Contribution from the Departments of Chemistry, University of Delaware, Newark, Delaware 19711,
and The Ohio State University, Columbus, Ohio 43210

Crystal Structure and Molecular Geometry of $[Rh(\mu\text{-}PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2$. A Coordinatively Unsaturated Complex Lacking Metal-Metal Bonding

WILLIAM C. FULTZ,[1a] ARNOLD L. RHEINGOLD,*[1a] PAUL E. KRETER,[1b,2] and DEVON W. MEEK*[1b]

Received May 17, 1982

The title compound with one molecule of THF crystallizes in the monoclinic space group *C*2/*c* with a = 19.508 (5) Å, b = 17.998 (3) Å, c = 19.514 (5) Å, β = 92.40 (2)°, and Z = 4. The structure was refined to discrepancy indices of R_F = 4.95% and R_{wF} = 5.19% for those 3977 unique data with $F_o > 2\sigma(F_o)$. Severe disorder in the solvent molecule accounts for the relatively high discrepancy indices. The compound is a neutral dirhodium complex in which the metal atoms are bridged by diphenylphosphido groups. The molecule is centered on a twofold, crystallographically imposed, rotational axis. The coordination sphere of each Rh atom is completed by chelating DPPE ligands. The Rh···Rh distance of 3.471 (1) Å precludes significant metal-metal bonding; each Rh atom, therefore, exists in a 16-electron environment. The Rh coordination geometry is distorted square planar with an interplanar dihedral angle of 133.4 (1)° and an intraplanar twist angle of 4.6 (2)° relating the two metal atom environments.

Introduction

The recent interest in organophosphido (R_2P) or -arsenido (R_2As) groups can be attributed to the realization that these metal-bridging ligands have a stability that is independent of bonding interactions between the metal atoms. This stability is of particular interest in homogeneous cluster catalysis where metal-metal bond breaking and formation play an important part in the catalytic mechanism.[3] Utilization of organophosphido or -arsenido bridging ligands may prevent undesirable fragmentation of the cluster unit on reaction with substrate molecules, thus stabilizing the catalyst complex.[4]

A number of groups have recently found that ^{31}P NMR spectroscopy can be very useful in assigning structural features of organophosphido-bridged metal complexes.[5] For example, it has been established that the ^{31}P NMR chemical shifts of the phosphido phosphorus nuclei are dramatically affected by the presence (or absence) of metal-metal bonding in a complex.[6,7] In complexes that lack metal-metal bonds such as $[MCl(\mu\text{-}PPh_2)PR_3]_2$ (M = Pd, Pt), $\delta_{P_{bridge}}$ occurs at approximately −130 (positive values downfield from the 85% H_3PO_4 standard). On the other hand, $\delta_{P_{bridge}}$ is +204.8 for $[Pd_3Cl(\mu\text{-}PPh_2)_2(PEt_3)_3][BF_4]$, which contains Pd-Pd bonds.[7] The large difference in $\delta_{P_{bridge}}$ between complexes lacking M-M bonding and complexes possessing M-M bonding is thought to be influenced by the same factors that give rise to the "ring contribution" to the ^{31}P NMR chemical shift for chelating diphosphines.[8] In order to substantiate the rapidly increasing number of structural assignments based on ^{31}P NMR data, it is necessary to obtain crystallographic data on representative complexes. The crystal structures of a number of phosphido-bridged, metal-metal bonded, di-, tri-, and tetrametallic complexes have been reported.[5,9] Reports of structures for phosphido-bridged complexes lacking a metal-metal bond, however, are rare and are limited to complexes for which ^{31}P NMR data are unavailable.[10] We are reporting the crystal and molecular structure of $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$ (DPPE = 1,2-bis(diphenylphosphino)ethane), which is one of a family of phosphido-bridged dirhodium complexes that contain no Rh-Rh bond, on the basis of recent ^{31}P NMR data.[11] Carty et al. have very recently reported the structural characterization of the isoelectronic complex $[Pt(\mu\text{-}PPh_2)(DPPE)]_2Cl_2$ in which the Pt_2P_2 parallelogram was found to be planar.[12]

Table I. Crystal and Refinement Data

formula	$Rh_2P_6C_{76}H_{68}\cdot C_4H_8O$
fw	1445.0
cryst syst	monoclinic
space group	$C2/c$ [C_{2h}^6 (No. 15)]
a, Å	19.508 (5)
b, Å	17.988 (3)
c, Å	19.514 (5)
β, deg	92.40 (2)
V, Å^3	6841.8 (28)
Z	4
mol wt	1445.0
ρ(calcd), g cm^{-3}	1.40
temp, °C	26
cryst color and dimens, mm	deep red, 0.22 × 0.31 × 0.41
radiation	graphite-monochromated Mo Kα (λ = 0.710 73 Å)
diffractometer	Nicolet R3
abs coeff, cm^{-1}	6.54
scan speed, deg min^{-1}	3.5
2θ scan range, deg	$3.0 < 2\theta < 45.0$
scan technique	$\theta/2\theta$
data collected	$h,k,\pm l$
scan width, deg	$2.0 + \Delta(\alpha_1-\alpha_2)$
weighting factor $(g)^a$	0.0012
unique data	4538 rflns (4700 collected)
unique data with $(F_o) > 2\sigma(F_o)$	3977
std rflns	3/141 rflns
LS parameters	390
data/parameters	10.2 (2σ data)
R, % (F_o)	4.95
R_w, % (F_o)	5.19

[a] Weight = $1/[\sigma^2(F) + |(g)(F^2)|]$.

---

(1) (1) University of Delaware. (b) The Ohio State University.

(2) Current address: ARCO Chemical Co., Newtown Square, PA 19073.

(3) (a) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27. (b) MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87-90.

(4) Braunstein, P.; Matt, D.; Bars, O.; Louer, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79.

(5) Kreter, P. E. Ph.D. Thesis, The Ohio State University, 1980. Eaborn, C.; O'dell, K. J.; Pidcock, A. *J. Organomet. Chem.* **1979**, *170*, 105. Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188. Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163.

(6) Meek, D. W.; Kreter, P. E.; Christoph. G. G. *J. Organomet. Chem.* **1982**, *231*, C53. Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186.

(7) Dixon, K. R.; Rattray, A. D. *Inorg. Chem.* **1978**, *17*, 1099. Cartwright, S. J.; Dixon, K. R.; Rattray, A. D. *Ibid.* **1980**, *19*, 1120.

(8) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(9) Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Organomet. Chem.* **1981**, *209*, C34.

(10) (a) Coleman, J. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 542. (b) Davies, G. R.; Mais, R. H. B.; Owston, P. G.; Thompson, D. T. *J. Chem. Soc. A* **1968**, 1251.

(11) Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319.

0020-1669/83/1322-0860$01.50/0

Experimental Section

A. Preparation of $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$. The title compound was obtained from the reaction of $[Rh(\mu\text{-}PPh_2)(1,5\text{-cyclooctadiene})]_2$ with DPPE in THF. The details of synthesis and characterization data will appear elsewhere.[11]

B. Collection of Diffraction Data. The details of data collection and crystal parameters are given in Table I. The crystal selected for study was cemented to the tip of a thin glass fiber with epoxy cement and was coated with a thin layer of varnish to minimize any air sensitivity. The crystal was centered on the diffractometer, and the crystal class (monoclinic), orientation matrix, and accurate unit-cell dimensions were determined from the angular settings of 24 reflections, $27° \le 2\theta \le 30°$.

All calculations were performed with the use of the Nicolet P3 and SHELXTL structure-solving package (revision 3.0) and a Data General NOVA 4 computer. Data were corrected for absorption by an empirical method using Ψ-scan data from close-to-axial (i.e., χ = 90 or 270 ± 10°) reflections and then refined by a six-parameter procedure to define a pseudoellipsoid used to calculate the corrections (transmission coefficient, max/min = 0.575/0.525). A profile-fitting procedure was applied to the data to improve the precision of the measurement of weak reflections. No correction for decay was required (<1.0% decay observed).

The observed systematic absences (hkl for $h + k = 2n$; $h0l$ for $l = 2n + 1$) indicated either the noncentrosymmetric space group Cc [C_s^4; No. 9] or the centrosymmetric $C2/c$ [C_{2h}; No. 15]. Successful refinement of the structure proved possible only in the space group $C2/c$. [Unrealistically large discrepancies in the aromatic C–C bond lengths (1.38 ± 0.21 Å) resulted when refinement in the space group Cc was attempted; the final residuals and GOF were, however, similar to those in $C2/c$.]

C. Solution and Refinement of Structure. Data were placed on an approximately absolute scale via a Wilson plot, which also provided the average overall thermal parameter ($\bar{U}$ = 0.036 Å^2). The structure was solved via the direct-methods routine SOLV, using 425 reflections with $|E| > 1.75$. The rhodium and phosphorus atoms were located from the E map based on the phase solution of highest internal consistency. The remaining non-hydrogen atoms of the organometallic molecule were located in a subsequent difference-Fourier synthesis. A difference map obtained after the isotropic refinement of the nonhydrogen atoms revealed the presence of a molecule of tetrahydrofuran for each complete dirhodium molecule. Blocked cascade refinement of the scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms (except for the solvent atoms which were refined isotropically) led to convergence with R = 8.20% and R_w = 8.81% ($R = \sum[|F_o| - |F_c|]/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)]^2/\sum w(F_o)^2$). Hydrogen atoms were then included in the organometallic molecule in idealized positions on the basis of d(C–H) = 0.96 Å and thermal parameters equal to 1.2 times the isotropic equivalent value for the atom to which it was attached. Hydrogen atoms were allowed to ride with the atoms to which they were attached during refinement but were not themselves refined. Refinement to convergence led to R = 4.95% and R_w = 5.19% (GOF = 1.387). The somewhat high residuals reflect, in part, our inability to propose an adequate model for the extreme disorder found in the THF molecule. Indications of the apparent disorder of the solvent molecule are the rather large thermal parameters and physically unreasonble bond parameters associated with it. The solvent molecule was located about the twofold rotational axis (the O atom is situated on the axis). Since THF does not possess such site symmetry, no "model" could be proposed to "fit" THF to the observed electron density maps. In all, 390 parameters were refined by using 3977 independent reflections, $F_o \ge 2\sigma|F_o|$, giving a data to parameter ratio of 10.2/1. The two highest peaks on the final difference map were ~0.7 e/Å^3 and were associated with the THF molecule of solvation.

The analytical scattering factors for neutral atoms were used and were obtined from the usual sources. Both $\Delta f'$ and $\Delta f''$ values were included for all non-hydrogen atoms.

Description of Crystal and Molecular Structure

The crystal structure consists of discrete neutral molecules of bis(μ-diphenylphosphido)bis[1,2-bis(diphenylphosphino)ethane]dirhodium with an equal number of tetrahydrofuran molecules in the lattice. The packing arrangement is illustrated stereographically in Figure 1. The molecular packing is governed by van der Waals forces, and closest intermolecular distances do not suggest any unusual interactions between tetrahydrofuran and the dirhodium complex.

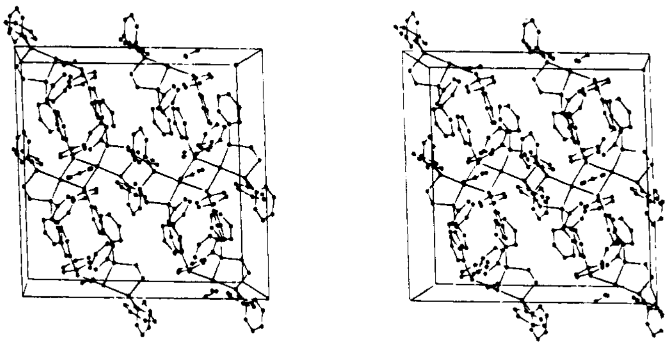

Figure 1. Molecular packing diagram for $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$ viewed down the b axis of the unit cell. Hydrogen atoms have been omitted.

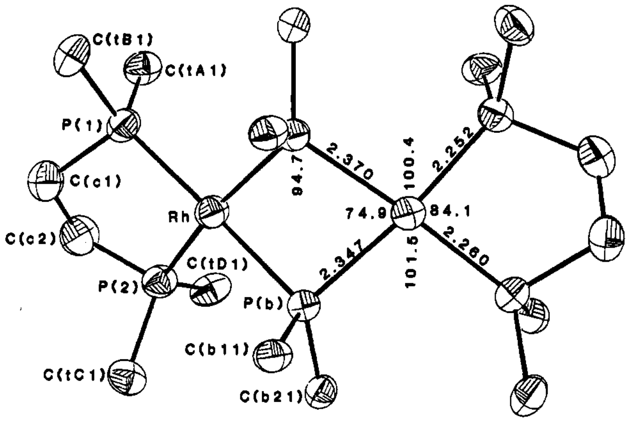

Figure 2. Molecular structure and labeling scheme for $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$ with the crystallographic twofold rotational axis nearly vertical to the plane of the page. In the text, primed atoms are related to the labeled atoms by this axis. (b = bridging, c = connecting, and t = terminal.) Only the first carbon atom of each phenyl ring is shown, and the thermal ellipsoids are depicted at the 50% probability level.

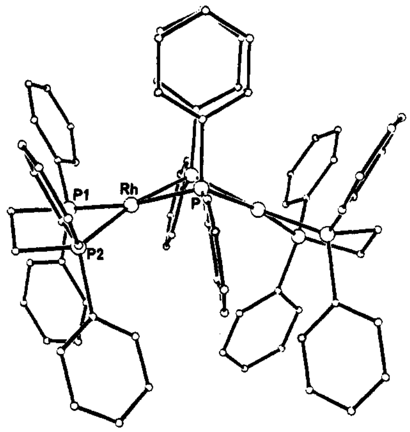

Figure 3. Perspective drawing of $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$ showing the dihedral angle (133.4°) relating the two Rh atom environments. Hydrogen atoms have been omitted for clarity.

Two enantiomorphs of the rhodium complex exist because of the coordination chirality induced by the chelating DPPE ligands. Both the $\delta\delta$ and $\lambda\lambda$ forms are present in the unit cell. Only one form, however, is unique in the crystal; the other is generated by the crystallographically imposed c-glide plane. The meso form of the complex ($\delta\lambda$ or $\lambda\delta$) is not observed in this structure.

---

(12) Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349.

Table II. Fractional Atomic Coordinates ($\times 10^4$) and Their Estimated Standard Deviations for $[Rh(\mu\text{-}PPh_2)(DPPE)]_2 \cdot C_4H_8O$[a]

atom	*x*	*y*	*z*
Rh	300 (1)	2896 (1)	3350 (1)
P(b)	690 (1)	3287 (1)	2274 (1)
P(1)	−117 (1)	2686 (1)	4395 (1)
P(2)	1265 (1)	2379 (1)	3809 (1)
C(c1)	631 (3)	2698 (4)	5014 (3)
C(c2)	1178 (3)	2210 (4)	4739 (3)
C(b11)	1505 (3)	2925 (3)	1976 (3)
C(b12)	2095 (3)	3341 (4)	1884 (3)
C(b13)	2685 (3)	3026 (4)	1647 (4)
C(b14)	2706 (4)	2292 (4)	1504 (4)
C(b15)	2142 (3)	1858 (4)	1594 (3)
C(b16)	1546 (3)	2166 (3)	1817 (3)
C(b21)	852 (3)	4290 (3)	2264 (3)
C(b22)	1146 (5)	4652 (4)	2815 (4)
C(b23)	1311 (6)	5402 (5)	2796 (5)
C(b24)	1162 (4)	5809 (4)	2219 (5)
C(b25)	871 (6)	5457 (5)	1674 (5)
C(b26)	716 (4)	4699 (4)	1693 (4)
C(tA1)	−486 (3)	1774 (4)	4605 (3)
C(tA2)	−810 (4)	1632 (4)	5214 (4)
C(tA3)	−1025 (4)	915 (4)	5371 (4)
C(tA4)	−929 (5)	349 (5)	4944 (5)
C(tA5)	−596 (4)	482 (4)	4336 (4)
C(tA6)	−385 (3)	1185 (4)	4167 (4)
C(tB1)	−706 (3)	3349 (4)	4779 (3)
C(tB2)	−1402 (3)	3251 (4)	4720 (3)
C(tB3)	−1849 (4)	3783 (5)	4962 (4)
C(tB4)	−1584 (5)	4413 (5)	5288 (4)
C(tB5)	−893 (5)	4508 (6)	5351 (5)
C(tB6)	−461 (5)	3986 (5)	5092 (4)
C(tC1)	1475 (3)	1439 (4)	3512 (3)
C(tC2)	1051 (4)	1108 (4)	3018 (4)
C(tC3)	1168 (5)	413 (5)	2773 (4)
C(tC4)	1734 (5)	26 (5)	3014 (5)
C(tC5)	2160 (5)	326 (5)	3512 (5)
C(tC6)	2034 (4)	1037 (4)	3766 (4)
C(tD1)	2087 (3)	2875 (3)	3783 (3)
C(tD2)	2610 (3)	2670 (5)	3391 (4)
C(tD3)	3193 (4)	3111 (6)	3352 (5)
C(tD4)	3257 (4)	3746 (5)	3719 (4)
C(tD5)	2737 (4)	3960 (4)	4128 (5)
C(tD6)	2152 (4)	3526 (4)	4160 (5)
Cs	4795 (7)	3328 (9)	1996 (8)
Cs′	4838 (7)	2528 (7)	2108 (6)
Os	5000	3758 (14)	2500

[a] Thermal parameters and hydrogen atom coordinates are available as supplementary material; b = bridging, c = connecting, t = terminal, s = solvent, THF.

The atom labeling scheme for $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$ is shown in Figure 2, and a view showing the distortions from planarity of the Rh atom environments is shown in Figure 3. Atomic coordinates are given in Table II, and important bond distances and angles are given in Table III. The molecule possesses a crystallographically imposed twofold axis of rotation; primed atoms in this discussion are related to nonprimed atoms by this axis. The symmetry axis is mutually perpendicular to the Rh–Rh′ and P(b)–P(b′) vectors. The Rh_2P_2 central ring is bent along the P–P vector, and the dihedral angle formed by the planes Rh–P(b)–P(b′) and Rh′–P(b)–P(b′) is 133.4 (4)°. This configuration of the Rh_2P_2 ring leads to axial and equatorial phenyl groups of the diphenylphosphido ligands. This would at first appear unfavorable because of the steric requirements of the axial phenyl groups. The axial phenyl groups, however, maintain efficient packing by being almost parallel to one another. This packing behavior is observed also in the alkylphenylphosphido-bridged complex $[Pt(\mu\text{-}PhP(CH_2)_3PPh_2)(CH_3)]_2$.[13] The bent Rh_2P_2 configuration found in the title compound may be contrasted with the rigorously planar Pt_2P_2 core in the isoelectronic complex $[Pt(\mu\text{-}PPh_2)(DPPE)]_2^{2+}$.[12]

Table III. Bond Distances and Bond Angles for $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$ with Estimated Standard Deviations

(A) Bond Distances (Å)

Rh···Rh′	3.471 (1)	P(1)–C(c1)	1.855 (6)
Rh–P(b)	2.370 (1)	P(1)–C(tA1)	1.845 (7)
Rh–P(b′)	2.347 (1)	P(1)–C(tB1)	1.837 (7)
Rh–P(1)	2.260 (2)	P(2)–C(c2)	1.854 (7)
Rh–P(2)	2.252 (2)	P(2)–C(tC1)	1.839 (7)
P(b)···P(b′)	2.868 (3)	P(2)–C(tD1)	1.839 (6)
P(b)–C(b11)	1.834 (6)	C(c1)–C(c2)	1.499 (10)
P(b)–C(b21)	1.833 (6)	⟨av⟩ aromatic (C–C)	1.380 (12)

(B) Bond Angles (deg)

Rh–P(b)–Rh′	94.7 (1)	P(2)–Rh–P(b′)	170.4 (1)
P(b)–Rh–P(b′)	74.9 (1)	Rh–P(B)–C(b11)	115.7 (2)
P(b)–Rh–P(1)	172.2 (1)	Rh–P(B)–C(b21)	115.3 (2)
P(b)–Rh–P(2)	100.4 (1)	Rh–P(1)–C(c1)	106.4 (2)
P(1)–Rh–P(2)	84.1 (1)	Rh–P(2)–C(c2)	110.4 (2)
P(1)–Rh–P(b′)	101.5 (1)	C(b11)–P(B)–C(b21)	101.2 (3)

The title compound is the first example of a rhodium–phosphido complex without metal–metal bonding; the Rh···Rh vector, 3.471 (1) Å, is outside the accepted range for significant metal–metal bonding.[14] This absence of Rh–Rh bonding is particularly significant, since the resulting four-coordinate rhodium atoms have 16, rather than 18, valence electrons. Previously reported rhodium–phosphido complexes contain Rh–Rh bonds; and, consequently, in general the metal centers satisfy the 18-electron rule.[7,11] The bond angles in the Rh_2P_2 ring clearly support the absence of the metal–metal bond. Vahrenkamp[15] reported the structures of the isoelectronic series $[(CO)_4M\text{–}P(CH_3)_2]_2$ (M = Mn, Cr, V) in which the formal M–M bond order increases from 0 to 2. He found that, in the absence of metal–metal (Mn, Mn) bonding, the P–M–P′ angle is acute, 76.9 (1)°, whereas the M–P–M′ angle is obtuse, 103.1 (1)°. The reverse relationship exists for the two compounds with metal–metal bonds. The related angles found for our title compound are P(b)–Rh–P(b)′ = 74.9 (1)° and Rh–P(b)–Rh′ = 94.7 (1)°. The P(b)–Fe–P(b)′ angle in $[Fe(CO)_3(\mu\text{-}PMe_2)I]_2$, which also has no metal–metal bonding, is 77.6 (1)°.[10b]

The coordination geometry of the rhodium atoms is almost tetragonal planar, with a distortion from planarity (torsion angle) of 4.6°. This distortion is probably due to strain introduced upon chelation of the DPPE ligands. The chelate strain also causes the P(1)–Rh–P(2) angle to be decreased to 84.1 (1)°.

The Rh–P(1), 2.260 (2) Å, and Rh–P(2), 2.252 (2) Å, distances are in the range of normal rhodium–phosphine distances.[16] On the other hand, the Rh–P(b) and Rh–P(b′) distances, 2.370 (1) and 2.347 (1) Å, are longer than corresponding Rh–P distances in most previous rhodium–phosphido complexes (2.28–2.32 Å).[9,14] The longer Rh–P(b) distance is probably due to the long Rh···Rh nonbonding distance, as well as to the greater localization of electron density at rhodium caused by the absence of metal–metal bonding. The unsaturation of the rhodium atoms in $[Rh(\mu\text{-}PPh_2)(DPPE)]_2$ implies a high degree of reactivity in this complex, and the chemical behavior of this and similar complexes has been studied.[11] Carty et al. have analyzed the Pt–P bond distances in $[Pt(\mu\text{-}PPh_2)(DPPE)]_2^{2+}$ in terms of the relative trans-directing influence of organophosphido bridges to terminal

---

(13) Meek, D. W.; Waid, R.; Tau, K. D.; Kirchner, R. M.; Morimoto, C. N. *Inorg. Chim. Acta* **1982**, *64*, L221.

(14) Billig, E.; Jamerson, J. D.; Pruett, R. L. *J. Organomet. Chem.* **1980**, *192*, C49. Jamerson, J. D.; Pruett, R. L.; Billig, E.; Fiato, F. A. *Ibid.* **1980**, *193*, C43.

(15) Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472.

(16) (a) Mason, R.; Meek, D. W. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 183–194. (b) Christoph, G. G.; Blum, P.; Liu, W. C.; Elia, A.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 894.

tertiary phosphines.[12] On the basis of Pt–P_{bridge} distances (average 2.348 Å) and Pt–P (terminal) distances (average 2.331 Å), they concluded that the two types of phosphorus substituents compete equally. In contrast to the nearly equal M–P bond distances found in the Pt complex, the two types of Rh–P bond distances differ significantly in the title compound: Rh–P_{bridge}, average 2.359 Å; Rh–$P_{terminal}$, average 2.256 Å. In terms of the relative bond-lengthening influences in the title compound, therefore, the bridging diphenylphosphido group would have to be considered to exert the weaker *trans*-directing influence.

The structural features as reported are fully consistent with predictions based on $^{31}P\{^1H\}$ NMR analysis.[5a,11] In substantiation of this structural report, we suggest that the observed $\delta_{P_{bridge}}$ resonance at −104 further demonstrates the lack of significant Rh–Rh bonding in this complex and of the utility of ^{31}P NMR spectroscopy for the structural characterization of transition-metal complexes that contain bridging organophosphido ligands.

Registry No. $[Rh(\mu\text{-}PPh_2)(DPPE)]_2\cdot C_4H_8O$, 84332-81-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, atom coordinates and isotropic thermal parameters, bond lengths, bond angles, and anisotropic thermal parameters (28 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of British Columbia, Vancouver, BC, Canada V6T 1Y6

Phosphine Complexes of Zirconium(IV) and Hafnium(IV) Obtained through the Use of Hybrid Multidentate Ligands. X-ray Crystal Structure of $ZrCl_2[N(SiMe_2CH_2PMe_2)_2]_2$

MICHAEL D. FRYZUK,* HUGH DAVID WILLIAMS, and STEVEN J. RETTIG

Received June 30, 1982

The reaction of $LiN(SiMe_2CH_2PR_2)_2$ with either $ZrCl_4$ or $HfCl_4$ generates new complexes of the formula $MCl_2[N(SiMe_2CH_2PR_2)_2]_2$ (M = Zr or Hf; R = Me or Ph). Both of the potentially tridentate hybrid ligands bind only in a bidentate fashion, generating coordinated and uncoordinated phosphines in the same molecule. The single-crystal X-ray structure of $ZrCl_2[N(SiMe_2CH_2PMe_2)_2]_2$ (space group *Pbca*; $a = 16.8307$ (9), $b = 18.4663$ (8), $c = 24.285$ (2) Å; $Z = 8$; $R = 0.036$ ($R_w = 0.046$)) indicates a distorted-octahedral geometry with trans chloride and cis phosphine ligands. The molecule is chiral both in the solid state and in solution by virtue of a "gear" effect of the two bulky disilylamide ligands.

Introduction

The chemistry of the group 4 metals, Ti, Zr, and Hf, is dominated by complexes containing the η^5-$C_5H_5^-$ or the η^5-$C_5Me_5^-$ ligand.[1] While these derivatives have established the unique reactivity patterns of these metals, new ligands and new combinations of ligands are currently being investigated to extend the potentially rich chemistry of this group.[2] One donor type that has only recently been incorporated into complexes of zirconium[2,4,5] and hafnium[6] is the *soft* phosphine ligand, PR_3 (R = aryl or alkyl). The evidence so far suggests that monodentate phosphine complexes of Zr(IV) are thermally labile[4] and subject to displacement by *hard* ligands such as NEt_3 or by chelating ligands. Clearly, mismatching the *soft* phosphine donors with the *hard* Zr(IV) and Hf(IV) centers is a major factor in this behavior. To overcome this mismatching of donors and acceptors, we have developed a new series of "hybrid" ligands[7] that incorporate the *soft* phosphine donor into a chelating array (Figure 1) that also contains the *hard* amido donor, $^-NR_2$ (R = alkyl, aryl, or silyl). Since amides of Zr(IV) and Hf(IV) are stable, well-known[8-10] complexes, we anticipated that the amide portion of the chelating ligand would serve as an *anchor* and reduce the tendency for phosphine dissociation. We present here full details of our initial work in this area, which has provided a new entry into phosphine derivatives of group 4B, specifically zirconium and hafnium.

Experimental Section

General Information. All manipulations were performed under prepurified nitrogen in a Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system or in standard Schlenk-type glassware. $ZrCl_4$ and $HfCl_4$ were obtained from Alfa and sublimed prior to use. Methylene chloride (CH_2Cl_2) was purified by distillation from CaH_2 under argon. Toluene, hexanes, and diethyl ether (Et_2O) were distilled from sodium–benzophenone ketyl under argon. Melting points were determined on a Mel-Temp apparatus in sealed capillaries under nitrogen and are uncorrected. Carbon, hydrogen, and nitrogen analyses were performed by Mr. P. Borda of this department. ^1H NMR spectra were recorded on one of the following instruments, depending on the complexity of the particular spectrum: Varian EM-360L, Bruker WP-80, Varian XL-100, or Bruker WH-400. $^{31}P\{^1H\}$ spectra were run at 32.442 MHz on the Bruker WP-80 in 10-mm tubes fitted with inserts for the internal standard $P(OMe)_3$ (set at +141.0 ppm relative to 85% H_3PO_4). Deuterated benzene (C_6D_6) and deuterated toluene (C_7D_8) were purchased from Aldrich, dried over activated 4-Å molecular sieves, and vacuum transferred prior to use. The starting ligand precursors $LiN(SiMe_2CH_2PR_2)_2$ (R = Ph[11b] or Me[12]) were prepared as described elsewhere.

$ZrCl_2[N(SiMe_2CH_2PPh_2)_2]_2$. A solution of $LiN(SiMe_2CH_2PPh_2)_2$ (8.56 g, 16.0 mmol) in Et_2O (150 mL) was added dropwise to a cold (−4 °C) suspension of $ZrCl_4$ (1.86 g, 8.0 mmol) in Et_2O (100 mL). The mixture was warmed to room temperature and stirred for 3 h. After the Et_2O was removed in vacuo, the residue was extracted with hexanes (2 × 20 mL) to remove the lemon yellow, "tris" derivative, $ZrCl[N(SiMe_2CH_2PPh_2)_2]_3$. Although this material was never ob-

---

(1) Labinger, J. A. *J. Organomet. Chem.* **1982**, *227*, 341.

(2) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1982**, *21*, 840.

(3) Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 245.

(4) Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319.

(5) Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941.

(6) Wreford, S. S.; Whitney, J. F. *Inorg. Chem.* **1981**, *20*, 3918.

(7) Bertini, I.; Dapporta, P.; Fallani, G.; Sacconi, L. *Inorg. Chem.* **1971**, *10*, 1703 and references therein.

(8) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 1724, 2928.

(9) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Wiley: New York, 1979.

(10) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

(11) (a) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3492. (b) Fryzuk, M. D.; MacNeil, P. A.; Secco, A. S.; Rettig, S. J.; Trotter, J. *Organometallics* **1982**, *1*, 918.

(12) Fryzuk, M. D.; Brzezowski, C.; MacNeil, P. A.; Williams, H. D., manuscript in preparation.

0020-1669/83/1322-0863$01.50/0