bicyclic aminophosphines have been shown to have basic nitrogen atoms. See, for example: Grec, D.; Hubert-Pfalzgraf, L. G.; Grand, A.; Riess, J. G. *Inorg. Chem.* **1985**, *24*, 4642, and references therein.

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[13] (a) Feser, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 940. (b) Werner, H.; Paul, W.; Feser, R.; Zolk, R.; Thometzek, P. *Chem. Ber.* **1985**, *118*, 261.

[14] A related carbene compound, $[(C_2H_5)_3P]_2RhCl_3[CHN(CH_3)_2]$, has been structurally characterized: Cetinkaya, B.; Lappert, M. F.; McLaughlin, G. M.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1974**, 1591.

Competitive Carbon–Carbon Bond Formation and Cleavage and Cluster Formation in the Reaction between 3-Hexyne and Hexaisopropoxyditungsten

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Summary: At −20 °C, $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and 3-hexyne (1 equiv) react in pentane in the presence of pyridine (2

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