Synthesis of Tetrakis[(tri-*tert*-butylphosphane)gold(I)]phosphonium Salts and Crystal Structure of the Tetraphenylboroxinate Salt $\{[(t\mathrm{Bu})_3\mathrm{PAu}]_4\mathrm{P}\}^+$ $[\mathrm{O(PhBO)_2BPh_2}]^-$

Edgar Zeller, Holger Beruda, and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München,
Lichtenbergstraße 4, D-85747 Garching

Received April 22, 1993

Key Words: Gold complexes / Phosphonium, tetrakis[(tri-*tert*-butylphosphane)gold(I)]

The reaction of $(\mathrm{Me_3Si})_3\mathrm{P}$ with $\{[(t\mathrm{Bu})_3\mathrm{PAu}]_3\mathrm{O}\}^+$ $\mathrm{BF_4^-}$ in tetrahydrofuran at −78°C affords the compound $\{[(t\mathrm{Bu})_3\mathrm{PAu}]_4\mathrm{P}\}^+$ $\mathrm{BF_4^-}$ (**1a**) in high yield. This product is converted into the tetraphenylborate salt (**1b**) by treatment with $\mathrm{Na[BPh_4]}$. The two compounds have been identified on the basis of their analytical and spectroscopic data, but could not be crystallized. In attempts to prepare single crystals of **1b**, a crystalline salt $\{[(t\mathrm{Bu})_3\mathrm{PAu}]_4\mathrm{P}\}^+$ $[\mathrm{O(PhBO)_2BPh_2}]^-$ (**1c**) has been obtained in very small quantities, probably by partial anion hydrolysis. A single crystal X-ray diffraction study of **1c** · $\mathrm{CH_2Cl_2}$ shows the compound to be built up of cations with a strongly distorted tetrahedral $(\mathrm{PAu})_4\mathrm{P}$ skeleton and anions with a planar six-membered boroxine ring. Two of the phenyl groups are attached to two trigonal-planar boron atoms and the other two phenyl groups to the third (tetrahedral) boron atom of the heterocycle. The origin of the peculiar cation structure is discussed in the light of findings with related ammonium- and arsonium-centered gold clusters.

Tetrakis[(triorganophosphane)gold(I)]*ammonium* salts of the type $\{[(\mathrm{R_3P})\mathrm{Au}]_4\mathrm{N}\}^+$ X^- have the conventional tetrahedral structures at the nitrogen center irrespective of the nature of the substituent R and the counterion X[1−5]. By contrast, the corresponding *arsonium* salts $\{[(\mathrm{R_3P})\mathrm{Au}]_4\mathrm{As}\}^+$ X^- have been shown[3,6,7] to possess a square-pyramidal structure at arsenic with acute angles Au—As—Au of ca. 70°. This configuration is at variance with classical concepts of structure and bonding[8,9], and it is only by considering[8] metal-metal bonding between seemingly closed-shell Au(I) atoms, based largely on relativistic effects[10], that this phenomenon has been rationalized in very recent theoretical treatments.

Quaternary *phosphonium* salts of the type $\{[(\mathrm{R_3P})\mathrm{Au}]_4\mathrm{P}\}^+$ X^-, for which a square-pyramidal structure has also been predicted in these theoretical studies[8,9], cannot be isolated with standard tertiary phosphanes $\mathrm{R_3P}$, except for systems with the bulky ligand $(t\mathrm{Bu})_3\mathrm{P}$, where at least NMR evidence has been obtained[11] for a cation $\{[(t\mathrm{Bu})_3\mathrm{PAu}]_4\mathrm{P}\}^+$. Chemical shifts and doublet/quintet multiplicities in the ^{31}P-NMR spectra are proof of the cation stoichiometry, but are inconclusive regarding the geometry at the central phosphorus atom[11] (tetrahedral vs. square-planar). We have now been able to isolate the $\mathrm{BF_4^-}$ and $\mathrm{BPh_4^-}$ salts of this cation and to convert it into an unusual boroxinate salt, the crystal structure of which has been determined.

Synthesis and Properties of the Phosphonium Salts

Treatment of tris(trimethylsilyl)phosphane[12] with tris[(tri-*tert*-butylphosphane)gold(I)]oxonium tetrafluoroborate[13] in tetrahydrofuran at −78°C with protection against directly incandescent light leads to a reaction mixture, from which a series of products can be precipitated by the addition of increasing quantities of pentane[11,14]. The tetrakis[(tri-*tert*-butylphosphane)gold(I)]phosphonium tetra*fluoro*borate salt (**1a**) appears as the last fraction and is obtained as an oily product, which is stable against air and water. Its NMR parameters have been confirmed[11], but attempts to crystallize the material have failed. The precipitates appearing upon addition of the first quantities of pentane to the reaction mixture are higher nuclearity clusters, the indentity of which is still under investigation. Penta- and hexanuclear compounds have been detected by analytical and spectroscopic techniques[11].

In an attempt to convert **1a** into the tetra*phenyl*borate salt **1b**, which was hoped to crystallize more readily, the tetrafluoroborate salt was treated with $\mathrm{Na[BPh_4]}$ in acetonitrile. A series of extraction and crystallization steps (Experimental) lead to a pure product, for which cation and anion FAB mass spectrometry has confirmed the presence of the tetragoldphosphonium cation $\{[(t\mathrm{Bu})_3\mathrm{PAu}]_4\mathrm{P}\}^+$ and the $\mathrm{BPh_4^-}$ anion beyond any doubt. Again, however, the material could not be crystallized.

The NMR spectra of **1b** are virtually identical with those of **1a**, except for the resonances of the $\mathrm{BPh_4^-}$ anion replacing those of the $\mathrm{BF_4^-}$ anion. This result indicates that both salts are dissociated in polar solvents to give the same cation.

This cation exhibits only one set of NMR signals (^{1}H, ^{13}C, ^{31}P) for four equivalent $[(t\mathrm{Bu})_3\mathrm{PAu}]$ units attached to a central phosphonium center. The resonance of the central phosphorus atom appears as a 1:4:6:4:1 quintet, again indicating the equivalence of the four (phosphane)gold ligands. As mentioned in the introductory remarks, these multiplicity data do not allow a distinction to be made between a tetrahedral and a square-pyramidal structure for the $(\mathrm{PAu})_4\mathrm{P}$

skeleton. Although the value of ^2J(PAuP) would seem to suggest a tetrahedral structure from a comparison with the data for the pentagold- and hexagoldphosphonium salts[11] (reasoning that sp^3, sp^{3}d, and sp^{3}d^2 hybrids of the central element should lead to decreasing J values), this evidence is not reliable. The same is true for the independence of the spectra of temperature (+35 to −65 °C in $CDCl_3$), since fluxionality cannot be ruled out even at the lowest temperature of the experiment.

During one of the many attempts to obtain single crystals of compound **1b** a colorless seed of crystals of good quality has been deposited from dichloromethane/diethyl ether after prolonged standing at room temperature. The X-ray diffraction study of a selected single crystal of this crop has shown, however, that this salt contains the proposed cation associated with a novel cyclic boroxinate counterion (**1c**). This anion has the stoichiometry $[O(BPhO)_2BPh_2]^-$ and probably arises from partial hydrolysis of the BPh_4^- anions under the influence of the other components of the solution [Eq. (1)]. From a literature survey it appears that this type of tetraorganoboroxinate anion has not been previously reported. It is only in one of our own studies that the analogous tetrafluoroboroxinate anion has been encountered and structurally characterized[15]. It may not be a coincidence, that this only other example has also arisen from partial anion hydrolysis (BF_4^-) in the presence of element-centered gold clusters, but no mechanism can be proposed at this stage.

$$\begin{aligned} &(\mathrm{Me_3Si})_3\mathrm{P} + \{[(t\mathrm{Bu})_3\mathrm{PAu}]_3\mathrm{O}\}^+\ \mathrm{BF_4^-} \\ &\qquad\xrightarrow{\qquad\qquad} \{[(t\mathrm{Bu})_3\mathrm{PAu}]_4\mathrm{P}\}^+\ \mathrm{X^-} \\ &\qquad\qquad\qquad\quad \mathbf{1a}\mathrm{:\ X = BF_4^-} \qquad\qquad (1) \\ &\mathbf{1a} \xrightarrow[\qquad]{\mathrm{Na[BPh_4]}} \mathbf{1b}\mathrm{:\ X = BPh_4^-} \\ &\mathbf{1b} \xrightarrow[\qquad]{\mathrm{H_2O}} \mathbf{1c}\mathrm{:\ X = [O(BPhO)_2BPh_2]^-} \end{aligned}$$

Owing to the formation of a number of byproducts (mainly high nuclearity phosphorus-centered gold clusters) in significant quantities, a balance of Eq. (1) is presently unrealistic. As in previous experiments with similar reagents (containing other tertiary phosphanes)[1–8], hexamethyldisiloxane is the main gold-free byproduct, which is readily detected by GC/MS studies.

The Crystal Structure of $\{[(t\mathrm{Bu})_3\mathrm{PAu}]_4\mathrm{P}\}^+[\mathrm{O(BPhO)_2BPh_2}]^- \cdot \mathrm{CH_2Cl_2}$ (1c′)

Compound **1c** forms colorless triclinic platelets (**1c′**), space group $P\bar{1}$ (No. 2 of Int. Tables), with two (symmetry-related) formula units of **1c** and two molecules of solvent CH_2Cl_2 in the unit cell. The lattice is built up of cations, anions, and solvent molecules which have no unusually close ion-ion or ion-molecule contacts and may be described as independent.

The *cations* have been found to contain what can be described as a distorted quasi-*tetrahedral* $(PAu)_4P$ skeleton (Figure 1).

Four gold atoms (Au1–Au4) are attached to the central phosphorus atom (P10) at very similar distances [2.306(2)–2.319(2) Å]. Each of these gold atoms is further coordinated to the phosphorus atom of its tertiary phosphane ligand at a distance again in the same range [2.314(2)–2.321(2) Å]. The angles P–Au–P at the gold atoms are close to 180° with individual values between 170.5(1) and 177.6(1)°. While these data are more or less as expected for phosphorus-centered gold clusters, the configuration at the central phosphorus atom with its severe distortion of the Au–P10–Au angles away from the tetrahedral value of 109° is particularly notworthy (Figure 2). These angles range from as low as 96.1(1) (for Au3–P10–Au4) to 139.5(1)° (for Au1–P10–Au4), and only one of them is close to the ide-

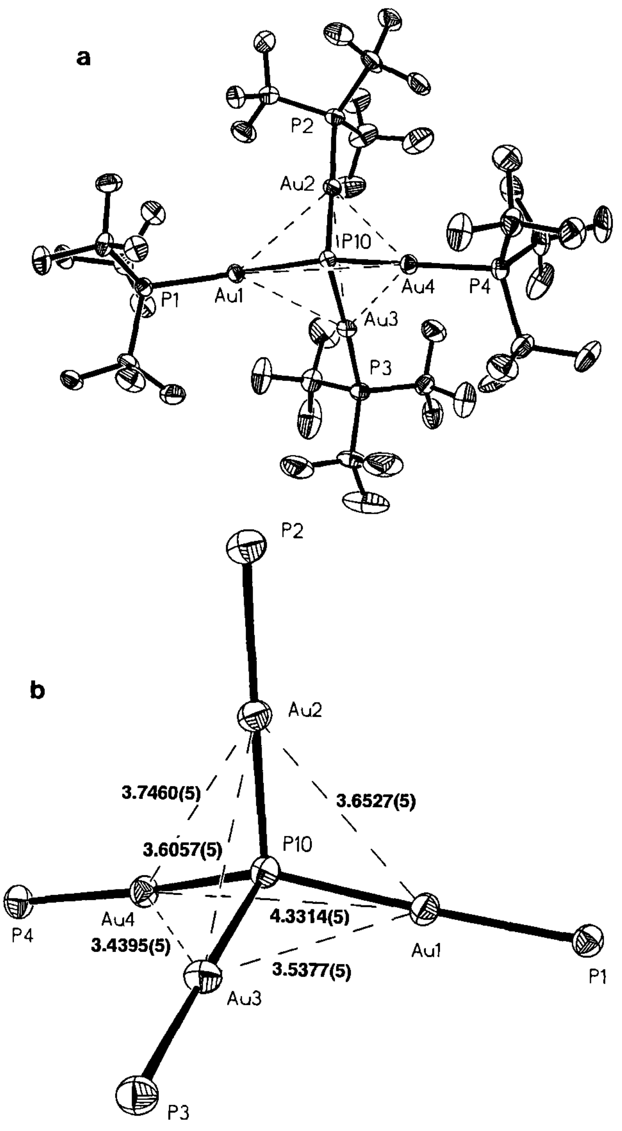

Figure 1. a) Structure of the cation of compound **1c′** with atomic numbering (ORTEP, 50% probability ellipsoids). Hydrogen atoms are omitted for clarity. b) Au···Au contacts in the $P(AuL)_4$ core of the cation. Other selected bond distances [Å] and angles [°]: Au1–P10 2.311(2), Au2–P10 2.313(2), Au3–P10 2.319(2), Au4–P10 2.306(2); Au1–P1 2.319(2), Au2–P2 2.321(2), Au3–P3 2.321(3), Au4–P4 2.314(2); P10–Au1–P1 172.38(8), P10–Au2–P2 177.57(9), P10–Au3–P3 177.00(9), P10–Au4–P4 170.49(9); Au1–P10–Au2 104.35(9), Au1–P10–Au3 99.66(8), Au1–P10–Au4 139.5(1), Au2–P10–Au3 102.2(1), Au2–P10–Au4 108.39(9), Au3–P10–Au4 96.12(9)

alized tetrahedral value [108.4(1)° for Au2—P10—Au4]. These angular distortions lead to widely different Au···Au contacts at the edges of the Au_4P unit, which are held to be important for the stability of most element-centered gold clusters. Even the shortest of these, Au3—Au4 = 3.439(1) Å, is still very long as compared to the reference value of ca. 3.0 Å in such clusters, indicating that contributions from metal-metal contacts to cluster bonding are very small. One Au···Au edge (Au1—Au4) is even as great as 4.331(2) Å, such that any bonding interactions can be ruled out.

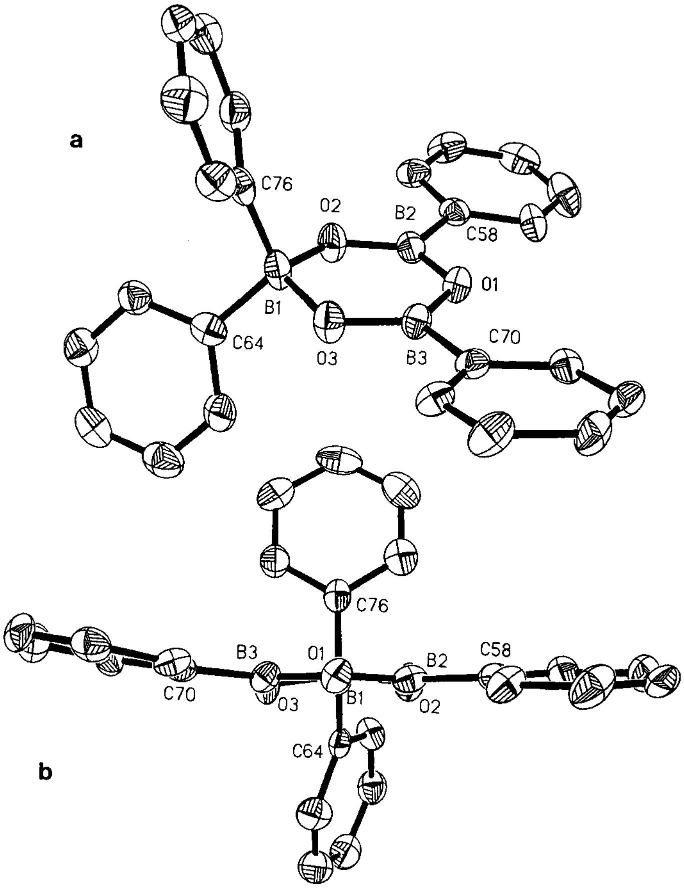

Figure 2. a) Structure of the anion of compound **1c′** with atomic numbering (ORTEP, 50% probability ellipsoids). Hydrogen atoms are omitted for clarity. b) Side view of the anion showing the coplanarity of the boroxine and two phenyl rings. Selected bond distances [Å] and angles [°]: B1—O2 1.52(1), B1—O3 1.51(1), B2—O1 1.40(1), B2—O2 1.31(1), B3—O1 1.38(1), B3—O3 1.35(1); B1—C64 1.61(2), B1—C76 1.61(2), B2—C58 1.57(2), B3—C70 1.55(2); O2—B1—O3 109.1(8), O1—B2—O2 122.4(10), O1—B3—O3 121.4(9), B1—O2—B2 123.5(9), B2—O1—B3 119.1(8), B1—O3—B3 122.8(8); C64—B1—C76 114.2(9)

In summary, it thus appears that the structure of the cations in **1a**—**c** can be described as quasi-tetrahedral. However, the severe distortions of the skeleton provide evidence, that the system is gaining energy from the shortened Au···Au contacts generated by contraction of some of the Au—P10—Au angles. Closer contacts than those found in the structure (3.4 Å) are clearly ruled out by the bulkiness of the $(tBu)_3P$ ligands, as is of course a full reversion to a square-pyramidal structure, which has been predicted for $(R_3PAu)_4P^+$ cations with less sterically demanding ligands.

The *anions* have been shown to have a cyclic boroxine structure with a six-membered ring of alternating boron and oxygen atoms. Two of the boron atoms (B2, B3) are three-coordinate with a planar configuration, while the third (B1) is tetracoordinate with a quasi-tetrahedral configuration, representing the center of the anionic charge. The boroxine ring is virtually planar with very small deviations of the ring atoms from the calculated "best plane". The phenyl rings at B2 and B3 are close to coplanar with the boroxine ring, suggesting π contributions to the B—C(*ipso*) bonds. This idea is supported by rather short distances B2—C58 = 1.57(2) and B3—C70 = 1.55(2) Å. For the same reason (π bonding between boron atoms B2 and B3 and neighboring oxygen atoms) the boron-oxygen bonds to B1 are also significantly longer than the boron-oxygen bonds to B2 and B3.

As mentioned in the introductory remarks, no tetra*organo*boroxinate anion has been previously reported, but the related tetra*fluoro* derivate has been encountered — equally unexpectedly — in the structure determination[13] of another large gold cluster: $\{[(iPr_3P)Au]_6C\}^{2+} \cdot 2\ [O(BFO)_2BF_2]^- \cdot 3\ CH_2Cl_2$. The dimensions are similar, but the quality of these reference data is limited, and a discussion of details may not be really meaningful.

Conclusion

The present study has shown that tetrahedral tetragoldphosphonium $[(R_3PAu)_4P]^+\ X^-$ salts can be prepared and are found to be stable compounds if bulky tertiary phosphanes R_3P are used as auxiliary ligands. The extreme distortion of the cation is indicative, however, of a preference for modified geometries which allow for peripheral metal-metal interactions (along the edges of the polyhedron). In the case of the title compound more severe distortions are prevented by the bulkiness of the tertiary phosphane ligand, but it needs little imagination to assume that with smaller ligands a complete rearrangement is induced to give a square-pyramidal PAu_4 core with much shorter Au···Au edges. While the Au···Au edges of a regular PAu_4 tetrahedron with radial Au—P bonds of 2.30 Å (above) are calculated to be as long as 3.90 Å (and thus well beyond the region of significant metal-metal bonding), the edges along the base of a PAu_4 square pyramid with the same Au—P distances and Au—P—Au angles of 80° (see ref.[6]) are calculated to be smaller than 3.00 Å (which represents a value typical of Au···Au bonding)[9]. The prediction[8–10] that cations $[(R_3PAu)_4P]^+$ with standard size tertiary phosphanes should have a non-classical square-pyramidal structure like their arsenic analogs[3,6,7] is therefore not yet to be discarded, but may well be valid for systems with the appropriate components.

This work has been supported by *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie*. Mr. *J. Riede* is thanked for establishing the X-ray data set.

Experimental

All experiments were carried out under dry, purified nitrogen. Samples and solutions were protected against directly incandescent light. Solvents were dried, distilled, and saturated with nitrogen.

Glassware was oven-dried and filled with nitrogen. $(Me_3Si)_3P$, $[(tBu_3P)Au]_3O^+ BF_4^-$ and $[(Ph_3P)Au]_3O^+ BF_4^-$ were prepared according to literature methods[12,13,16]. – NMR: Jeol GX 400. – MS: MAT 311 (FAB). – GC/MS: Hewlett-Packard HP 5890/MSD 5971A.

Tetrakis[(tri-tert-butylphosphane)gold(I)]phosphonium(+1) Tetrafluoroborate(–1) (**1a**): A solution of tris(trimethylsilyl)phosphane (0.125 g, 0.5 mmol) in tetrahydrofuran (10 ml) is treated at –78°C with a solution of tris[(tri-*tert*-butylphosphane)gold-(I)]oxonium tetrafluoroborate (0.870 g, 0.67 mmol) in 40 ml of the same solvent. The pale yellow reaction mixture is stirred for 3 h at low temp. and then allowed to warm to room temp. Addition of pentane (30 ml) leads to the separation of a small amount of a red oil, which contains several gold cluster species (detected by NMR and MS analysis: **1a**, a pentanuclear species, and other as yet unidentified compounds). The supernatant yellow solution is treated with another 20 ml of pentane to precipitate a colorless oil, which transforms into a colorless solid when dried in vacuo. The product cannot be crystallized. It is stable against air and water, yield 0.77 g (90%), decomposition at 190°C. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): $\delta = -78.9$ [quin, 1 P, J(P,P) = 208.4 Hz, PAu_4]; 99.1 [d, 4 P, J(P,P) = 208.4 Hz, $(PAu)_4$]. – ^1H NMR ($CDCl_3$, 25°C): $\delta = 1.55$ [d, J(P,H) = 12.2 Hz, Me]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): $\delta = 32.39$ [d, J(P,C) = 5.0 Hz, Me]; 39.38 [d, J(P,C) = 12.21 Hz, CP]. – MS (FAB-pos), m/z (%): 1627.6 (100) [M^+]. – $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25°C): $\delta = -4.0$ [s, BF_4^-]. – $C_{48}H_{108}Au_4BF_4P_5$ (1714.9): calcd. C 33.62, H 6.35, Au 45.94; found C 33.12, H 6.30, Au 46.1.

Tetrakis[(tri-tert-butylphosphane)gold(I)]phosphonium(+1) Tetraphenylborate(–1) (**1b**): A solution of compound **1a** (0.814 g, 0.5 mmol) in acetonitrile (10 ml) is treated with a solution of sodium tetraphenylborate (1.71 g, 5 mmol) in 10 ml of the same solvent. The mixture is stirred for 2 h at ambient temp. The solvent is removed in vacuo and the residue washed three times with small amounts of water in order to extract $NaBF_4$ and $NaBPh_4$. The residue is dried in vacuo and extracted with diethyl ether. From the diethyl ether solution **1b** is obtained after evaporation of the solvent as a colorless, air-stable solid, yield 0.79 g (85%), decomposition temperature 170°C. – The NMR resonances for the cation of **1b** are similar to those of **1a**. – ^1H NMR ($CDCl_3$, 25°C): $\delta = 6.75-6.81$, $6.90-6.95$, and $7.22-7.28$ (m, BPh_4). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): $\delta = 121.2$, 124.9, 135.8, and 163.5 (m, BPh_4). – $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25°C): $\delta = -20.5$ (s, BPh_4). – MS (FAB-pos), m/z (%): 1627.6 (100) [M^+], 1425.5 (26) [$(tBu_3PAu)_3PAu^+$]. – (FAB-neg), m/z (%): 319.2 (100) [BPh_4^-].

Tetrakis[(tri-tert-butylphosphane)gold(I)]phosphonium(+1) Tetraphenylboroxinate(–1) (**1c**): A solution of a sample of compound **1b** in a mixture of diethyl ether and dichloromethane is carefully layered with heptane. Very few colorless crystals grow at the interphase during a period of 3 weeks. These are identified as **1c** · CH_2Cl_2 by an X-ray diffraction study. No other analytical or spectroscopic data could be collected.

Crystal and Structure Solution Data for **1c** · CH_2Cl_2[21]: $C_{73}H_{130}Au_4B_3Cl_2O_3P_5$ ($M_{rel} = 2101.9$), $a = 13.523(1)$, $b = 16.526(1)$, $c = 20.777(4)$ Å, $\alpha = 67.29(1)$, $\beta = 78.71(1)$, $\gamma = 84.89(1)°$, space group $P\bar{1}$ (No. 2, Int. Tables), $V = 4199.9$ Å^3, $Z = 2$, $d_{calc} = 1.725$ gcm^{-3}, $T = -50$°C, $\mu(Mo\text{-}K_\alpha) = 62.4$ cm^{-1}, $\lambda(Mo\text{-}K_\alpha) = 0.71069$ Å, CAD4 diffractometer, 18209 reflections measured, 18206 unique, and 10331 observed [$F_o \geqslant 4.00\sigma(F_o)$]; Lorentz, polarization and absorption corrections [DIFABS][17] ($t_{min/max} = 0.67/1.36$) have been applied. Structure solution has been performed by direct methods (SHELXS-86)[18]. Missing hydrogen atoms have been located by successive difference Fourier syntheses using CRYSTALS[19]. Final refinement of 812 parameters in 8 blocks with anisotropic parameters for all non-hydrogen atoms and the use of the structure factors of calculated hydrogen atoms in fixed positions ($U_{iso} = 0.075$) converged at $R = 0.040$ ($R_w = 0.044$) by using the weighting scheme of Prince[20].

---

[1] Y. L. Slovokhotov, Y. T. Struchkov, *J. Organomet. Chem.* **1984**, *277*, 143.

[2] A. Grohmann, J. Riede, H. Schmidbaur, *Nature* **1990**, *345*, 140.

[3] E. Zeller, H. Beruda, A. Kolb, P. Bissinger, J. Riede, H. Schmidbaur, *Nature* **1991**, *352*, 141.

[4] A. W. Brodbeck, J. Strähle, *Acta Crystallogr., Sect. A*, **1991**, *46*, C232.

[5] H. Schmidbaur, *Gold Bull.* **1990**, *23*, 11.

[6] E. Zeller, Dissertation, Techn. Univ. München, **1993** (in preparation).

[7] H. Beruda, Dissertation, Techn. Univ. München, **1993** (in preparation).

[8] H. Schmidbaur, *Interdisc. Sci. Rev.* **1993**, *17*, 213.

[9] H. Schmidbaur, *Pure Appl. Chem.* **1993**, *65*, 691.

[10] P. Pyykkö, Y. Li, *Inorg. Chem.* **1993**, *32*, 2630–2634.

[11] E. Zeller, H. Schmidbaur, *J. Chem. Soc., Chem. Commun.* **1993**, 69.

[12] H. Schumann, L. Rösch, *Chem. Ber.* **1974**, *107*, 854.

[13] E. Zeller, A. Kolb, H. Schmidbaur, *Z. Anorg. Allg. Chem.*, in press.

[14] E. Zeller, H. Beruda, H. Schmidbaur, *Chem. Ber.*, in preparation.

[15] H. Schmidbaur, B. Brachthäuser, O. Steigelmann, H. Beruda, *Chem. Ber.* **1992**, *125*, 2705.

[16] See also: A. N. Nesmeyanov, E. G. Perevalova, Y. T. Struchkov, M. Y. Antipin, K. I. Grandberg, V. P. Dyadchenko, *J. Organomet. Chem.* **1980**, *201*, 343.

[17] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, **1983**, *39*, 158.

[18] G. M. Sheldrick, *SHELXS-86*, Universität Göttingen, **1986**.

[19] D. J. Watkin, P. W. Betteridge, J. R. Carruthers, *CRYSTALS User Manual*, Oxford University Computing Laboratory, Oxford, **1986**.

[20] E. Prince, *Mathematical Techniques in Crystallography*, Springer Verlag, Berlin, **1982**.

[21] Supplementary material has been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-76344 Eggenstein-Leopoldshafen, and may be obtained by quoting the depository number CSD-57329, the names of the authors, and the complete journal citation.

[128/93]