

[Ph₂P(CH₂)₃]₂Zn: X-ray Crystal Structure Determination and Reaction with Group 11 Metal Salts

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The structure of bis[3-(diphenylphosphino)propyl]zinc, [Ph₂P(CH₂)₃]₂Zn (I), has been determined by X-ray diffraction analysis. Crystals of I are monoclinic, space group *P*₂₁/*a*, with four molecules in a unit cell of dimensions *a* = 14.224 (6) Å, *b* = 19.340 (9) Å, *c* = 9.984 (2) Å, and β = 102.14 (3)°. The structure was refined to *R* = 0.069 (*R*_w = 0.054) for 1732 observed reflections. The zinc atom is four-coordinate, both phosphorus atoms being involved in intramolecular coordination. The value of the carbon-zinc-carbon angle of 147.1 (4)° is intermediate between that of a linear and of a tetrahedral bond arrangement. NMR spectroscopy shows that the chelating monomeric structure persists in solution. Reactions of I with group 11 metal salts are described. Only the gold derivative, dimeric [3-(diphenylphosphino)propyl]gold, [Ph₂P(CH₂)₃Au]₂, is sufficiently stable to allow isolation. A cyclic structure containing a ten-membered Au₂P₂C₆ ring is proposed.

Introduction

In recent years we have studied the coordination chemistry of organozinc compounds containing functional substituents in the groups bound to zinc via carbon.¹⁻⁷ When the functional group is attached to the α-carbon atom, useful synthetic reagents are obtained, e.g. the Reformatsky reagent "BrZnCH₂COOR" and the related zinc enolates. We recently reported on the structure and reactivity of these reagents.^{4,5} Compounds in which the functional group and the metal are separated by more than two (carbon) atoms have not been used in organic synthesis, nor are they likely to be used for this purpose in the near future. However, elucidation of their structures provides an insight into the more subtle aspects of organozinc coordination chemistry. We recently reported the structures of a number of ω-substituted diorganozinc compounds, viz. Zn[(CH₂)_nX]₂ (*n* = 3, X = OMe,⁶ SMe,⁷ NMe₂;⁷ *n* = 4, X = OMe,⁶ and discussed the hybridization of the zinc in them.⁷ We now report the molecular structure of [Ph₂P(CH₂)₃]₂Zn (I) and the utilization of this compound for the synthesis of corresponding alkylcopper, -silver, and -gold compounds.

Experimental Section

All manipulations were performed in an atmosphere of oxygen- and moisture-free nitrogen, with normal Schlenk techniques. Solvents used were distilled from sodium/benzophenone prior to use. ¹H NMR spectra were recorded on a Varian EM-390

Table I. Crystal Data and Details of the Structure Determination

| a. Crystal Data | |
|---|--|
| formula | C ₃₀ H ₃₂ P ₂ Zn |
| mol wt | 519.91 |
| cryst system | monoclinic-b |
| space group | No. 14, <i>P</i> ₂ ₁ / <i>a</i> |
| <i>a</i> , Å | 14.224 (6) |
| <i>b</i> , Å | 19.340 (9) |
| <i>c</i> , Å | 9.984 (2) |
| β, deg | 102.14 (3) |
| <i>V</i> , Å ³ | 2685 (2) |
| <i>Z</i> | 4 |
| <i>D</i> _{calcd} , g/cm ³ | 1.286 |
| <i>F</i> (000), electrons | 1088 |
| μ(Cu Kα), cm ⁻¹ | 25.3 |
| cryst size, mm | 0.13 × 0.25 × 0.58 |
| b. Data Collection | |
| θ _{min} , θ _{max} , deg | 2.3, 45 |
| radiatn, Å | Cu Kα (Ni filtered), 1.5418 |
| ω/2θ scan, deg | Δω = 0.70 + 0.15 tan θ |
| horiz and vert aperture, mm | 3, 5 |
| dist to crystal, mm | 173 |
| ref reflectns | 200; 040; 002 |
| data set | <i>h</i> , 0 to 13; <i>k</i> , -17 to +17; <i>l</i> , -9 to +8 |
| total data | 4572 |
| unique data | 3244 |
| obsd data (<i>I</i> > 2.5σ(<i>I</i>)) | 1732 |
| c. Refinement | |
| NO, NV, S | 1732, 311, 2.1 |
| <i>R</i> , <i>R</i> _w | 0.069, 0.054 |
| weighting scheme | ω = 1/σ ² (<i>F</i>) |
| (Δ/σ) _{av} | 0.1 |
| min and max resd dens, e Å ⁻³ | 0.44, -0.41 |

spectrometer with Me₄Si as an internal standard. ¹³C and ³¹P NMR spectra were recorded on a Bruker WP-200 spectrometer with Me₄Si as an internal standard and 85% H₃PO₄ as an external standard, respectively. Microanalyses were performed at the Institute of Applied Chemistry TNO (Zeist, The Netherlands) under the supervision of Mr. G. J. Rotscheid. [Ph₂P(CH₂)₃]₂Zn³ and Au(CO)Cl⁸ were prepared according to literature methods.

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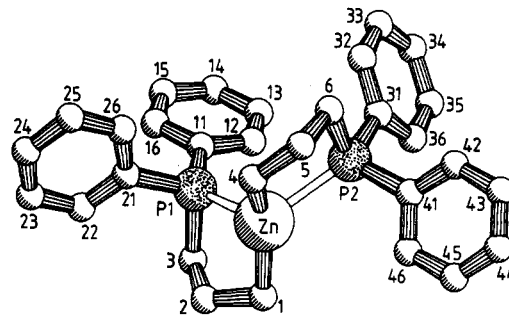
Table II. Fractional Atomic Coordinates for the Non-Hydrogen Atoms and Equivalent Isotropic Temperature Factors

| atom | x | y | z | $U_{\text{eq}}^a, \text{\AA}^2$ |
|-------|-------------|-------------|-------------|---------------------------------|
| Zn | 0.1291 (1) | 0.25852 (6) | 0.0913 (1) | 0.0772 (5) |
| P(1) | 0.0364 (2) | 0.2404 (1) | -0.1596 (2) | 0.070 (1) |
| P(2) | 0.0245 (2) | 0.3407 (1) | 0.2006 (2) | 0.065 (1) |
| C(1) | 0.2339 (7) | 0.3004 (4) | 0.008 (1) | 0.078 (4) |
| C(2) | 0.224 (1) | 0.262 (1) | -0.128 (1) | 0.084 (6) |
| C(3) | 0.1388 (7) | 0.2736 (5) | -0.226 (1) | 0.091 (4) |
| C(4) | 0.0931 (8) | 0.1863 (4) | 0.2155 (8) | 0.088 (4) |
| C(5) | 0.0476 (8) | 0.2142 (5) | 0.324 (1) | 0.109 (5) |
| C(6) | -0.0308 (7) | 0.2695 (4) | 0.281 (1) | 0.086 (4) |
| C(11) | -0.0645 (6) | 0.2846 (4) | -0.2701 (8) | 0.066 (4) |
| C(12) | -0.0831 (7) | 0.3521 (5) | -0.2404 (9) | 0.090 (4) |
| C(13) | -0.1533 (8) | 0.3902 (5) | -0.324 (1) | 0.103 (5) |
| C(14) | -0.2056 (8) | 0.3615 (6) | -0.442 (1) | 0.091 (5) |
| C(15) | -0.1906 (7) | 0.2938 (6) | -0.473 (1) | 0.083 (4) |
| C(16) | -0.1179 (7) | 0.2540 (5) | -0.3889 (8) | 0.075 (4) |
| C(21) | 0.0219 (7) | 0.1497 (5) | -0.212 (1) | 0.059 (4) |
| C(22) | 0.0683 (8) | 0.1199 (6) | -0.305 (1) | 0.098 (5) |
| C(23) | 0.059 (1) | 0.0495 (7) | -0.333 (1) | 0.131 (6) |
| C(24) | 0.002 (1) | 0.0102 (6) | -0.266 (1) | 0.104 (5) |
| C(25) | -0.0450 (8) | 0.0383 (7) | -0.175 (1) | 0.095 (5) |
| C(26) | -0.0347 (7) | 0.1090 (6) | -0.144 (1) | 0.080 (4) |
| C(31) | -0.0761 (7) | 0.3994 (4) | 0.1435 (9) | 0.066 (4) |
| C(32) | -0.1697 (7) | 0.3778 (5) | 0.110 (1) | 0.105 (5) |
| C(33) | -0.2450 (8) | 0.4228 (5) | 0.048 (1) | 0.128 (5) |
| C(34) | -0.2249 (8) | 0.4891 (6) | 0.022 (1) | 0.090 (5) |
| C(35) | -0.1322 (9) | 0.5115 (5) | 0.058 (1) | 0.090 (5) |
| C(36) | -0.0545 (8) | 0.4681 (4) | 0.1168 (9) | 0.079 (4) |
| C(41) | 0.0969 (9) | 0.3846 (4) | 0.3474 (9) | 0.061 (4) |
| C(42) | 0.0592 (8) | 0.4122 (5) | 0.449 (1) | 0.091 (5) |
| C(43) | 0.117 (1) | 0.4445 (6) | 0.565 (1) | 0.112 (5) |
| C(44) | 0.214 (1) | 0.4488 (6) | 0.570 (1) | 0.115 (5) |
| C(45) | 0.254 (1) | 0.4214 (5) | 0.472 (1) | 0.115 (5) |
| C(46) | 0.1962 (9) | 0.3897 (5) | 0.353 (1) | 0.088 (5) |

$$^a U_{\text{eq}} = \frac{1}{3} \sum \sum U_{ij} a_i^* a_j^* a_i a_j$$

Reaction of I with Au(CO)Cl. $[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Au}]_2$ was prepared by adding a solution of 0.63 g (2.42 mmol) of Au(CO)Cl in 30 mL of benzene to a stirred solution of 0.78 g (1.50 mmol) of I in 30 mL of benzene. The addition took 10 min and was carried out at 10 °C. A spontaneous, vigorous evolution of carbon monoxide took place, and a clear, light-brown solution resulted. The reaction mixture was stirred for an additional hour at room temperature and then hydrolyzed to decompose excess of I. The resulting slurry was evaporated to dryness, and diphenylpropylphosphine was removed by extraction with cold pentane. The product (0.62 g, 1.46 mmol) was obtained (67% yield) by extraction of the residue with benzene. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{AuP}$ (Found): Au, 46.3 (45.5); P, 7.3 (6.7). The compound is dimeric in benzene (ebulliometry) and decomposes at 80 °C (DTA; 5 °C/min).

Data Collection and Structure Determination of I. Suitable crystals were obtained by recrystallization from toluene at -20 °C. Data for a poorly diffracting colorless transparent crystal, mounted under nitrogen in a Lindemann glass capillary, were collected on a Enraf-Nonius CAD4F diffractometer. Crystal data and numerical details of the structure determination are given in Table I. Lattice parameters with standard deviations were determined from the setting angles of 11 reflections ($9 < \theta < 23^\circ$). The observed extinctions ($h0l, h = 2n + 1; 0k0, k = 2n + 1$) indicated space group $P2_1/a$. Standard deviations in the intensities were increased according to an analysis of the variance of the reference reflections:⁹ $\sigma^2(I) = \sigma_{\text{ref}}^2(I) + (0.02I)^2$. The redundant reflection set was corrected for Lp and for a small decay of 3.5% over 71 hours of X-ray exposure time and averaged ($R_{\text{av}} = 0.06$) after correction for absorption with DIFABS¹⁰ (minimum and maximum correction 0.68 and 1.68, respectively). The structure was solved by direct methods using the program SHELX84¹¹ and

**Figure 1.** PLUTO drawing (EUCLID version¹⁵ of I with the adopted numbering scheme indicated. C(2) is disordered (0.53/0.47); the minor disorder component is not shown. The hydrogen atoms have been omitted for clarity.**Table III. Selected Data on the Molecular Geometry of I**

| (a) Bond Distances (Å) | | | |
|--------------------------|------------|--|-----------|
| Zn-P(1) | 2.598 (3) | P(2)-C(41) | 1.82 (1) |
| Zn-P(2) | 2.572 (3) | C(1)-C(2) | 1.53 (2) |
| Zn-C(1) | 2.02 (1) | C(2)-C(3) | 1.41 (2) |
| Zn-C(4) | 2.00 (1) | C(4)-C(5) | 1.48 (1) |
| P(1)-C(3) | 1.84 (1) | C(5)-C(6) | 1.54 (1) |
| P(1)-C(11) | 1.83 (1) | $\langle \text{C}(11)\cdots\text{C}(16) \rangle$ | 1.383 (5) |
| P(1)-C(21) | 1.83 (1) | $\langle \text{C}(21)\cdots\text{C}(26) \rangle$ | 1.382 (7) |
| P(2)-C(6) | 1.85 (1) | $\langle \text{C}(31)\cdots\text{C}(36) \rangle$ | 1.385 (7) |
| P(2)-C(31) | 1.82 (1) | $\langle \text{C}(41)\cdots\text{C}(46) \rangle$ | 1.387 (7) |
| (b) Bond Angles (deg) | | | |
| P(1)-Zn-P(2) | 105.72 (9) | Zn-P(2)-C(6) | 93.5 (3) |
| P(1)-Zn-C(1) | 85.8 (3) | Zn-P(2)-C(31) | 137.6 (3) |
| P(1)-Zn-C(4) | 111.0 (3) | Zn-P(2)-C(41) | 110.6 (4) |
| P(2)-Zn-C(1) | 118.0 (2) | C(6)-P(2)-C(31) | 102.8 (4) |
| P(2)-Zn-C(4) | 85.5 (3) | C(6)-P(2)-C(41) | 102.6 (4) |
| C(1)-Zn-C(4) | 147.1 (4) | C(31)-P(2)-C(41) | 103.7 (4) |
| Zn-P(1)-C(3) | 91.2 (3) | Zn-C(1)-C(2) | 103.5 (8) |
| Zn-P(1)-C(11) | 133.9 (3) | C(1)-C(2)-C(3) | 116 (1) |
| Zn-P(1)-C(21) | 114.1 (3) | P(1)-C(3)-C(2) | 109.0 (8) |
| C(3)-P(1)-C(11) | 101.5 (4) | Zn-C(4)-C(5) | 114.1 (6) |
| C(3)-P(1)-C(21) | 106.4 (5) | C(4)-C(5)-C(6) | 116.9 (8) |
| C(11)-P(1)-C(21) | 104.4 (4) | P(2)-C(6)-C(5) | 106.8 (7) |
| (c) Torsion Angles (deg) | | | |
| Zn-P(1)-C(3)-C(2) | 26.7 (9) | Zn-P(2)-C(6)-C(5) | 35.5 (6) |
| P(1)-C(3)-C(2)-C(1) | -65 (1) | P(2)-C(6)-C(5)-C(4) | -57 (1) |
| C(3)-C(2)-C(1)-Zn | 66 (1) | C(6)-C(5)-C(4)-Zn | 45 (1) |
| C(2)-C(1)-Zn-P(1) | -30.2 (7) | C(5)-C(4)-Zn-P(2) | -12.8 (7) |
| C(1)-Zn-P(1)-C(3) | 3.7 (4) | C(4)-Zn-P(2)-C(6) | -13.1 (4) |
| Zn-P(1)-C(11)-C(12) | 22.8 (9) | Zn-P(2)-C(41)-C(46) | 22.6 (7) |
| C(3)-P(1)-C(21)-C(22) | -11 (1) | C(6)-P(2)-C(31)-C(32) | -28 (1) |

refined with a locally modified Eclipse S/230 minicomputer implementation of SHELX76.¹² Hydrogen atoms were introduced on calculated positions and refined with fixed geometry (C-H = 1.08 Å, $U = 0.16 \text{\AA}^2$). One of the chelating rings was found to be disordered for the position of C(2) [C(20): mirror image related with respect to the ring plane] and refined with a disorder model (0.53/0.47) including soft bond constraints. Blocked full-matrix refinement on F converged at $R = 0.069$. The non-hydrogen atoms were refined with anisotropic thermal parameters. Final positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are listed in Table II. Scattering factors were taken from Cromer and Mann¹³ and anomalous dispersion terms from Cromer and Liberman.¹⁴ Geometrical calculations were done with PLATO.¹⁵

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Table IV. NMR Spectroscopic Data for $\text{XC}_\alpha\text{H}_2\text{C}_\beta\text{H}_2\text{C}_\gamma\text{H}_2\text{P}(\text{C}_6\text{H}_5)_2$

| | | X | | | | |
|-------------------|----------|------------------------|--------------------------|------------------------|--------------------------|-------------------------------|
| | | H | | $^{1/2}\text{Zn}$ | | |
| | | C_6D_6 | CD_2Cl_2 | C_6D_6 | CD_2Cl_2 | Au (C_6D_6) |
| $^{13}\text{C}^a$ | α | 15.92 (13.5) | 15.79 (13.5) | 12.19 (c) | 11.60 (d) | 30.98 (96.4/4.4) |
| | β | 19.81 (17.0) | 19.72 (16.7) | 25.99 (13.4) | 25.71 (6) | 27.67 (~s) |
| | γ | 30.81 (12.3) | 30.48 (11.5) | 33.65 (4.1) | 33.15 (~2) | 33.11 (28.2) |
| $^1\text{H}^b$ | α | | | 1.07 (t) ^f | | 2.31 (m) ^e |
| | β | | | 2.26 (m) | | 2.27 (m) ^e |
| | γ | | | 2.17 (m) | | 2.52 (m) ^e |
| $^{31}\text{P}^b$ | | | | -13.9 (s) | | 44.5 (s) |

^a $J_{\text{C-P}}$ coupling in parentheses. ^bPeak multiplicity in parentheses. ^c"Filled-in" doublet; spacing 33.0 Hz. ^dEqual-intensity triplet; spacing 19.5 Hz. ^eAssignment tentative. ^fAbbreviations: t, triplet; m, multiplet; s, singlet.

Results and Discussion

The Crystal Structure of Bis[3-(diphenylphosphino)propyl]zinc, $[\text{Ph}_2\text{P}(\text{CH}_2)_3]_2\text{Zn}$ (I). The monoclinic unit cell contains four discrete molecules of the title compound. A PLUTO plot, with the adopted numbering scheme indicated, is given in Figure 1. Selected data on the molecular geometry are assembled in Table III. The molecule has no twofold axial symmetry. It consists of a four-coordinate zinc atom carrying two 3-(diphenylphosphino)propyl groups that form chelate rings by intramolecular phosphorus to zinc coordination.

When the structure was refined, a disorder in one of the two chelate rings was observed. For the β -carbon atom C(2) two positions were found with nearly equal population (53:47). A ring puckering analysis according to Cremer and Pople¹⁶ could not discriminate between an envelope-type conformation and a half-chair-type conformation of both rings. This is probably due to the large differences in the individual bond lengths in each ring. Puckering parameters found for ring 1 ($\text{ZnP}_1\text{C}_3\text{C}_2\text{C}_1$) are $Q = 0.52$ (1) Å and $\phi = 117.1$ (9)° and for ring 2 ($\text{ZnP}_2\text{C}_6\text{C}_5\text{C}_4$) are $Q = 0.47$ (1) Å and $\phi = 81.8$ (8)°.

The asymmetry parameter analysis according to Duax et al.¹⁷ indicated a mirror plane symmetry for ring 1 with the mirror through C(2) and bisecting the Zn-P(1) bond; asymmetry parameter $\Delta C_s = 2.6$ (8)°. For ring 2 a twofold axial symmetry, with the twofold axis through Zn and the middle of the C(5)-C(6) bond, gives the best description of the conformation of the ring; asymmetry parameter $\Delta C_2 = 6.7$ (8)°.

The coordinate bonds between zinc and phosphorus (averaged 2.58 Å) are only 0.15 Å longer than the sum of the covalent radii of these elements.¹⁸ In the corresponding OMe,⁶ SMe,⁷ and NMe₂⁷ derivatives the coordinate bond lengths were about 0.35 Å longer than the sum of the covalent radii of the elements involved. This indicates that the interaction between zinc and phosphorus is stronger than that between zinc and other heteroatoms. These short zinc-phosphorus bond lengths are even more surprising when it is taken into account that the phosphorus atoms carry electron-withdrawing phenyl groups, whereas the other heteroatoms are methyl-substituted (cf. also ref 7 for a discussion on the coordination chemistry of this type of organozinc compounds). One has, of course, to be careful not to attach too much importance to these differences, since relatively weak forces are involved (may be down to a few kilocalories per mole), with corresponding flat potential energy surfaces. Small steric or electronic effects thus can give rise to rather large distortions in the

ligand to metal internal coordination.

The Structure of I in Solution. Ebulliometry showed that the compound is monomeric in benzene. The structure of I in solution was investigated by using ^{13}C and ^{31}P NMR spectroscopy. The results are gathered in Table IV. A comparison of the resonance position of the γ -carbon atom with that of the corresponding carbon in diphenylpropylphosphine shows an upfield shift of 2.84 ppm in benzene and of 3.36 ppm in CD_2Cl_2 . Corresponding shifts in the other heteroatom-containing organozinc compounds have been interpreted as proof for the existence of internal coordination.² This indicates that I occurs as the internally coordinated complex, both in benzene and in CD_2Cl_2 .

The presence of intramolecular coordination in solution is also corroborated by the nature and magnitude of the phosphorus-carbon coupling constants. In the ^1H -decoupled ^{13}C spectra of I in C_6D_6 and in CD_2Cl_2 , the carbon atom next to zinc (α -carbon) appears as a "filled-in doublet" and a triplet containing three equal-intensity lines, respectively. The other aliphatic carbon atoms appear as doublets (cf. Table IV). Although a complete analysis of these spectra was not attempted, the α -carbon absorptions are strongly indicative for the presence of an AXX' spin system^{19,20} ($A = ^{13}\text{C}$; $X, X' = ^{31}\text{P}$) in which both the AX (AX') and XX' couplings necessarily occur across zinc. The latter, then, is proof for intramolecular zinc-phosphorus coordination. Also the magnitude of the P-C couplings is easily understood when coupling across zinc is accepted (C_α , multiplet of two different $^2J_{\text{P-Zn-C}}$; C_β , apparent doublet of $^2J_{\text{P-C-C}} + ^3J_{\text{P-Zn-C-C}}$; C_γ , apparent doublet of $^1J_{\text{P-C}} + ^3J_{\text{P-Zn-C-C}}$).

The coupling constants are very dependent on the nature of the solvent (cf. Table IV). This can be understood in terms of the different contributions of solvent-dependent conformations, although the trends in numerical values are not easily explained.

Reaction of I with Group 11 Metal Salts. Organozinc compounds are well-known and very suitable reagents for alkylation or arylation of transition-metal salts.²¹ Since the introduction of potentially coordinating groups in alkyl derivatives of group 11 metals might enhance their—normally low—thermal stability, we carried out some reactions with copper, silver, and gold salts.

Upon the addition of I to a suspension of CuBr in THF at -20 °C, a clear yellow solution resulted. The ^1H NMR spectrum of this clear solution at -20 °C showed only the presence of (diphenylphosphino)propyl groups bound to zinc. When the solution was warmed to 0 °C, these ab-

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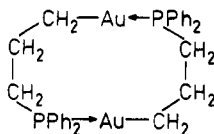


Figure 2. Schematic structure proposed for $[\text{Au}(\text{CH}_2)_3\text{PPh}_2]_2$.

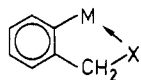


Figure 3. Functionally substituted aryl derivatives of group 11 metals. For M and X see text.

sorptions were replaced by a broad signal at 0.70 ppm. On continued warming of the solution, this signal disappeared within 10 min at 30 °C, accompanied by a rapid darkening of the solution. In the final spectrum of this solution, signals of both *n*-propyl and allyl groups were found, indicating a radical decomposition.

Similar experiments with silver nitrate yielded solutions that already darkened rapidly at -50 °C, indicating a faster formation and an even faster decomposition of the corresponding silver species.

Only from the reaction of I with $\text{Au}(\text{CO})\text{Cl}$ was a stable product obtained. The product is dimeric in benzene, and its ^1H , ^{13}C , and ^{31}P NMR data are given in Table IV. The assignments in the ^1H NMR spectrum of the three methylene groups linking the phosphorus to gold are uncertain because of the small chemical shift differences. Attempts to simulate the ^1H NMR spectrum were unsuccessful. The assignment of the aliphatic carbons in the ^{13}C spectrum is based on a comparison with those of the zinc analogue I but remains somewhat tentative. When it is assumed that the dimer has a structure analogous to that of $(\text{AuSCH}_2\text{CH}_2\text{PEt}_2)_2$,²² i.e. a ten-membered ring with linear coordination of the gold atoms, the observed phosphorus-carbon couplings can be readily explained (cf. Figure 2).

The α -carbon shows two phosphorus couplings of 96.3 and 4.4 Hz. The large one can be attributed to a $^2J_{\text{P-Au-C}}$ coupling. The value is very similar to that observed in $t\text{-Bu}_3\text{P}\cdot\text{AuMe}$,²³ i.e. 89 Hz. The smaller coupling then is

a $^3J_{\text{P-C-C}}$ coupling to the other phosphorus. The other couplings can be similarly explained and have reasonable values. Model studies show that the suggested cyclic structure is completely strain-free when the coordination of the gold is taken to be linear.

The group 11 metal compounds described here can be considered aliphatic analogues of the functionally substituted aryl derivatives (Figure 3) described by Van Koten et al.^{24,25} ($\text{X} = \text{OMe}, \text{NMe}_2$; $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) and Abicht and Issleib²⁶ ($\text{X} = \text{PPh}_2$; $\text{M} = \text{Cu}, \text{Au}$). In these compounds coordination, both intra- and intermolecular, via heteroatoms and bridging aryl groups has been established. The latter type of coordination will be far less important in aliphatic derivatives since alkyl groups are only weakly bridging ligands. The small stabilization by heteroatom coordination in the (diphenylphosphino)propyl derivatives supports the suggestion made by Van Koten and Noltes²⁷ that a full coordination sphere around a group 11 metal brought about by heteroatom coordination, and not the coordination itself, is the decisive factor in the stabilization of the metal-carbon bond. This crowding does not occur to any significant extent in our case.

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Registry No. 1, 85380-68-3; $[\text{Au}(\text{CH}_2)_3\text{PPh}_2]_2$, 107847-85-8; $\text{Au}(\text{CO})\text{Cl}$, 50960-82-2; CuBr , 7787-70-4; AgNO_3 , 7761-88-8.

Supplementary Material Available: Tables of thermal parameters, positional parameters for the minor disorder component and hydrogen atoms, and bond distances and angles and a plot of the disorder model (6 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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