ortho-Metalation of Triarylphosphane at Cobalt and Template Synthesis of Chelating 2-(Diarylphosphanyl)aroyl Ligands

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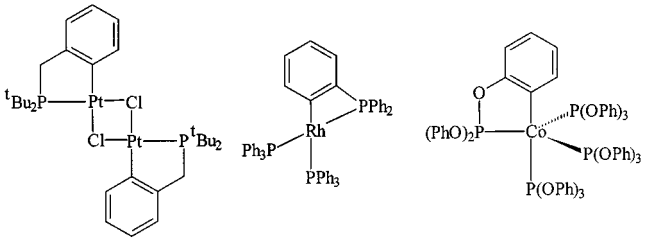
Elimination of methane from thermally labile $CoMe(PPh_3)(PMe_3)_3$ generates *ortho*-metalated $Co(2\text{-}Ph_2PC_6H_4)(PMe_3)_3$ (**1**). Addition of dihydrogen causes ring-opening which is followed by a ligand dismutation reaction giving $CoH(PMe_3)_4$ and $CoH(PMe_3)_2(PPh_3)_2$. The system does not catalytically hydrogenate olefins. CO insertion into the Co–C bond of **1** results in ring expansion and constitutes a template synthesis of the anionic 2-phosphanylbenzoyl chelate ligand as shown in the molecular structure of $Co(2\text{-}Ph_2PC_6H_4CO)(CO)(PMe_3)_2$ (**3**). Oxidative addition of iodomethane transforms **1** into diamagnetic $CoMeI(2\text{-}Ph_2PC_6H_4)(PMe_3)_2$ (**7**), while benzoyl chloride oxidizes **1** to paramagnetic $CoCl(2\text{-}Ph_2PC_6H_4)(PMe_3)_2$ (**8**). The preservation of the four-membered metallacycle in three successive oxidation states is supported by single-crystal X-ray analyses of **1**, **7**, and **8**.

Introduction

C−H activation of hydrocarbons,[1] particularly that involving aromatic compounds, and cyclometalation[2] of arylphosphanes are important areas of research with respect to homogeneous catalysis. *ortho*-Metalations of triarylphosphanes, e.g. the metalation of benzylphosphanes (**A**) or phenyl phosphites (**C**), represent some early examples.



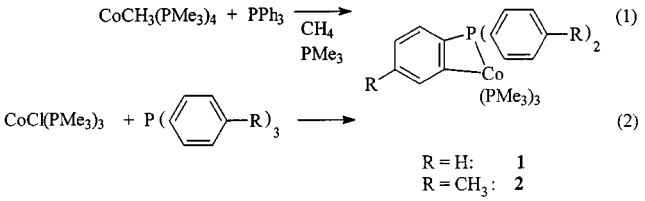
A B C

When coordinated to platinum metals, e.g. as in Keim's rhodium complex **B**,[3a] triphenylphosphane has in many cases been shown to form four-membered metallacycles.[3] With iron, cobalt, or nickel, only a few examples have been reported. While $Fe(C_2H_4)(Ph_2PCH_2CH_2PPh_2)_2$ is *ortho*-metalated only under irradiation,[4] $CoH(N_2)(PPh_3)_3$ has been shown by several groups to undergo H/D exchange in all *ortho* positions.[5] In solution, $CoCH_3(PPh_3)_3$ spontaneously eliminates methane. No *ortho*-metalated species have been isolated from these systems. Only in the presence of styrene was an *ortho*-metalated species generated, which has still to be fully characterized.[6] Although no *ortho*-metalation through C−H activation has been described for alkyl- or hydridonickel(II) or -nickel(0) complexes with phenylphosphanes, the reaction of (pentachlorophenyl)diphenylphosphane with nickel(0) affords a metallacyclic complex,[7] which undergoes ring-opening through substitution of its P-donor function with triphenylphosphane. Although H_2 smoothly hydrogenates the rhodium(I) complex **B** under ring-opening, retention of the four-membered metallacycle was observed in both oxidative addition reactions and ring-expansion reactions with CO[8] and diphenylacetylene.[9]

With trimethylphosphanes as supporting ligands, we have observed quite similar properties and reactivities in the cobalt(I) system and report here on the syntheses, reactions, and structural investigations of such complexes.

Results and Discussion

When combined with triphenylphosphane in tetrahydrofuran, $CoCH_3(PMe_3)_4$ eliminates methane to form the metallacyclic complex **1** according to Equation (1). Addition of triphenylphosphane to $CoCl(PMe_3)_3$, followed by methyllithium (Equation 2), affords **1** in essentially quantitative yield.



Using tris(4-methylphenyl)phosphane in place of triphenylphosphane in a synthesis according to Equation 2, the analogous complex **2** is obtained in 95% yield. Both complexes form large quadrangular crystals with black faces,

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which appear dark red when illuminated. In dry air, solid **1** and **2** remain unchanged for ca. two hours, although their solutions are decomposed within a few minutes if air is admitted.

Their infrared spectra display the characteristic *ortho*-metalation bands at $\tilde{\nu}$ = 722 cm^{-1} (**1**) and 726 cm^{-1} (**2**), which correspond to out-of-plane CH vibrations.[3c] The ^{31}P NMR spectra (−40 °C) feature an AM_2X pattern of three signals with J(AM) = 49 Hz (**1**) and 48 Hz (**2**), which is consistent with a trigonal-bipyramidal arrangement of donor atoms with one axial (A) and two equatorial (M) trimethylphosphanes. The equatorial chelate P nucleus X displays a high-field signal characteristic of four-membered metallacycles[10] with J(AX) = 70 Hz and J(MX) = 87 Hz.

The trigonal-bipyramidal configuration of **1** has been confirmed in the crystal. Figure 1 shows the first molecular structure of an *ortho*-metalated arylcobalt complex. The bond lengths are as expected for Co^{I} centered in a trigonal bipyramid of CP_4 donor atoms.[11] The bond angles at cobalt deviate from ideal symmetry because of steric repulsions. Those of the axial P4 atom appear to be augmented by 5°, and the small chelate bite angle [C16−Co−P1 = 71.48(10)°] causes a bending of the main axis towards the chelate ring [C16−Co−P4 = 168.00(11)°]. Thus, the properties and the molecular structure prove **1** (18 metal-valence electrons) to be a true homologue of its 16-electron rhodium congener **B**.

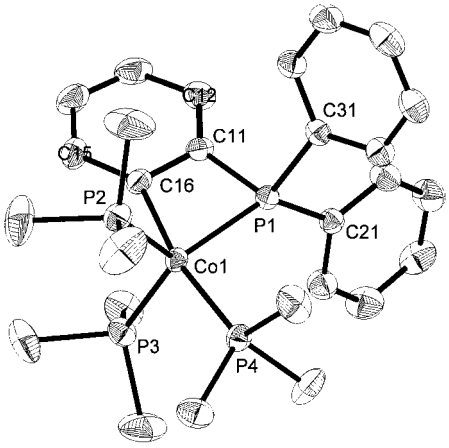
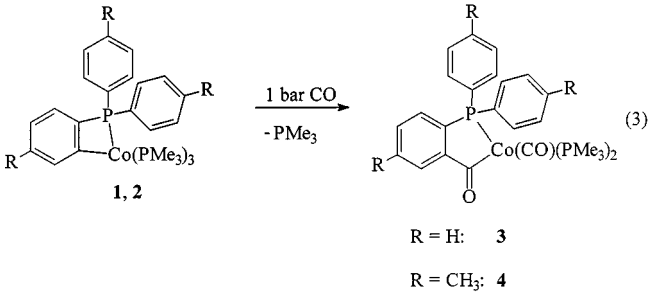


Figure 1. Molecular structure of **1** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C16 1.990(3), Co−P1 2.2170(10), Co−P2 2.1744(11), Co−P3 2.1710(12), Co−P4 2.1826(11), P1−C11 1.795(3), P1−C31 1.842(3), P1−C21 1.843(3), C11−C16 1.399(5), C11−C12 1.377(5), C12−C13 1.392(5), C13−C14 1.357(6), C14−C15 1.387(5), C15−C16 1.400(5); C16−Co−P3 86.89(10), C16−Co−P2 88.80(11), P3−Co−P2 118.64(5), C16−Co−P4 168.00(11), P3−Co−P4 98.91(4), P2−Co−P4 97.48(4), C16−Co−P1 71.48(10), P3−Co−P1 118.22(4), P2−Co−P1 117.92(4), P4−Co−P1 96.53(4), C11−P1−C31 106.13(16), C11−P1−C21 104.57(16), C31−P1−C21 101.64(15), C11−P1−Co 83.81(12), C31−P1−Co 124.66(11), C21−P1−Co 128.92(11), C11−C16−C15 114.8(3), C11−C16−Co 104.1(2), C16−C11−P1 100.3(2)

Reaction with Carbon Monoxide

At ambient temperature under 1 bar CO, THF solutions of complexes **1** and **2** react with two molar equivalents of CO according to Equation 3. An in situ transformation also occurs after *ortho*-metallation, as described by Equations 1 or 2.



Compound **3** has previously been obtained by C,H activation of 2-diphenylphosphanylbenzaldehyde.[11] Compounds **3** and **4** show analogous infrared absorptions of their carbonyl ligands at $\tilde{\nu}$ = 1953 and 1946 cm^{-1} (C≡O) and benzoyl groups $\tilde{\nu}$ = 1916 and 1909 cm^{-1} (C=O), respectively. When compared with the ^{31}P NMR spectroscopic data for **1** and **2**, the largest difference is seen in the shift of the chelate P atom. On going from a four-membered to a five-membered metallacycle, a low-field shift of 115 ppm is found, which is of the expected order.[10] The two trimethylphosphane ligands give rise to a broad singlet at δ = 9, which splits into a doublet at −40 °C. The coupling constant [J(PP) = 81 Hz] is indicative of a P−Co−P angle of about 120°, which is in perfect agreement with the molecular structure of **3**[12] (Figure 2). The cobalt atom is centered in a trigonal bipyramid comprising three equatorial P-donor functions. The chelate bite angle [P1−Co−C1 = 85.03(9)°] is similar to that in **1**, and the metallacycle shows a normal Co−C bond length only slightly longer than in **1** [Co−C1 = 1.960(3) Å]. Surprisingly, the groups with the largest *trans* influence are almost perfectly aligned along an axis [C1−Co−C20 = 176.3(2)°].

In the observed configuration, the carbonyl ligand can be expected to dissociate freely from **3**. A further carbonyl ligand may be mobilized through a decarbonylation reaction of the acyl function, restoring the four-membered metallacycle. In an attempted ligand equilibration reaction, regarding **3** as a source and **1** as an acceptor of carbonyl groups, no exchange of ligands was observed.

In further attempts to prepare the desired compound from either $CoMe(CO)(PMe_3)_3$ [13] and triphenylphosphane or from $CoCl(CO)(PMe_3)_3$ [14] and MeLi in the presence of triphenylphosphane, no *ortho*-metalation was observed.

Hydrogenation of Metallacycles

Under ambient conditions (20 °C, 1 bar H_2) in pentane or diethyl ether, **1** undergoes a ring-opening reaction to form mixed-ligand cobalt hydrides according to Equations 4 and 5. While **5** can be crystallized from pentane, **6** may be obtained through a ligand dismutation reaction and precipitated as an orange solid as it is insoluble in diethyl ether.

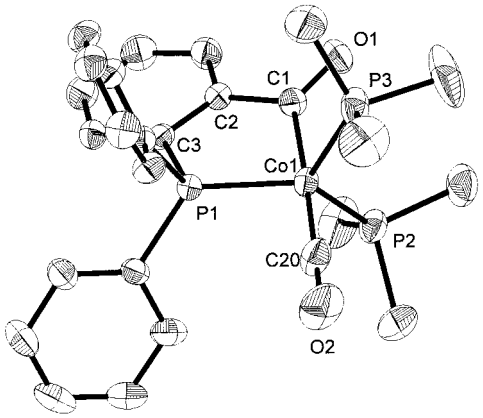
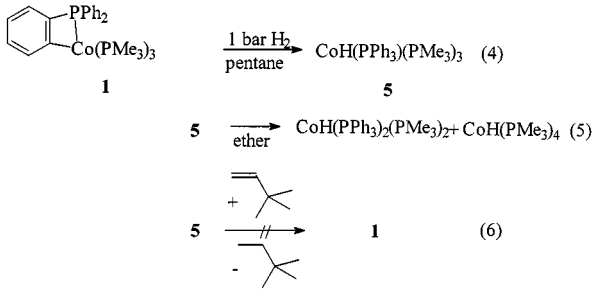


Figure 2. Molecular structure of **3** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C1 196.0(3), Co−P1 215.02(10), Co−P2 217.38(9), Co−C3 181.7(3), Co−C20 174.3(4), C20−O2 115.3(4), C1−O1 122.1(3), C1−C2 154.0(4), C2−C3 138.2(4), P1−C3 181.7(3); C1−Co−P1 85.03(9), C1−Co−P2 83.70(9), C1−Co−P3 89.56(9), C1−Co−C20 176.3(2), P1−Co−P2 123.91(3), P1−Co−P3 115.42(4), P1−Co−C20 93.47(12), P2−Co−P3 119.23(4), P2−Co−C20 94.35(13), C20−Co−P3 94.18(13), Co−C1−C2 117.2(2), C1−C2−C3 117.9(2), C2−C3−P1 111.2(2), C3−P1−Co 104.65(9), Co−C1−O1 126.9(2), O1−C1−C2 115.9(3)



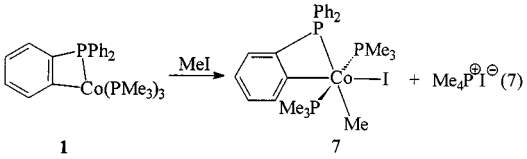
The hydrogenation reaction cannot be reversed by adding an olefin. Cyclohexene, 1-octene, and even 3,3-dimethylbut-1-ene, with its large heat of hydrogenation, remain unreactive. Such equilibria would, in principle, make the pair of compounds **1** and **5** a homogeneous hydrogenation catalyst involving *ortho*-metalated intermediates as are supposedly involved in Parshall's ruthenium system.[15] However, with (trimethylphosphane)cobalt compounds, hydrogenation reactions appear to be generally rather slow.

The catalytic activity of **1** and **5** in the hydrogenation of 1-octene was tested under 70 bar H_2 at 80 °C, but none was found. Hydrogen uptake was only observed with **1**, which was found to correspond to a stoichiometric reaction according to Equation 4.

Oxidative Addition and Oxidation

The ease with which it is hydrogenated under ambient conditions makes complex **1** a candidate for oxidative addition reactions. Using iodomethane as a substrate, the interesting question arises as to whether attack by the metal would proceed as a regioselective addition or promote ring-opening through a subsequent reductive C−C coupling reaction.

Within 15 h, the appearance of a light-brown coloration and a white precipitate of tetramethylphosphonium iodide indicated reaction according to Equation 7. However, trimethylphosphane was only partly quaternated in a side reaction, and addition of a second molar equivalent of iodomethane did not improve the yield of dark-brown crystals of **7** obtained from either diethyl ether or pentane. The use of a tenfold excess of iodomethane completely suppressed the formation of **7** and led to some $CoMe_2(I)(PMe_3)_3$ [16] as a product of a subsequent ring-opening reaction, as well as a cobalt-containing dark-green solid, which proved insoluble and was not identified.



In the ^{1}H NMR spectrum of **7**, the $CoCH_3$ protons resonate at δ = 0.51, which is close to the chemical shift seen for $CoMe_2(I)(PMe_3)_3$,[16] and are coupled to two *cis*-trimethylphosphane ligands [^3J(PH) = 9.5 Hz] and a *trans*-chelating phosphorus atom [^3J(PH) = 1.8 Hz], which gives rise to a high-field signal (δ(P) = −40) in the ^{31}P NMR spectrum, indicative of a four-membered metallacycle. All spec-

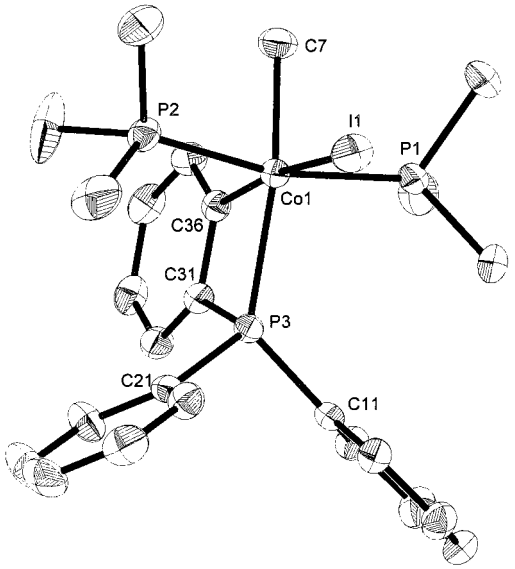
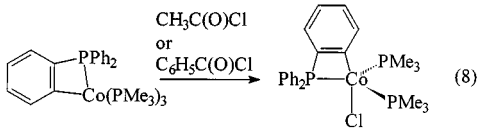


Figure 3. Molecular structure of **7** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: I−Co 2.7099(6), Co−C36 1.942(3), Co−C7 2.039(3), Co−P1 2.2381(11), Co−P2 2.2425(11), Co−P3 2.3467(10), P3−C31 1.799(3), P3−C11 1.829(3), P3−C21 1.830(3), C31−C36 1.395(4), C31−C32 1.389(4), C32−C33 1.374(5), C33−C34 1.375 (5), C34−C35 1.384(5), C35−C36 1.398(4); C36−Co−C7 89.60(15), C36−Co−P1 94.06(10), C7−Co−P1 84.50(11), C36−Co−P2 91.88(10), C7−Co−P2 83.90(12), P1−Co−P2 166.92(4), C36−Co−P3 69.98(10), C7−Co−P3 159.57(11), P1−Co−P3 96.01(4), P2−Co−P3 96.97(4), C36−Co−I 171.33(10), C7−Co−I 98.96(11), C31−P3−C21 110.33(16), C31−P3−Co 80.77(11), C21−P3−Co 125.96(11), C11−P3−Co 127.73(11), P1−Co−I 88.17(3), P2−Co−I 87.69(3), P3−Co−I 101.46(3), C31−P3−C11 107.12(15), C31−P3−C21 110.32(16), C11−P3−C21 100.23(15), C31−P3−Co 80.77(11), C36−C31−P3 101.2(2), C31−C36−Co 108.0(2), C35−C36−Co 134.5(3)

troscopic data are thus compatible with an octahedral configuration of **7** in solution.

Crystals of **7** proved to be stable in air for more than two days and could thus be mounted on an X-ray diffractometer without inert gas protection. The molecular structure (Figure 3) confirms the configuration of **7** as derived from the spectroscopic data. The iodo and methyl ligands lie in the plane of the chelate ring, and the two carbon−cobalt bonds are mutually orthogonal [C7−Co−C36 = 89.60(15)°]. The trimethylphosphane ligands are positioned in an axis perpendicular to the chelate ring and appear slightly bent [P1−Co−P2 = 116.92(4)°] towards the $CoCH_3$ group. This bending and the small bite angle of the chelating ligand [C36−Co−P3 = 69.98(10)°] reflect the spatial requirements of the iodo ligand. The strong *trans* influence of the $CoCH_3$ group and the weak effect of the iodo ligand cause an elongation of Co−P3 by 0.1 Å compared with Co−P1 and Co−P2 and a contraction of Co−C36 by 0.045 Å compared with the corresponding Co−C16 distance in **1**. Therefore, the molecular structure of **7** appears to be the result of a regioselective *cis* addition of iodomethane.

With benzoyl chloride or acetyl chloride, oxidation is observed rather than oxidative addition, as in the rhodium system.[8]



(8)

1 **8**

The cobalt(II) complex **8** (17 valence electrons) was obtained as the only cobalt-containing species in 50−60% yield, while the remaining hydrocarbon moieties have yet to be characterized.

Dark-brown quadrangular crystals could be grown from pentane or diethyl ether and proved to be stable in moist air for more than two hours. The thermal stability, color, and multitude of infrared bands in the fingerprint region are very similar to those observed for **7**, although the crystal habit is different.

The molecular structure of **8** (Figure 4) can be related to a trigonal bipyramid similar to that of **1**. The chelate bite angle [C36−Co−P1 = 71.28(12)°] has a value intermediate between those of **1** and **7**. Distances from the cobalt atoms to the trimethylphosphanes are 0.04 Å longer than those not subject to a strong *trans* influence in **1**. The chelate P atom is almost 0.15 Å farther away from the metal center, although in the opposite direction there is a methyl group in **1** and a void in **8**, which is defined by bond angles P2−Co−P3 = 157.70(5)° and Cl−Co−C36 = 170.49(12)°. This space is large enough for, although not occupied by, a hydride ligand, as indicated by the fact that there no bands in the Co−H region of the infrared spectrum (1980−1880 cm^{-1}), and solid **8** has paramagnetic properties as would be expected for a total of 17 metal-valence electrons.

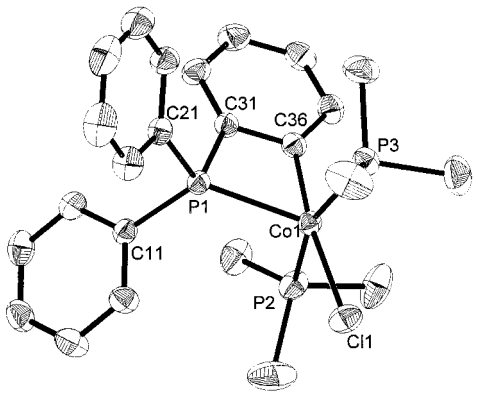
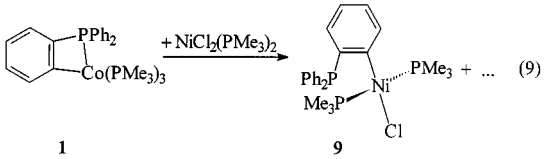


Figure 4. Molecular structure of **8** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Co−C36 1.926(4), Co−P1 2.3631(11), Co−P2 2.2179(12), Co−P3 2.2096(12), Co−Cl 2.3014(13), P1−C11 1.831(4), P1−C31 1.811(4), P1−C21 1.840(4), C31−C36 1.397(6), C31−C32 1.390(6), C32−C33 1.388(6), C33−C34 1.377(7), C34−C35 1.386(7), C35−C36 1.402(6); C36−Co−P1 71.28(12), C36−Co−P2 86.85(12), P3−Co−P2 157.70(5), C36−Co−Cl 170.49(12), P3−Co−Cl 88.48(5), P2−Co−Cl 89.79(5), C36−Co−P1 71.28(12), P3−Co−P1 98.53(5), P2−Co−P1 101.87(4), Cl−Co−P1 118.15(4), C31−P1−C11 109.17(19), C31−P1−C21 107.08(19), C11−P1−C21 102.53(19), C31−P1−Co 78.85(14), C11−P1−Co 118.65(13), C21−P1−Co 134.16(14), C36−C31−P1 103.1(3), C31−C36−C35 117.2(4), C31−C36−Co 106.7(3), C35−C36−Co 136.0(3)

Although the actual molecular symmetries of **1**, **7**, and **8** are lower than those of idealized coordination polyhedra, the angles around the cobalt atom change in a way as to suggest a smooth transition from a trigonal bipyramid in **1** through an intermediate geometry in **8** to an approximate octahedron in **7**.

Transmetalation Reaction

In reactions of $NiCl_2(PMe_3)_2$ with one or two molar equivalents of methyllithium in the presence of triphenylphosphane, no evidence of *ortho*-metalation has been observed. Besides elemental nickel, the mixture of soluble species produced was invariably found to contain $Ni(PMe_3)_4$, $Ni(PPh_3)(PMe_3)_3$, and $Ni(PPh_3)_2(PMe_3)_2$. However, the *ortho*-metalated chelate ligand might be transferred to nickel according to Equation 9.

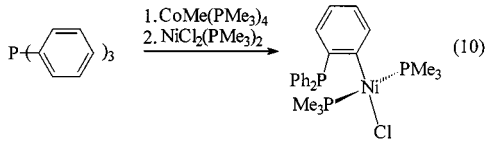


(9)

1 **9**

A light-green powder was obtained as a cobalt-containing residue, from which no soluble compound could be extracted. From a diethyl ether solution containing a considerable quantity of $Ni(PMe_3)_4$, honey-colored cubes of **9** were crystallized in 55% yield, which proved to be stable in air for more than two hours. The infrared spectrum features all the bands typical of *ortho*-metalated triphenylphos-

phane, while the NMR spectra show singlets indicating fast exchange of the ligands as in *trans*-NiCl(Me)(PMe_3)$_2$. At −40 °C, the ^{31}P NMR spectrum shows an A_2B pattern of resonances at δ = −5.4 (2 P) and δ = −7.0 (1 P) with a coupling constant [^2J(PP) = 21 Hz] falling in the range reported for related square-planar nickel(II) compounds.[7] These data are consistent with the presumption that the configuration of **9** is *trans*-square planar and the arylphosphane donor is uncoordinated.



(10)

The transmetalation reaction (Equation 9) provides access to an *ortho*-metalated triphenylphosphane without the need for halogenated arylphosphane precursors through a two-step synthetic procedure (Equation 10).

Conclusion

Methylcobalt(I) complexes incorporating triphenylphosphane ligands spontaneously eliminate methane forming four-membered metallacycles, which remain unchanged in oxidation or oxidative addition reactions. Ring-opening by dihydrogen occurs in a slow reaction and cannot be easily reversed. Under the conditions employed, the system is not an active hydrogenation catalyst. Insertion of carbon monoxide into the metallacycle constitutes a template synthesis of the C,P-chelating (2-diphenylphosphanyl)benzoyl ligand.

Experimental Section

General Procedures and Materials: All air-sensitive and volatile materials were handled using standard vacuum techniques and were stored under argon. − Microanalyses: Kolbe Microanalytical Laboratory, Mülheim/Ruhr, FRG. − Melting points/decomposition temperatures: Sealed capillaries, uncorrected values. − Chemicals (Merck/Schuchardt) were used as purchased, although liquids were degassed in vacuo by a freeze-pump-thaw procedure. Literature methods were followed for the preparation of CoMe(PMe_3)$_4$,[13] CoCl(PMe_3)$_3$,[14] and $NiCl_2(PMe_3)_2$.[17] − IR: Nujol mulls between KBr discs, Bruker spectrophotometer type FRA 106. − NMR: ^{1}H and ^{13}C NMR spectra (300 and 75 MHz, respectively) were recorded with a Bruker ARX-300 spectrometer, ^{31}P NMR spectra (81 MHz) with a Bruker AM-200 instrument. ^{13}C and ^{31}P resonances were obtained with broad-band proton decoupling.

[(2-Diphenylphosphanyl)phenyl-*C*^{1},*P*]tris(trimethylphosphane)cobalt (1). − Method a: CoCl(PMe_3)$_3$ (3.38 g, 11.0 mmol) in THF (60 mL) was combined with triphenylphosphane (2.75 g, 10.5 mmol) in THF (10 mL) at −70 °C to give a green solution. After 5 min, 0.9 M MeLi solution in diethyl ether (6.6 mL, 10.5 mmol) was added to afford an orange solution, which turned deep red on warming to 20 °C. After 4 h, the volatiles were removed in vacuo and the residue was extracted with toluene (50 mL) through a glass sinter disc (G3). Evaporation of the solvent from the extract and drying of the residue in vacuo afforded a black microcrystalline solid. Crude yield 5.70 g (99%) of **1**; yield after recrystallization from 30 mL of pentane 4.5 g (79%). − **Method b:** CoMe(PMe_3)$_4$ (880 mg, 2.30 mmol) in THF (50 mL) and triphenylphosphane (630 mg, 2.40 mmol) in THF (10 mL) were combined at −70 °C. On warming to 20 °C, the mixture took on a deep-red color. After 60 h, the volatiles were removed in vacuo and the residue was extracted with pentane (30 mL). Crystallization at 4 °C afforded dark-red quadrangular rods. Yield 690 mg (55%) of **1**; decomp. > 115 °C. − ^{1}H NMR ([D$_8$]THF): δ = 1.13 (br. s, 9 H, PCH_3), 1.26 (br. s, 18 H, PCH_3), 6.29 (m, 1 H, CH), 6.45 (m, 1 H, CH), 6.65 (m, 1 H, CH), 6.85 (m, 1 H, CH), 7.22 (m, 6 H, CH), 7.69 (m, 4 H, CH). − ^{13}C NMR (300 MHz, [D$_8$]THF): δ = 22.1 (m, PCH_3), 22.9 (m, PCH_3), 118.4 (m, 4-C/6-C), 119.6 (m, 6-C/4-C), 126.2 (s, 5-C), 126.4 (s, *p*-C), 126.6 (s, *m*-C), 131.8 [d, ^2J(PC) = 9 Hz, *o*-C], 140.1 [d, ^2J(PC) = 9 Hz, 2-C], 154.2 (m, *i*-C), 170.0 (m, 1-C). − ^{31}P NMR ([D$_8$]THF, 233 K): δ = −32 [dt, $^2J(P_{eq}P_{eq})$ = 87 Hz, $^2J(P_{ax}P_{eq})$ = 70 Hz, 1 P, PPh_2], −4 [dd, $^2J(P_{eq}P_{eq})$ = 87 Hz, $^2J(P_{ax}P_{eq})$ = 49 Hz, 2 P, PMe_3], 23 [dt, $^2J(P_{eq}P_{ax})$ = 70 Hz, $^2J(P_{eq}P_{ax})$ = 49 Hz, 1 P, PMe_3]. − $C_{27}H_{41}CoP_4$ (548.2): calcd. C 59.13, H 7.53, P 22.59; found C 59.21, H 7.40, P 22.68.

{2-[Bis(4-methylphenyl)phosphanyl]-5-methylphenyl-*C*^{1},*P*}-tris(trimethylphosphane)cobalt (2). − Method a: CoCl(PMe_3)$_3$ (840 mg, 2.60 mmol) in THF (50 mL) was combined with tris(4-methylphenyl)phosphane (790 mg, 2.60 mmol) in THF (10 mL) at −70 °C to give a green solution. After 5 min, 2.6 M MeLi solution in diethyl ether (1.6 mL, 2.60 mmol) was added to afford an orange solution, which turned deep red on warming to 20 °C. After 15 h, the volatiles were removed in vacuo and the residue was extracted with pentane (30 mL). Crystallization at 4 °C afforded dark-red quadrangular rods. Yield 580 mg (38%) of **2**; m.p. 142−144 °C. − ^{1}H NMR (200 MHz, [D$_8$]THF): δ = 1.10 [d, ^2J(PH) = 9 Hz, 9 H, PCH_3], 1.25 (br. s, 18 H, PCH_3), 2.01 (s, 3 H, CCH_3), 2.29 (s, 6 H, CCH_3), 6.18 (m, 2 H, CH), 6.71 (br. s, 1 H, CH), 7.04 [d, ^3J(HH) = 7 Hz, 4 H, CH], 7.56 [dd, ^3J(HH) = 8 Hz, ^3J(PH) = 8 Hz, 4 H, CH]. − ^{13}C NMR (75.4 MHz, [D$_8$]THF): δ = 19.4 (s, CH_3), 20.7 (s, CH_3), 22.1 (m, PCH_3), 22.9 (m, PCH_3), 119.2−171.6 (C). − ^{31}P NMR ([D$_8$]THF, 233 K): δ = −34 [dt, $^2J(P_{eq}P_{eq})$ = 87 Hz, $^2J(P_{ax}P_{eq})$ = 70 Hz, 1 P, PPh_2], −5 [dd, $^2J(P_{eq}P_{eq})$ = 87 Hz, $^2J(P_{ax}P_{eq})$ = 49 Hz, 2 P, PMe_3], 22 [dt, $^2J(P_{eq}P_{ax})$ = 70 Hz, $^2J(P_{eq}P_{ax})$ = 49 Hz, 1 P, PMe_3]. − $C_{30}H_{47}CoP_4$ (548.2): calcd. C 61.02, H 8.02, P 20.98; found C 60.69, H 7.80, P 21.39.

Carbonyl[2-(diphenylphosphanyl)benzoyl-*C*^{1},*P*]bis-(trimethylphosphane)cobalt (3): CoMe(PMe_3)$_4$ (880 mg, 2.30 mmol) in THF (50 mL) and triphenylphosphane (610 mg, 2.30 mmol) in THF (10 mL) were combined at −70 °C and then the resulting solution was allowed to warm to 20 °C in vacuo. After 3 h, CO was admitted, and the mixture was stirred under 1 bar CO for 15 h. The volatiles were then removed in vacuo and the residue was extracted with pentane (30 mL). Crystallization at 4 °C afforded dark-red crystals. Yield 300 mg (24%) of **3**; m.p. 141−143 °C. − IR (Nujol): $\tilde{\nu}$ = 1917 cm^{-1} (C≡O), 1582 (C=C), 1551 (C=O). − ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 1.13 [t′, $|^2J(PH) + {}^4J(PH)|$ = 7.1 Hz, 18 H, PCH_3], 7.33 (m, 8 H, CH), 7.47 (m, 1 H, CH), 7.56 (m, 4 H, CH), 7.66 (m, 1 H, CH). − ^{13}C NMR (75.4 MHz, [D$_8$]THF): δ = 18.3 (m, PCH_3), 119.4−156.0 (C), 222.4 (m, C≡O), 261.1 (m, C=O). − ^{31}P NMR ([D$_8$]THF): δ = 8.7 [d, $^2J(P_{eq}P_{eq})$ = 69 Hz, 2 P, PMe_3], 83.0 (br. s, 1 P, PPh_2).

{2-[Bis(4-methylphenyl)phosphanyl]-5-methylbenzoyl-*C*^{1},*P*}carbonyl-bis(trimethylphosphane)cobalt (4): CoMe(PMe_3)$_4$ (760 mg, 2.00 mmol) in THF (50 mL) and tri-*p*-tolylphosphane (610 mg, 2.30 mmol) in THF (10 mL) were combined at −70 °C and then

the resulting mixture was allowed to warm to 20 °C in vacuo. After 3 h, CO was admitted, and the mixture was stirred under 1 bar CO for 15 h. Workup as in the case of **3** afforded dark-red crystals. Yield 300 mg (26%); m.p. 162−164 °C. − IR (Nujol): $\tilde{\nu}$ = 1909, 1863 cm^{-1} (C≡O), 1598 (C=C), 1572, 1546 (C=O). − ^1H NMR (300 MHz, [D$_8$]THF): δ = 1.11 [t′, $|^2J(PH) + {}^4J(PH)|$ = 7.2 Hz, 18 H, PCH_3], 2.31 (s, 6 H, CCH_3), 2.35 (s, 3 H, CCH_3), 7.12 [d, $^3J(HH)$ = 7.9 Hz, 4 H, CH], 7.16 [d, $^3J(HH)$ = 7.6 Hz, 1 H, CH], 7.26 (s, 1 H, C^6-H), 7.42 [dd, $^3J(PH)$ = 10.0 Hz, $^3J(HH)$ = 8.1 Hz, 4 H, C^2−H], 7.51 [dd, $^4J(PH)$ = 5.8 Hz, $^3J(HH)$ = 7.5 Hz, 4 H, C^3−H]. − ^{13}C NMR (75.4 MHz, [D$_8$]THF): δ = 15.7 (s, CH_3), 20.2 [t′, $|^1J(PC) + {}^3J(PC)|$ = 26 Hz, PCH_3], 21.3 (s, CH_3), 121.6 [d, $^2J(PC)$ = 20 Hz, 3-C], 129.5 [d, $^3J(PC)$ = 9 Hz, *m*-C], 130.6 (s, 4-C/6-C), 131.1 (s, 6-C/4-C), 132.8 [d, $^2J(PC)$ = 13 Hz, *o*-C], 137.8 [d, $^1J(PC)$ = 35 Hz, *ipso*-C], 139.3 (s, *p*-C), 140.6 [d, $^2J(PC)$ = 32 Hz, 2-C], 140.8 (s, 5-C), 158.7 [d, $^1J(PC)$ = 62 Hz, 1-C], 222.7 (m, C≡O), 263.1 (m, C=O). − ^{31}P NMR ([D$_8$]THF, 233 K): δ = 9.0 [d, $^2J(P_{eq}P_{eq})$ = 81 Hz, 2 P, PMe_3], 80.5 [t, $^2J(P_{eq}P_{ax})$ = 81 Hz, 1 P, PPh_2]. − $C_{29}H_{38}CoO_2P_3$ (570.1): calcd. C 61.06, H 6.71, P 16.29; found C 60.88, H 6.95, P 15.71.

Hydrogenation of 1: Hydrogenation of **1** (250 mg, 0.50 mmol) in diethyl ether (30 mL) by stirring for 15 h under 1 bar of H_2 furnished a red solid, which was isolated by decantation and washing. Yield 50 mg of **5** (27% based on PPh_3); decomp. > 158 °C. − IR (Nujol): $\tilde{\nu}$ = 1941 cm^{-1} (Co−H), 1582 (C=C). − ^1H NMR (200 MHz, [D$_8$]THF): δ = −17.30 (br. s, 1 H, CoH), 1.11 (br. s, 27 H, PCH_3), 7.18−7.41 (m, 15 H, CH). − ^{31}P NMR ([D$_8$]THF): δ = 4.8 (br. s, 3 P, PCH_3), 58.5 (br. s, 1 P, PPh_3). − $C_{27}H_{43}CoP_4$ (550.5): calcd. C 58.91, H 7.87, P 22.51; found C 57.92, H 7.34, P 21.73. − All volatiles were removed in vacuo from the light-red solution, and the solid residue was taken up in pentane (30 mL). At −25 °C, red plates crystallized. Yield 180 mg of **6** (60% based on PPh_3); decomp. > 171 °C. − IR (Nujol): $\tilde{\nu}$ = 1967 cm^{-1} (Co−H), 1582 (C=C). − ^1H NMR (300 MHz, [D$_8$]THF): δ = −17.70 (m, 1 H, CoH), 0.93 (br. s, 18 H, PCH_3), 7.11 (m, 18 H, CH), 7.36 (m, 12 H, CH). − ^{31}P NMR ([D$_8$]THF): δ = 5.5 (br. s, 2 P, PCH_3), 56.3 (br. s, 2 P, PPh_3).

[2-(Diphenylphosphanyl)phenyl-*C*^{1},*P*]iodo(methyl)bis(trimethylphosphane)cobalt (7): 1 (840 mg, 1.50 mmol) in THF (30 mL) was combined with iodomethane (0.10 mL, 210 mg, 1.50 mmol) in THF (30 mL) at −70 °C. The solution was allowed to warm to ambient temperature and within 30 min took on a light-brown color and became turbid. After 15 h at 20 °C, the volatiles were removed in vacuo and the brown solid was extracted with diethyl ether. On storage of the extract at 4 °C, dark-brown crystals were obtained. Yield 390 mg (42%); m.p. 123−124 °C. − ^1H NMR (300 MHz, [D$_8$]THF): δ = 0.51 [dt, $^3_{cis}J(PH)$ = 9.5 Hz, $^3_{trans}J(PH)$ = 1.8 Hz, 3 H, $CoCH_3$], 0.98 [t′, $|^2J(PH) + {}^4J(PH)|$ = 3.7 Hz, 18 H, PCH_3], 6.73 (br. s, 1 H, CH), 7.05 (m, 2 H, CH), 7.22 [d, $^3J(HH)$ = 8 Hz, 1 H, CH], 7.33 (m, 6 H, CH), 7.77 (m, 4 H, CH). − ^{13}C NMR (75.4 MHz, [D$_8$]THF): δ = 14.2 [t′, $|^1J(PC) + {}^3J(PC)|$ = 27 Hz, PCH_3], 121.6 [d, $^3J(PC)$ = 6 Hz, 4-C], 126.6 (s, 5-C/6-C), 127.6 [d, *J*(PC) = 8 Hz, *o*-C/*m*-C], 128.0 (s, *p*-C), 130.9 [d, *J*(PC) = 9 Hz, *m*-C/*o*-C], 134.4 [d, $^2J(PC)$ = 20 Hz, 3-C], 137.5 [d, $^1J(PC)$ = 14 Hz, *ipso*-C]. − ^{31}P NMR ([D$_8$]THF, 233 K): δ = 9.6 (s, 2 P, PMe_3), −40.2 (s, 1 P, PPh_2). − $C_{25}H_{35}CoIP_3$ (614.0): calcd. C 48.88, H 5.74, P 15.13; found C 48.78, H 5.62, P 15.88.

Chloro[2-(diphenylphosphanyl)phenyl-*C*^{1},*P*]bis(trimethylphosphane)cobalt (8). − Method a: 1 (310 mg, 0.6 mmol) in THF (40 mL) was combined with benzoyl chloride (80 mg) in THF (1 mL) at −70 °C. Warming to 20 °C afforded a dark-brown solution which, after stirring for 16 h, was concentrated to dryness in vacuo. The residue was extracted with pentane to remove traces of $CoCl(PMe_3)_3$ (IR control) and then with diethyl ether, from which dark-brown quadrangular rods were crystallized. Yield 150 mg (50%) of **8**. − **Method b:** At −70 °C in vacuo, acetyl chloride (210 mg, 1.50 mmol) in THF (30 mL) was condensed into a vessel containing **1** (740 mg, 1.40 mmol) in THF (30 mL). The resulting mixture was allowed to warm to ambient temperature; within 5 min a light-green solid separated, which slowly redissolved. After 15 h at 20 °C, a red-brown solution was obtained, which was concentrated to dryness in vacuo. The residue was extracted with pentane, and on storage of the extract at 4 °C dark-brown crystals were obtained. Yield 660 mg (59%) of **8**; m.p. 123−124 °C. − IR (Nujol): $\tilde{\nu}$ = 1582 cm^{-1}, 1552 (C=C). − $C_{24}H_{32}ClCoP_3$ (507.1): calcd. C 56.76, H 6.35, P 18.30; found C 56.68, H 6.35, P 18.22.

Chloro[2-(diphenylphosphanyl)phenyl]bis(trimethylphosphane)nickel (9): 1 (830 mg, 1.5 mmol) and $NiCl_2(PMe_3)_2$ (420 mg) were combined in diethyl ether (60 mL) at −70 °C. Warming to 20 °C afforded a dark-brown solution which, after 16 h, had taken on a greenish-brown appearance. It was then concentrated to dryness in vacuo. Extraction of the residue with diethyl ether afforded a greenish-brown solution, storage of which at 4 °C led to the deposition of honey-colored quadrangular rods. Yield 420 mg (55%) of **9**; m.p. 165−168 °C. − IR (Nujol): $\tilde{\nu}$ = 1581 cm^{-1}, 1554 (C=C). − ^1H NMR (300 MHz, [D$_8$]THF): δ = 0.89 (br. s, 1 H, 18 H, PCH_3), 6.70 [t, $^3J(PH)$ = 7.2 Hz, 1 H, CH], 6.85 [t, $^3J(PH)$ = 7.1 Hz, 1 H, CH], 6.93 [d, $^2J(PH)$ = 5 Hz, 1 H, CH], 7.31 (m, 7 H, CH), 7.44 (m, 4 H, CH). − ^{13}C NMR (75.4 MHz, [D$_8$]THF): δ = 13.2 [t′, $|^1J(PC) + {}^3J(PC)|$ = 30 Hz, PCH_3], 121.4, 127.3, 132.3 (s, 4-C, 5-C, 5-C), 129.0 (s, *p*-C), 129.1 [d, $^3J(PC)$ = 6 Hz, *m*-C], 134.9 [d, $^2J(PC)$ = 17 Hz, *o*-C], 136.6 [dt, $^2J(PC)$ = 25 Hz, $^4J(PC)$ = 6 Hz, 3-C], 140.4 [d, $^1J(PC)$ = 15 Hz, *ipso*-C], 137.5 (m, 2-C), 169.4 (m, 1-C). − ^{31}P NMR ([D$_8$]THF, 233 K): δ = −5.4 (B_2, PMe_3), −7.0 (A, PPh_2); AB_2 spin system, *J*/δ = 0.16 with $^2J(PP)$ = 21 Hz. − $C_{24}H_{32}ClNiP_3$ (506.1): calcd. C 56.79, H 6.35, P 18.31; found C 56.64, H 6.60, P 18.22.

Table 1. Crystal data for compounds **1** and **3**

	1	**3**
Empirical formula	$C_{27}H_{41}CoP_4$	$C_{26}H_{32}CoO_2P_3$
Molecular mass	548.4	528.4
Crystal size [mm]	0.32 × 0.52 × 0.38	0.52 × 0.38 × 0.47
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1/n$
a [Å]	16.366(3)	13.2532(14)
b [Å]	18.919(6)	16.618(2)
c [Å]	19.049(3)	13.887(2)
α [°]	90	90
β [°]	90	96.304(8)
γ [°]	90	90
V [Å^3]	5898(2)	3039.9(5)
Z	8	4
$D_{calcd.}$ [g/cm^3]	1.235	1.142
μ(Mo-K_α) [mm^{-1}]	0.812	−
Temperature [K]	293(2)	293(2)
Data coll. range [°]	4.3 ≤ 2Θ ≤ 55	−
h	0 ≤ *h* ≤ 21	−1 ≤ *h* ≤ 5
k	−24 ≤ *k* ≤ 1	−19 ≤ *k* ≤ 19
l	−1 ≤ *l* ≤ 24	−16 ≤ *l* ≤ 16
No. reflect. measured	7594	2411
No. unique data	6775 (R_{int} = 0.0421)	−
Parameters	298	271
GoF on F^2	0.996	1.029
*R*1 [$I \geq 2\sigma(I)$]	0.0446	0.0526
*wR*2 (all data)	0.1076	0.1617

Hydrogenation Tests: A 1-L stainless steel autoclave was charged with 1-octene (15.4 g) in pentane (130 mL) under argon. A solution of either **5** or **1** (430 mg) in pentane (10 mL) was added under hydrogen pressure, which was maintained at 70 bar by continuous feeding. The system was kept at 30 °C for 8 h until no further uptake of hydrogen was observed. The volatiles were then collected in a cold trap in vacuo and were shown to contain 1-octene and less than 1% octane (GC).

Crystal Structure Analyses: Crystal data are presented in Table 1 and Table 2. Data collection: Complex **1**: A dark-red specimen was sealed under argon in a glass capillary and mounted on a Siemens P4 diffractometer. Intensities were collected (ω scans) using graphite-monochromated Mo-K_α radiation; Lp corrections and absorption corrections based on ψ-scans were applied. The structure was solved by direct and conventional Fourier methods. All non-hydrogen atoms were treated anisotropically; hydrogen atoms were treated with a riding model in idealized positions. − Complex **3**: A dark-brown specimen was sealed and mounted as described for **1**. Data collection as for **1**. The structure was solved using Patterson and Fourier methods. Refinement as for **1**. − Complex **7**: A dark-brown specimen was sealed and mounted as described for **1**. Data collection, structure solution, and refinement as for **1**. − Complex **8**: A dark-brown specimen was sealed and mounted as described for **1**. Data collection, structure solution, and refinement as for **1**. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-116690 for **1**, CCDC-136410 for **3**, CCDC-116691 for **7**, and CCDC-116692 for **8**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data for compounds **7** and **8**

	7	**8**
Empirical formula	$C_{25}H_{35}CoIP_3$	$C_{24}H_{32}ClCoIP_3$
Molecular mass	614.3	507.8
Crystal size [mm]	0.28 × 0.38 × 0.30	0.28 × 0.58 × 0.48
Crystal system	monoclinic	monoclinic
space group	$P2_1/n$	Cc
a [Å]	10.529(2)	10.065(1)
b [Å]	17.364(2)	17.617(2)
c [Å]	14.877(2)	14.838(2)
α [°]	90	90
β [°]	92.41(1)	96.96(1)
γ [°]	90	90
V [Å^3]	2717.5(7)	2611.6(5)
Z	4	4
$D_{calcd.}$ [g/cm^3]	1.501	1.291
μ(Mo-K_α) [mm^{-1}]	1.955	0.952
Temperature [K]	293(2)	293(2)
Data coll. range [°]	$4.5 \le 2\Theta \le 55$	$4.6 \le 2\Theta \le 55$
h	$-13 \le h \le 1$	$-1 \le h \le 13$
k	$-1 \le k \le 22$	$-1 \le k \le 22$
l	$-19 \le l \le 19$	$-19 \le l \le 19$
No. reflect. measured	7725	3731
No. unique data	6241 (R_{int} = 0.0239)	3503 (R_{int} = 0.0205)
Parameters	272	262
GoF on F^2	0.973	1.013
$R1$ [$I \ge 2\sigma(I)$]	0.0378	0.0345
$wR2$ (all data)	0.0776	0.0839

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[1] A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879−2932.
[2] S. Trofimenko, *Inorg. Chem.* **1973**, *12*, 1215−1221.
[3] [3a] W. Keim, *J. Organomet. Chem.* **1968**, *14*, 179−184. − [3b] B. Longato, F. Morandini, S. Bresadola, *J. Organomet. Chem.* **1975**, *88*, C7−C8. − [3c] M. A. Bennett, D. L. Milner, *J. Chem. Soc., Chem. Commun.* **1967**, 581−582. − [3d] B. R. James, L. D. Markham, D. K. W. Wang, *J. Chem. Soc., Chem. Commun.* **1974**, 439−440. − [3e] D. J. Cole-Hamilton, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1977**, 797−804. − [3f] A. J. Cheney, B. E. Mann, B. L. Shaw, R. M. Slade, *J. Chem. Soc., Chem. Commun.* **1970**, 1176−1177. − [3g] M. A. Bennett, T. Dirnberger, D. C. R. Hockless, E. Wenger, A. C. Willis, *J. Chem. Soc., Dalton Trans.* **1998**, 271−277.
[4] G. Hata, H. Kondo, *J. Am. Chem. Soc.* **1968**, *90*, 2278−2281. A. Misono, Y. Uchida, T. Saito, K. M. Song, *J. Chem. Soc., Chem. Commun.* **1967**, 419−420. − [5b] A. Sacco, M. Rossi, *Inorg. Chim. Acta* **1968**, *2*, 127−132. − [5c] J. H. Enemark, B. R. Davis, J. A. McGinnety, J. A. Ibers, *J. Chem. Soc., Chem. Commun.* **1968**, 96−97. − [5d] A. Yamamoto, S. Kitazume, L. S. Pu, S. Ikeda, *J. Am. Chem. Soc.* **1971**, *93*, 371−380. − [5a]
[6] Y. Kubo, A. Yamamoto, S. Ikeda, *J. Organomet. Chem.* **1973**, *59*, 353−364.
[7] M. Font-Bardia, J. González-Platas, G. Muller, D. Panyella, M. Rocamora, X. Solans, *J. Chem. Soc., Dalton Trans.* **1994**, 3075−3084.
[8] W. Keim, *J. Organomet. Chem.* **1969**, *19*, 161−168.
[9] J. S. Ricci, J. A. Ibers, *J. Organomet. Chem.* **1971**, *27*, 261−271.
[10] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229−266.
[11] H.-F. Klein, U. Lemke, M. Lemke, A. Brand, *Organometallics* **1998**, *17*, 4196−4201.
[12] U. Lemke, Dissertation, TU Darmstadt, **1998**.
[13] H.-F. Klein, H. H. Karsch, *Chem. Ber.* **1975**, *108*, 944−955.
[14] H.-F. Klein, H. H. Karsch, *Inorg. Chem.* **1975**, *14*, 473−477.
[15] G. W. Parshall, *Acc. Chem. Res.* **1970**, *3*, 139−144.
[16] H.-F. Klein, H. H. Karsch, *Chem. Ber.* **1975**, *108*, 956−966.
[17] K. A. Jensen, O. Dahl, *Acta Chem. Scand.* **1968**, *22*, 1044−1045.

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