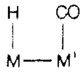
scribed as occurring by rotation of the $Pt(CO)(PCy_3)$ fragment about an axis perpendicular to the Os_3 plane.[51]

The chemistry of heteronuclear bridging hydrides is currently actively investigated, from a synthetic, structural, and catalytic point of view.[4,52] The dynamic behavior and the reactivity of the heterobimetallic complexes reported here show their versatility and the potential of this class of complexes. Binuclear systems of the type



$$\overset{\overset{H}{|}}{M}-\overset{\overset{CO}{|}}{M'}$$

deserve theoretical and further experimental studies. In the systems reported here, migration of the hydride ligand bonded to platinum occurs toward the adjacent metal rather than toward a carbonyl ligand.

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Registry No. **1**, 81423-60-1; **2**, 104033-91-2; **3**, 104051-35-6; **4**, 98063-33-3; $Na[Mo(CO)_3Cp]\cdot 2DMF$, 104033-92-3; *trans*-$PtH(Cl)(PPh_3)_2$, 16841-99-9; $Na[W(CO)_3Cp]\cdot 2DMF$, 104033-93-4; $Na[Mn(CO)_5]$, 13859-41-1; *trans*-$PtH(Cl)(PEt_3)_2$, 16842-17-4; $Pt_4(\mu\text{-}CO)_5(PPh_3)_4$, 27518-14-5; $Pt_2Cl_2(\mu\text{-}CO)PPh_3)_3$, 89742-11-0; $Pt_3(\mu\text{-}CO)_3(PPh_3)_4$, 16222-02-9; $Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4$, 68875-50-3; $[Mo(CO)_3Cp]_2$, 12091-64-4; $Pt_2Mo_2Cp_2(CO)_6(PPh_3)_2$, 93084-57-2.

Supplementary Material Available: Calculated hydrogen atom positions for 1 and 4 (Tables VI and VII), anisotropic thermal parameters for 1 and 4 (Tables VIII and IX), and selected least-squares planes for 1 and 4 (Tables X and XI) and views of the structures of 1 and 4 with the complete atom labeling scheme (Figures 4 and 5) (12 pages); tables of observed and calculated structure factors for 1 and 4 (Tables XII and XIII) (33 pages). Ordering information is given on any current masthead page.

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Preparation, Properties, and Reactions of Metal-Containing Heterocycles. 51.[1] Three- and Five-Membered Phosphacobaltacycloalkanes

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The synthesis of three- and five-membered phosphacobaltacycloalkanes $(OC)_3\overline{CoPPh_2CH_2}$ (**3a**), $(OC)_3\overline{CoPPh_2(CH_2)_3}$ (**4a**), and $(OC)_3\overline{CoP(C_6H_{11})_2(CH_2)_3}$ (**4b**) by reductive cycloelimination of $[(OC)_3CoPPh_2CH_2Cl]_2$ (**1a**), $[(OC)_3CoPPh_2(CH_2)_3Cl]_2$ (**2a**), and $[(OC)_3CoP(C_6H_{11})_2(CH_2)_3Cl]_2$ (**2b**) is described. Reaction of the five-membered ring with CO or PPh_3 results either in CO insertion into the metal–alkyl C bond forming $(OC)_3\overline{CoPPh_2(CH_2)_3C}{=}O$ (**5a**), $(OC)_3\overline{CoP(C_6H_{11})_2(CH_2)_3C}{=}O$ (**5b**), and $Ph_3P(OC)_2\overline{CoPPh_2(CH_2)_3C}{=}O$ (**6a**), respectively, or in CO substitution yielding $Ph_3P(OC)_2\overline{CoP(C_6H_{11})_2(CH_2)_3}$ (**7b**). The products were characterized by IR, NMR (^1H, ^{13}C, and ^{31}P), and mass spectroscopy. Single crystals of $(OC)_3\overline{CoPPh_2CH_2}$ (**3a**) are monoclinic of space group $P2_1/c$ with $a = 10.498$ (4) Å, $b = 7.697$ (3) Å, $c = 18.783$ (5) Å, $\beta = 98.29$ (2)°, and $Z = 4$. Single crystals of $(OC)_3\overline{CoP(C_6H_{11})_2(CH_2)_3}$ (**4b**) are triclinic of space group $P\bar{1}$ with $a = 9.999$ (5) Å, $b = 12.910$ (5) Å, $c = 8.364$ (3) Å, $\alpha = 101.81$ (3)°, $\beta = 101.28$ (3)° $\gamma = 112.44$ (4)°, and $Z = 2$. The cobalt coordination in $(OC)_3\overline{CoPPh_2CH_2}$ (**3a**) is a distorted trigonal bipyramid. According to a short P–C(4) bond of 1.725 (5) Å the $\overline{Co\text{–}P\text{–}C}$ ring is described as a phosphorus ylide with a complexed ylidic C(4) atom. $(OC)_3\overline{CoP(C_6H_{11})_2(CH_2)_3}$ (**4b**) is essentially a metallacyclopentane with a trigonal-bipyramidal coordinated cobalt.

Introduction

Interest in metallacycloalkanes recently increased due to their presumed role in transition-metal-catalyzed reactions.[2] This is also true for complexes with donor atoms in the metallacycle.[3,4] Cobalt is of increasing importance as a component of highly reactive catalytic systems.[5] Continuing earlier studies of three- to seven-membered

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phosphametallacycloalkanes with different transition metals[6] we extended our investigations to three- and five-membered phosphacobaltacycloalkanes. A key function in C–H activation has been ascribed to $\overline{\text{M–P–C}}$ rings.[7] They are characterized by a shortened P–C bond[6f,g,8] and may be considered as ylide complexes.

Experimental Section

General Procedures. All preparations were carried out under an atmosphere of argon purified with a surface compound consisting of chromium(II) on silica gel.[9] THF was freshly distilled from $LiAlH_4$; *n*-hexane and toluene were rendered water- and oxygen-free by distillation from sodium. Purification of CO was achieved by passing the gas through Schlenk tubes cooled to −80 °C. For chromatographic purification of the products columns (diameter 2.6 cm) with silica gel 60 (Merck) were used. Instrumentation: mass spectra, Varian MAT 711 A; IR, Beckman IR 12 and Bruker FT-IR spectrometer, Model IFS 113c; ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR, Bruker WP 80 and Bruker AC 80 at 80, 20.12, 32.39, and 80.13, 20.15, 32.44 MHz, respectively. Elemental analyses were carried out with a Carlo Erba Model 1104, and a Perkin-Elmer atomic absorption spectrometer, Model 4000. (3-Chloropropyl)diphenylphosphane[10] and (3-chloropropyl)dicyclohexylphosphane[6e,11] were prepared by literature methods. (Chloromethyl)diphenylphosphane was synthesized by modification of the described procedure.[10]

(Chloromethyl)diphenylphosphane. Pure $HPPh_2$ (5.4 mL, 31 mmol, $d = 1.07$ g/cm^3) was added dropwise to 1.7 g (74 mmol) of sodium granules stirred in 200 mL of THF at 0 °C. After the reaction mixture had turned to deep orange (30 min), excess sodium was filtered off (P3) at room temperature and the filtrate was added dropwise to 40 mL of cooled CH_2Cl_2 (−40 °C) within 3 h. Removal of the solvent at −10 °C under reduced pressure led to a yellow viscous noncrystallizing liquid still containing dissolved NaCl (yield ≈ 80%). Ph_2PCH_2Cl was identified by its ^{31}P{^{1}H} NMR spectrum (δ −11.4, THF, −30 °C). Because the phosphane decomposes within few hours at −10 °C,[10] no attempts for further purification were made. The toluene solution of the residual liquid was immediately used for substitution of CO in $Co_2(CO)_8$.

Bis[tricarbonyl[(chloromethyl)diphenylphosphane]cobalt](*Co–Co*) (1a). To 4.1 g (12 mmol) of $Co_2(CO)_8$ dissolved in 50 mL of toluene at 50 °C was quickly added the solution of 5.9 g (25 mmol) of Ph_2PCH_2Cl in 50 mL of toluene in one portion, resulting in a vigorous gas evolution. After being stirred for 45 min, the reaction mixture was cooled to room temperature and solid byproducts were separated by filtration (P3) as quickly as possible. Removal of the solvent afforded a brown residue which was first suspended in 50 mL of *n*-hexane. After separation from the solution the product was washed twice, each time with 20-mL portions of *n*-hexane, yielding 6.3 g (69.5%) of **1a** as a brown powder soluble in polar organic solvents: decomp >116 °C; IR [ν(C≡O) (toluene, cm^{-1})] 2046 (w), 1968 (vs, br); ^{1}H NMR (C_6D_6, 30 °C) δ 1.35 (s, CH_2), 6.7–7.5 (m, PPh_2); FDMS (8 kV), *m/e* (relative intensity) 754 (100) (M$^+$, ^{35}Cl calcd 754), 342 (25) (M$^+$ − Cl/2). Anal. Calcd for $C_{32}H_{24}Cl_2Co_2O_6P_2$: C, 50.89; H, 3.20; Cl, 9.39; Co, 15.61. Found: C, 50.78; H, 3.06; Cl, 9.66; Co, 15.30.

General Preparation of [$(OC)_3CoPR_2(CH_2)_3Cl]_2$ (2a and 2b). To $Co_2(CO)_8$ dissolved in 50 mL of benzene was added a solution of $PR_2(CH_2)_3Cl$ in 10 mL of benzene dropwise resulting in a vigorous gas evolution. After the solution was stirred for 12 h, the solvent was removed under reduced pressure. The residue was suspended in 40 mL of *n*-hexane. After separation from the solution the product was washed twice, each time with 20-mL portions of *n*-hexane.

Bis[tricarbonyl[(3-chloropropyl)diphenylphosphane]cobalt](*Co–Co*) (2a). $Co_2(CO)_8$ (3.0 g, 8.8 mmol) and 4.7 g (18 mmol) of (3-chloropropyl)diphenylphosphane were reacted. The whole procedure was carried out at room temperature. **2a** was isolated as a brown powder which dissolves well only in polar organic solvents in 79.8% yield (5.7 g): decomp >115 °C; IR [ν(C≡O) (CCl_4, cm^{-1})] 1986 (w), 1973 (vs, br); ^{1}H NMR (C_6D_6, 30 °C) δ 2.0 (m, PCH_2CH_2), 2.4 (m, PCH_2), 3.0 (t, $^3J_{HH}$ = 6.3 Hz, CH_2Cl), 6.9–7.8 (m, PPh_2); FDMS (8 kV), *m/e* 810 (M$^+$, ^{35}Cl calcd 810). Anal. Calcd for $C_{36}H_{32}Cl_2Co_2O_6P_2$: C, 53.29; H, 3.97; Cl, 8.37; Co, 14.53. Found: C, 53.26; H, 3.79; Cl, 9.08; Co, 14.22.

Bis[tricarbonyl[(3-chloropropyl)dicyclohexylphosphane]cobalt](*Co–Co*) (2b). $Co_2(CO)_8$ (3.0 g, 8.8 mmol) and 4.9 g (18 mmol) of (3-chloropropyl)dicyclohexylphosphane were used. The reaction was carried out at 40 °C. **2b** was isolated in 81.6% yield (6.0 g) as a reddish brown powder soluble in polar organic solvents: decomp >135 °C; IR [ν(C≡O) (CCl_4, cm^{-1})] 2025 (w), 1973 (sh), 1952 (vs, br); ^{1}H NMR (C_6D_6, 30 °C) δ 1.0–1.7 (m, $P(C_6H_{11})_2CH_2CH_2$), 3.1 (m, CH_2Cl); FDMS (8 kV), *m/e* 834 (M$^+$, ^{35}Cl calcd 834). Anal. Calcd for $C_{36}H_{56}Cl_2Co_2O_6P_2$: C, 51.75; H, 6.76; Cl, 8.49; Co, 14.11. Found: C, 51.53; H, 6.81; Cl, 8.24; Co, 13.99.

General Preparation of $(OC)_3\overline{CoPR_2(CH_2)_n}$ (3a, 4a, and 4b). A solution of [$(OC)_3CoPR_2(CH_2)_nCl]_2$ (**1a**, **2a**, or **2b**) in 200 mL of THF was added to amalgamized sodium at −10 °C. Once the color of the dark brown solution cleared, the THF solution was decanted and the solvent was removed under reduced pressure at −10 °C. The residual dark oil was extracted three times with 50-mL portions of *n*-hexane (−10 °C), and from the combined extracts solvent was removed by evaporation.

2,2,2-Tricarbonyl-1,1-diphenyl-1-phospha-2-cobaltacyclopropane (3a). **1a** (1.5 g, 2 mmol) and 214 g of 0.6% sodium amalgam were reacted. The reaction time was 15 min. The obtained product was purified by chromatography on a 14-cm silica gel column eluting with *n*-hexane at —30 °C. **3a** was isolated as a yellow powder which is well soluble in nonpolar and in polar organic solvents (261 mg, 19.1% yield after purification) and sublimes at −5 °C (10^{-6} torr): mp 39 °C; ^{1}H NMR (toluene-d_8, −30 °C) δ 1.19 (s, CH_2), 6.5–7.3 (m, PPh_2); ^{13}C{^{1}H} NMR (THF-d_8, −20 °C)[12,13] δ 128.74 (d, $^1J_{PC}$ = 62.7 Hz, C^1-Ph), 129.76 (d, $^3J_{PC}$ = 12.8 Hz, C^{3,5}-Ph), 132.00 (d, $^4J_{PC}$ = 3.4 Hz, C^4-Ph), 133.88 (d, $^2J_{PC}$ = 13.0 Hz, C^{2,6}-Ph); MS (70 eV), *m/e* (relative intensity) 342 (3, M$^+$), 314 (25, M$^+$ − CO), 286 (29, M$^+$ − 2 CO), 258 (100, M$^+$ − 3 CO), 183 (26, $P(C_6H_4)_2^+$), 180 (48, $CoP(C_6H_4)CH_2^+$), 166 (20, $CoP(C_6H_4)^+$). Anal. Calcd for $C_{16}H_{12}CoO_3P$: C, 56.16; H, 3.53; Co, 17.22. Found: C, 56.13; H, 3.71; Co, 17.02.

2,2,2-Tricarbonyl-1,1-diphenyl-1-phospha-2-cobaltacyclopentane (4a). **2a** (2.0 g, 2.5 mmol) and 216 g of 0.6% sodium amalgam were reacted. The reaction time was 75 min. The obtained product was purified by chromatography on a 17-cm silica gel column eluting with *n*-hexane at −10 °C. **4a** was isolated as a yellow powder which is soluble in nonpolar and polar organic solvents (709 mg, 38.3% yield after purification): decomp >51 °C; ^{1}H NMR (C_6D_6) δ 1.35 (m, CH_2), 1.96 (m, CH_2), 2.38 (m, CH_2), 6.9–7.5 (m, PPh_2); ^{13}C{^{1}H} NMR (THF-d_8, −33 °C)[12,13] δ 129.29 (d, $^3J_{PC}$ = 9.5 Hz, C^{3,5}-Ph), 130.56 (d, $^4J_{PC}$ = 2.1 Hz, C^4-Ph), 132.21 (d, $^2J_{PC}$ = 11.5 Hz, C^{2,6}-Ph), 137.86 (d, $^1J_{PC}$ = 36.6 Hz, C^1-Ph);

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MS (70 eV), *m/e* (relative intensity) 370 (2, M^+), 342 (19, M^+ − CO), 314 (17, M^+ − 2 CO), 300 (19, M^+ − 2 CO − CH_2), 286 (39, M^+ − 3 CO), 272 (35, M^+ − 3 CO − CH_2), 258 (12, M^+ − 3 CO − 2 CH_2), 244 (71, M^+ − 3 CO − 3 CH_2), 183 (100, $P(C_6H_4)_2^+$). Anal. Calcd for $C_{18}H_{16}CoO_3P$: C, 58.36; H, 4.35; Co, 15.92. Found: C, 58.94; H, 4.41; Co, 16.18.

2,2,2-Tricarbonyl-1,1-dicyclohexyl-1-phospha-2-cobaltacyclopentane (4b). **2b** (1.5 g, 1.8 mmol) was reacted with 200 g of 0.6% sodium amalgam. The reaction time was 60 min. Recrystallization of the crude product from *n*-hexane yielded a yellow crystalline compound which dissolves in nonpolar and polar organic solvents (684 mg, 49.7% yield): mp 85 °C; ^1H NMR (toluene-d_8, −20 °C) δ 0.9–2.0 (m, CH_2); MS (70 eV), *m/e* (relative intensity) 382 (2, M^+), 354 (16, M^+ − CO), 326 (29, M^+ − 2 CO), 298 (28, M^+ − 3 CO), 296 (30, M^+ − 3 CO − 2 H), 294 (14, M^+ − 3 CO − 4 H), 284 (4, M^+ − 3 CO − CH_2), 268 (13, M^+ − 3 CO − 2 CH_2 − 2 H), 266 (14, M^+ − 3 CO − 2 CH_2 − 4 H), 254 (43, M^+ − 3 CO − 3 CH_2 − 2 H), 252 (43, M^+ − 3 CO − 3 CH_2 − 4 H), 250 (31, M^+ − 3 CO − 3 CH_2 − 6 H). Anal. Calcd for $C_{18}H_{28}CoO_3P$: C, 56.55; H, 7.38; Co, 15.42. Found: C, 56.36; H, 7.20; Co, 14.82.

2,2,2-Tricarbonyl-1,1-diphenyl-1-phospha-2-cobalta-3-cyclohexanone (5a). A CO stream was passed through a solution of 730 mg (2.0 mmol) of **4a** in 70 mL of *n*-hexane at −10 °C during 7 h resulting in a yellow precipitate which was filtered off (P4) and then washed three times with 15-mL portions of *n*-hexane. **5a** was isolated as a yellow powder (447 mg, 56.1% yield) soluble in polar organic solvents: mp 69 °C; ^1H NMR (toluene-d_8, −20 °C) δ 1.1–1.9 (m, CH_2), 2.38 (t, $^3J_{HH}$ = 1.44 Hz, CH_2), 6.9–7.4 (m, PPh_2); $^{13}C\{^1H\}$ NMR (THF-d_8, −45 °C)[12,13] δ 129.47 (d, $^3J_{PC}$ = 9.9 Hz, $C^{3,5}$-Ph), 131.00 (d, $^4J_{PC}$ = 2.1 Hz, C^4-Ph), 132.80 (d, $^2J_{PC}$ = 11.2 Hz, $C^{2,6}$-Ph), 136.18 (d, $^1J_{PC}$ = 42.3 Hz, C^1-Ph); FDMS (8 kV), *m/e* (relative intensity) 398 (100, M^+), 370 (43, M^+ − CO). Anal. Calcd for $C_{19}H_{16}CoO_4P$: C, 57.30; H, 4.04; Co, 14.80. Found: C, 57.53; H, 4.23; Co, 15.25.

2,2,2-Tricarbonyl-1,1-dicyclohexyl-1-phospha-2-cobalta-3-cyclohexanone (5b). A CO stream was passed through a solution of 820 mg (2.1 mmol) of **4b** in 70 mL of *n*-hexane at −10 °C during 7 h. Removal of the solvent resulted in the formation of a yellow residue which was washed at −60 °C with four 5-mL portions of *n*-hexane. **5b** (401 mg, 44.4% yield) is sparingly soluble in *n*-hexane and better soluble in polar organic solvents: mp 64 °C; ^1H NMR (toluene-d_8, −20 °C) δ 0.6–2.0 (m, CH_2); FDMS (8 kV), *m/e* (relative intensity) 410 (63, M^+), 382 (100, M^+ − CO). Anal. Calcd for $C_{19}H_{28}CoO_4P$: C, 55.62; H, 6.88; Co, 14.36. Found: C, 55.86; H, 7.03; Co, 14.00.

2,2-Dicarbonyl-1,1-diphenyl-2-(triphenylphosphane)-1-phospha-2-cobalta-3-cyclohexanone (6a). To a solution of 310 g (0.8 mmol) of **4a** in 40 mL of *n*-hexane at −10 °C was added 880 mg (3.36 mmol) of PPh_3. The mixture was stirred for 4 h whereby a yellow solid precipitated which was filtered off and washed three times with 15-mL portions of *n*-hexane, yielding 334 mg (66.0%) of **6a**. The product is sparingly soluble even in polar organic solvents: decomp >35 °C; ^1H NMR (toluene-d_8, −20 °C) δ 0.8–1.5 (m, CH_2), 2.8 (m, CH_2), 6.8–7.2 (m, PPh); FDMS (8 kV), *m/e* (relative intensity) 632 (86, M^+), 604 (34, M^+ − CO), 370 (41, M^+ − PPh_3), 262 (100, PPh_3). Anal. Calcd for $C_{36}H_{31}CoO_3P_2$: C, 68.36; H, 4.93; Co, 9.32. Found: C, 67.13; H, 4.69; Co, 8.90.

2,2-Dicarbonyl-1,1-dicyclohexyl-2-(triphenylphosphane)-1-phospha-2-cobaltacyclopentane (7b). To a solution of 900 mg (2.4 mmol) of **4b** in 70 mL of *n*-hexane at −10 °C was added 1200 mg (4.6 mmol) of PPh_3, and the temperature was elevated to 60 °C. The reaction mixture was stirred for 1 h at this temperature and for another 12 h at 20 °C. A yellow residue was obtained after the solvent was removed from the muddy solution and was washed three times with 15-mL portions of *n*-hexane, yielding 826 mg (55.8%) of **7b**. The product is sparingly soluble even in polar organic solvents: decomp >101 °C; ^1H NMR (C_6D_6, 30 °C) δ 0.9–2.2 (m, CH_2), 7.0–7.9 (m, PPh_3); FDMS (8 kV), *m/e* 616 (M^+). Anal. Calcd for $C_{35}H_{43}CoO_2P_2$: C, 68.18; H, 7.03; Co, 9.56. Found: C, 68.30; H, 7.15; Co, 9.35.

X-ray Structure Determinations of 3a and 4b. Clear, yellow crystals of **3a** were obtained by slow crystallization from *n*-hexane. A suitable crystal with approximate dimensions 0.3 × 0.2 × 0.3 mm^3 was mounted on a glass fiber and then transferred to an Enraf-Nonius CAD-4 diffractometer with low-temperature equipment. The lattice constants were determined with 25 precisely centered high-angle reflections. The final cell parameters and specific data collection parameters for **3a** and **4b** are summarized in Table I. Systematic extinctions ($h0l$, $l = 2n$; $0k0$, $k = 2n$) suggested the space group to be $P2_1/c$ (no. 14). The usual corrections for Lorentz and polarization effects were applied to the intensity data. No decay in the intensities of three standard reflections was observed.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement of $(OC)_3\overline{\mathrm{CoPPh_2C}}\mathrm{H_2}$ (3a) and $(OC)_3\overline{\mathrm{CoP(C_6H_{11})_2(C}}\mathrm{H_2)_3}$ (4b)

	$(OC)_3\overline{\mathrm{CoPPh_2C}}\mathrm{H_2}$ **3a**	$(OC)_3\overline{\mathrm{CoP(C_6H_{11})_2(C}}\mathrm{H_2)_3}$ **4b**
formula	$C_{16}H_{12}CoO_3P$	$C_{18}H_{28}CoO_3P$
fw	342.18	382.33
space group	$P2_1/c$	$P\bar{1}$
a, Å	10.498 (4)	9.999 (5)
b, Å	7.697 (3)	12.910 (5)
c, Å	18.783 (5)	8.364 (3)
α, deg	90	101.81 (3)
β, deg	98.29 (2)	101.28 (3)
γ, deg	90	112.44 (4)
V, $Å^3$	1501.9	931.1
Z	4	2
d_{calcd}, g cm^{-3}	1.513	1.364
T, °C	−100	−90
$F(000)$, e	696	404
μ(Mo Kα), cm^{-1}	12.49	10.14
radiatn (graphite monochromator, λ = 0.710 73 Å)	Mo Kα	Mo Kα
θ limits, deg	3–26	3–25
scan type	ω/θ	ω/θ
max scan speed	40 s	40 s
h,k,l range	$-12\rightarrow0, -9\rightarrow0, -23\rightarrow23$	$-11\rightarrow11, -15\rightarrow15, -9\rightarrow0$
reflctns measd	6672	6991
no. of unique data with $I \geq 3\sigma(I)$	1886	2853
no. of variables	119	233
R	0.035	0.028
R_w	0.037	0.034
weighting scheme	$w^{-1} = \sigma^2(F)$	$w^{-1} = \sigma^2(F)$

The structure was solved by direct methods,[14] and difference Fourier syntheses were used to locate the remaining non-hydrogen atoms. The DIFABS[15] method of absorption correction was applied after isotropic refinement of all non-hydrogen atoms. The methylene hydrogen atoms were located with the aid of a difference Fourier map and refined. The positions of the phenyl hydrogen atoms were calculated on the basis of the usual trigonal geometry and included in the structure factor calculation but were not refined. A secondary extinction parameter[16] was refined in the final cycles of least squares (refined value, $g = 1.5\ (4) \times 10^{-7}$). The atomic scattering factors used were those from Cromer and Waber.[17]

A yellow single crystal of **4b** with dimensions 0.2 × 0.2 × 0.3 mm^3 was chosen for X-ray investigation. Automatic peak search and indexing procedure yielded a triclinic reduced primitive cell, and there were no conventional cells of higher symmetry. Corrections for Lorentz and polarization effects were applied to the intensity data. No correction for crystal decomposition was necessary. The structure was solved by direct methods.[14] The assumption that the space group was centric was confirmed by

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[14] (a) MULTAN 82, P. Main et al., Department of Physics, University of York, York, England. (b) All calculations were performed on a Digital PDP 11/60 using the Structure Determination Package (SDP) of B. A. Frenz & Ass., Inc., College Station, TX, and Enraf-Nonius, Delft, Netherlands.

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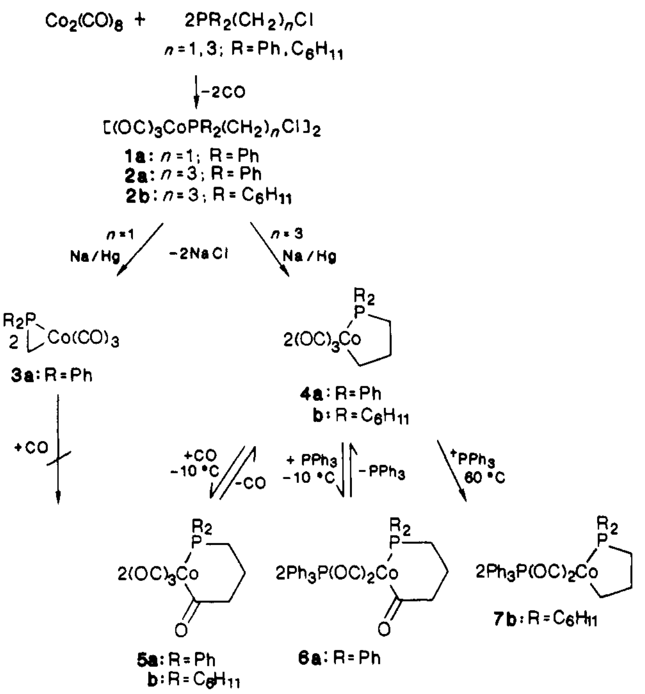
Scheme I



the successful refinement of the structure. An empirical correction for absorption (DIFABS[15]) was applied to the intensities. Calculated positions of the cyclohexyl hydrogens were included in the structure factor calculation but were not refined, while the positions of the hydrogen atoms belonging to the metallacycle were located and refined. In the final cycles of least squares a secondary extinction parameter was refined to a value of $g = 9.1 (6) \times 10^{-8}$.

Results and Discussion

The bifunctional ligands $R_2P(CH_2)_nCl$ (n = 1, 3) are necessary for the synthesis of the three- and five-membered phosphacobaltacycloalkanes **3a**, **4a**, and **4b**. As reported previously the preparation of Ph_2PCH_2Cl causes difficulties.[10] Reaction of $NaPPh_2$ with CH_2Cl_2 allows the synthesis of Ph_2PCH_2Cl as a yellow viscous liquid which is stable for some hours below −10 °C. Immediate conversion with $Co_2(CO)_8$ results in CO substitution, yielding stable $[(OC)_3CoPPh_2CH_2Cl]_2$ (**1a**) (Scheme I). The homologous complexes $[(OC)_3CoPR_2(CH_2)_3Cl]_2$ (**2a** and **2b**) are obtained by similar procedures. Formation of the compounds $(OC)_3\overline{CoPR_2(CH_2)_n}$ (**3a**, **4a**, and **4b**) can be achieved by reductive cycloelimination.[4a,6a,c,d,g]

The different nature of the M–C function in the three- and five-membered heterocycles **3a**, **4a**, and **4b** is shown by its behavior toward carbon monoxide. **3a** does not react with CO between −10 and 20 °C and behaves as the already known phosphametallacyclopropanes,[6f,g,7b] whereas n-hexane solutions of the cyclopentanes **4a** and **4b** absorb CO already at −10 °C, affording the phosphacobaltacyclohexanones **5a** and **5b**. The mechanism of these reactions is probably analogous to the alkyl migrations characterized by a coordinatively unsaturated intermediate which has been confirmed by several pertinent examples.[18] The easy cleavage of the Co–C bond[13,19] is especially demonstrated by comparison with CO insertions in phosphamanganacycloalkanes[4a,b,6b] which occur only under significantly more severe conditions. In accordance with experimental evidence lower activation barriers have been predicted for alkyl migrations in trigonal-bipyramidal cobalt complexes as compared to octahedrally coordinated alkylmanganese derivatives.[20] Numerous investigations show that CO insertion is influenced by solvents,[18b,c,20] type and stability of the M–C bond,[18b,20,21] and steric or electronic factors of the ligands.[18b,20,22] The ligand effect is also observed in our own experiments. With use of the sterically more demanding PPh_3, no CO insertion into the M–C σ bond of **4b** is observable. The reason of this steric hindrance are probably the voluminous cyclohexyl substituents in **4b**. CO replacement and formation of **7b** occurs only at 60 °C without any change of the five-membered ring. As was demonstrated for a carbonylcyclopentadienyliron complex,[23] such substitutions can proceed in two stages via primary CO insertion followed by decarbonylation.

Cleavage of the Co–C bond however is presumed for the reaction of the sterically less demanding compound **4a** with PPh_3 which already occurs at −10 °C. This behavior may be rationalized in terms of the Tolman cone angle[24] which is certainly smaller for the Ph_2PCH_2 fragment than for the $(C_6H_{11})_2PCH_2$ group (compare the smaller cone angle of PPh_2Me with $P(C_6H_{11})_2Me$).[24a]

The reactions **4a** ⇌ **5a**, **4b** ⇌ **5b**, and **4a** ⇌ **6a** are reversible. **5a**, **5b**, and **6a** decarbonylate at 30 °C (N_2 stream) and at 0 °C, respectively, forming **4a** and **4b**. In the case of **5a** and **5b** the process is accompanied by partial decomposition of the thermolabile **4a** and **4b**.

In the electron-impact mass spectra of **3a**, **4a**, and **4b** all three CO ligands are eliminated gradually starting from the molecular peak. The further fragmentation proceeds in specific dependance on the ring size.[6g] In the case of **3a** a phenyl group is cleaved before the CH_2 unit. For the five-membered rings **4a** and **4b** a successive splitting of CH_2 units occurs, forming the fragments $CoPR_2^+$ which have lost up to six H atoms. As a result of the easy cleavage of CO from **5a**, **5b**, and **6a** and the low volatility of **7b**, their molecular peaks only appear in field desorption mass spectra. Moreover in the corresponding spectra of **5a** and **5b** the (M^+ − CO) peak is observed as well, in the case of **5b** even with the highest intensity. The field desorption mass spectrum of **6a** reveals three characteristic peaks, i.e., the molecular peak and signals for two fragments reduced by PPh_3 and CO, respectively.

In the 5-μm region of the IR spectrum of **3a** (in n-hexane) two sharp absorptions of terminal CO groups appear (Table II), corresponding to the irreducible representations A_1 and E, local C_{3v} symmetry supposed.[25]

The IR spectra of **4a** and **4b** reveal three CO bands between 2050 and 1960 cm^{-1} (Table II). The lower symmetry may result from an interaction of the P substituents and the $Co(CO)_3$ moiety. In the IR spectra (5-μm region) of the cyclic acyl complexes **5a** and **5b** the frequency difference between the two CO absorptions with longer wavelengths is significantly increased compared to **4a** and

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Table II. CO Vibrations (cm^{-1}) in the IR Spectra of 3-7

compds	no.	$\nu(C{\equiv}O)$	$\nu(C{\equiv}O)$	$\nu(C{\equiv}O)$	$\nu(>C{=}O)$
$(OC)_3CoPPh_2CH_2$	**3a**[a]	2049 s	1984 vs		
$(OC)_3CoPPh_2(CH_2)_3$	**4a**[a]	2049 s	1989 vs	1976 vs	
	4a[b]	2042 s	1981 sh	1967 vs	
$(OC)_3CoP(C_6H_{11})_2(CH_2)_3$	**4b**[a]	2041 s	1978 vs	1972 vs	
	4b[b]	2035 s	1967 sh	1960 vs	
$(OC)_3CoPPh_2(CH_2)_3C{=}O$	**5a**[b]	2057 s	2000 s	1970 vs	1653 m
$(OC)_3CoP(C_6H_{11})_2(CH_2)_3C{=}O$	**5b**[b]	2050 s	1992 s	1969 vs	1650 m
$Ph_3P(OC)_2CoPPh_2(CH_2)_3C{=}O$	**6a**[c]	1976 s	1913 vs		1621 m
$Ph_3P(OC)_2CoP(C_6H_{11})_2(CH_2)_3$	**7b**[c]	1958 s	1895 vs		

[a] In *n*-hexane. [b] In THF. [c] In KBr.

Table III. $^{31}P\{^1H\}$ NMR Data[a]

compds	no.	δ	no.	δ	*J*, Hz	no.	δ	*J*, Hz
$[(OC)_3CoPR_2(CH_2)_nCl]_2$[b]	**1a**	67.5	**2a**	59.7		**2b**	70.3	
$(OC)_3CoPR_2(CH_2)_n$[c]	**3a**	5.0	**4a**	76.9		**4b**	92.0	
$(OC)_3CoPR_2(CH_2)_3C{=}O$[d]			**5a**	21.3		**5b**	36.6	
$Ph_3P(OC)_2CoPR_2(CH_2)_3C{=}O$[e]			**6a**	19.2 (d, Co*P*R_2CH_2) 50.8 (d, Co*P*Ph_3)	$^2J_{PP} = 34.3$			
$Ph_3P(OC)_2CoPR_2(CH_2)_3$[d]						**7b**	65.2 (d) 61.5 (d)	$^2J_{PP} = 21.4$

[a] All spectra were recorded at 32.39 MHz; chemical shifts in δ units (positive values to low field) relative to external 85% H_3PO_4. [b] In THF at 30 °C. [c] In *n*-hexane at -50 °C. [d] In THF at -50 °C. [e] In toluene at -70 °C.

4b. Due to the electron-withdrawing effect of the acyl group all CO bands are shifted to higher wavenumbers in comparison with **4a** and **4b**. The keto >C=O vibrations absorb at higher frequencies than in comparable manganese compounds.[4a,b,6a,b] For **6a** and **7b** two intensive CO peaks are found in the 5-μm region. The acyl band in **6a** appears at 1621 cm^{-1} (Table II).

In the 80-MHz ^1H NMR spectra of the metallacycles **4**–**7** only unresolved multiplets are present.[2a] The spectrum of **3a** however shows a singlet at δ 1.19 characteristic for ylidic protons[6f,g,26] (in toluene-d_8). Analogous features comparable to those of metallacyclopropanes[6f,g,26c,27] become evident in the $^{31}P\{^1H\}$ NMR spectrum of **3a** (Table III). Recently it was found that the position of the ^{31}P signal in P-containing heterocycles depends both on the ring size[4a,27,28] and on the torsional angle C–M–P–C.[1] With respect to these findings the $^{31}P\{^1H\}$ spectra confirm the five-membered ring structure of **4a** and **4b** (Table III). The $^{31}P\{^1H\}$ singlet of the phosphorus atom in **5a** and **5b** and the doublet of the endocyclic P atom in **6a** appear at higher field compared to **4a**, **4b**, and **7b**. For **6a** the doublet shifted to lower field corresponds to the PPh_3 ligand. In the spectrum of **7b** a distinction of the different P atoms is no longer possible. The low-field $^{31}P\{^1H\}$ signals in the spectra of **2b**, **4b**, and **5b** indicate[28] that the C–P–C bond angles in the $(C_6H_{11})_2PCH_2$ fragment are increased as compared to those in the phenyl substituted analogues **2a**, **4a**, and **5a**.[24]

On account of their high-field position the $^{13}C\{^1H\}$ signals of **3a** (Table IV) remind of the already known phosphametallacyclopropanes characterized by an ylidic bonding system.[6f] The resonances of the methylene C and of the phenyl C(11) and C(21) atoms (Figure 1) are split into doublets by ^{31}P coupling. They are shifted to higher field compared to the $^{13}C\{^1H\}$ signals in the larger metallacycles.[4a] By recording $^{13}C\{^1H\}$ NMR spectra with the solvent peaks (THF-d_8) suppressed by the DEPT method,[29] the C atoms in the cyclic framework of **4a**, **4b**, **5a**, and **5b** were assigned as well. Puls experiments[29] also allow an assignment of the cyclohexyl C atoms adjacent to phosphorus appearing as doublets in the spectra of **4b** and **5b**. In the spectrum of **4b** the signal of the middle ring C atom is superposed by the multiplet of the cyclohexyl C atoms. The interpretation is supported by the well-

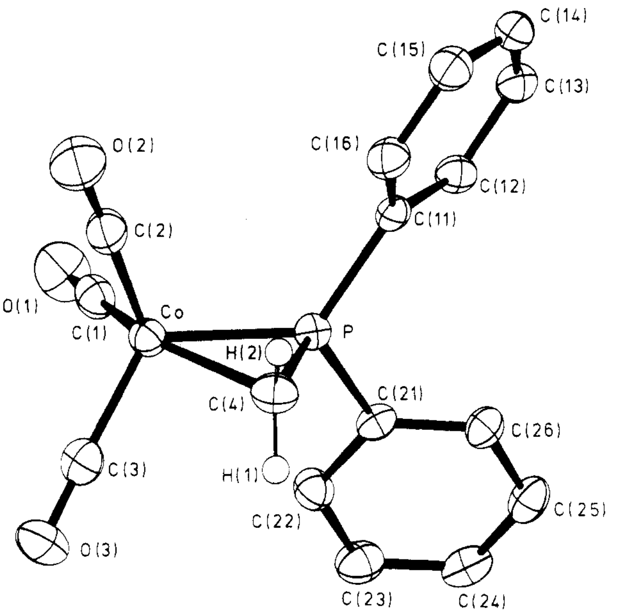

Figure 1. ORTEP plot of $(OC)_3CoPPh_2CH_2$ (**3a**).

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Table IV. $^{13}C\{^1H\}$ NMR Data[a]

compds	no.	δ (J, Hz)						
		δ(CoCH$_2$)	δ(CoC(O)CH$_2$)	δ(CoC(O)CH$_2$)	δ(CoPCH$_2$)	δ(CoPCH$_2$CH$_2$)	δ(PC)[b]	δ(CoCO)
$(OC)_3CoPPh_2CH_2$[c,d]	3a	-0.90 (d, $^1J_{PC}$ = 15.7)					128.74 (d, $^1J_{PC}$ = 62.7)	207.41
$(OC)_3CoPPh_2(CH_2)_3$[c,e]	4a	27.00 (d, $^2J_{PC}$ = 4.9)			37.21 (d, $^1J_{PC}$ = 7.4)	36.03	137.86 (d, $^1J_{PC}$ = 36.6)	207.16 (d, $^2J_{PC}$ = 7.1)
$(OC)_3CoP(C_6H_{11})_2(CH_2)_3$[e]	4b	24.86 (d, $^2J_{PC}$ = 24.2)			37.44 (d, $^1J_{PC}$ = 17.1)	27–29 (m)[f]	35.80 (d, $^1J_{PC}$ = 19.3)	208.84
$(OC)_3CoPPh_2(CH_2)_3C{=}O$[c,g]	5a		203.80	56.81 (d, $^3J_{PC}$ = 12.7)	27.86 (d, $^1J_{PC}$ = 27.4)	22.61 (d, $^2J_{PC}$ = 3.8)	136.18 (d, $^1J_{PC}$ = 42.3)	225.27 (d, $^2J_{PC}$ = 24.8)
$(OC)_3CoP(C_6H_{11})_2(CH_2)_3C{=}O$[g]	5b		205.58 (d, $^2J_{PC}$ = 3.0)	52.63 (d, $^3J_{PC}$ = 12.2)	13.82 (d, $^1J_{PC}$ = 22.0)	23.30 (d, $^2J_{PC}$ = 5.0)	35.91 (d, $^1J_{PC}$ = 24.0)	220.95 (d, $^2J_{PC}$ = 19.6)

[a] All spectra were recorded at 20.15 MHz; chemical shifts in δ vunits (positive values to low field) relative to internal Me_4Si. [b] P adjacent C atoms belonging to phenyl and cyclohexyl rings, respectively. [c] For assignment of phenyl C atoms see Experimental Section. [d] In THF-d_8 at -20 °C. [e] In THF-d_8 at -33 °C. [f] The multiplet is caused by superposition of cyclohexyl C atoms. [g] In THF-d_8 at -45 °C.

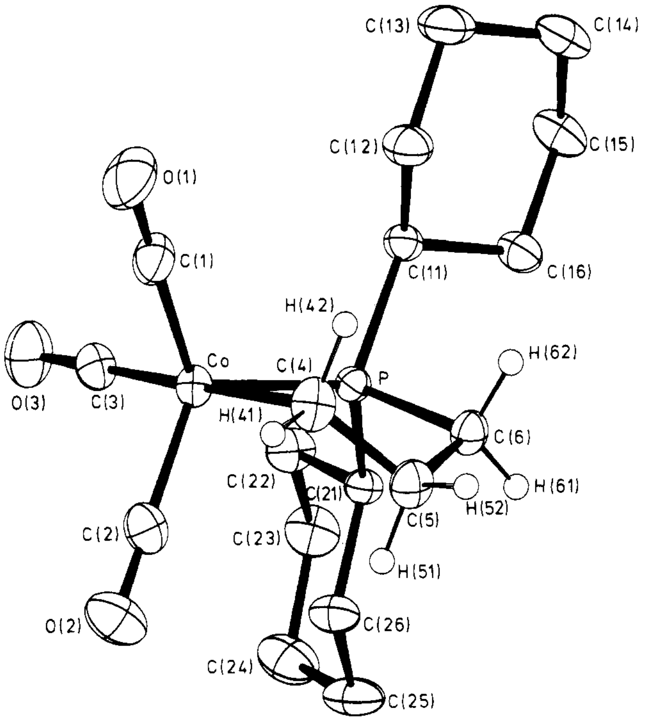

Figure 2. ORTEP plot of $(OC)_3CoP(C_6H_{11})_2(CH_2)_3$ (4b).

Table V. Selected Interatomic Distances (Å) for $(OC)_3CoPPh_2CH_2$ (3a) and $(OC)_3CoP(C_6H_{11})_2(CH_2)_3$ (4b)

	$(OC)_3CoPPh_2CH_2$ 3a	$(OC)_3CoP(C_6H_{11})_2(CH_2)_3$ 4b
Co–P	2.134 (1)	2.220 (1)
Co–C(1)	1.765 (5)	1.756 (3)
Co–C(2)	1.788 (4)	1.781 (3)
Co–C(3)	1.771 (4)	1.762 (2)
Co–C(4)	2.073 (5)	2.085 (2)
P–C(4)	1.725 (5)	
P–C(6)		1.842 (2)
P–C(11)	1.807 (4)	1.856 (3)
P–C(21)	1.806 (4)	1.839 (2)
C(1)–O(1)	1.143 (6)	1.148 (3)
C(2)–O(2)	1.141 (5)	1.145 (4)
C(3)–O(3)	1.141 (5)	1.149 (3)
C(4)–C(5)		1.510 (4)
C(5)–C(6)		1.521 (4)

known spectra of cyclic phosphanes, phosphonium cations,[30] and η^1-alkyl complexes.[31]

The position of the acyl C resonances in the $^{13}C\{^1H\}$ NMR spectra of **5a** and **5b** is similar to that of organic ketones.[32] The C atoms adjacent to the acyl groups are deshielded.[4a,13] Signals of the remaining C atoms were assigned by comparing the coupling constants. The low-field absorptions of the terminal carbonyl C atoms in the spectra of **5a** and **5b** correlate with the higher CO frequencies in the IR spectra, demonstrating the electron-withdrawing effect of the acyl CO groups.[33]

Description of the Crystal Structures of 3a and 4b. An ORTEP plot with atom labelling scheme of **3a** is shown

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Table VI. Selected Interatomic Angles (deg) for $(OC)_3\overline{CoPPh_2CH_2}$ (3a) and $(OC)_3\overline{CoP(C_6H_{11})_2(CH_2)_3}$ (4b)

	$(OC)_3\overline{CoPPh_2CH_2}$ **3a**	$(OC)_3\overline{CoP(C_6H_{11})_2(CH_2)_3}$ **4b**
P-Co-C(1)	102.2 (1)	119.6 (1)
P-Co-C(2)	111.5 (1)	115.3 (1)
P-Co-C(3)	121.2 (2)	96.5 (1)
P-Co-C(4)	48.4 (1)	82.4 (1)
C(1)-Co-C(2)	102.2 (2)	121.1 (1)
C(1)-Co-C(3)	102.0 (2)	95.9 (1)
C(1)-Co-C(4)	149.2 (2)	83.4 (1)
C(2)-Co-C(3)	114.3 (2)	97.4 (1)
C(2)-Co-C(4)	98.6 (2)	84.5 (1)
C(3)-Co-C(4)	89.7 (2)	178.1 (1)
Co-P-C(4)	64.0 (2)	
Co-P-C(6)		104.9 (1)
Co-P-C(11)	124.1 (1)	119.0 (1)
Co-P-C(21)	122.2 (1)	118.9 (1)
C(4)-P-C(11)	114.0 (2)	
C(4)-P-C(21)	113.6 (2)	
C(6)-P-C(11)		105.4 (1)
C(6)-P-C(21)		104.0 (1)
C(11)-P-C(21)	109.6 (2)	103.0 (1)
Co-C(4)-P	67.7 (2)	
Co-C(4)-C(5)		110.7 (1)
C(4)-C(5)-C(6)		109.0 (2)
P-C(6)-C(5)		107.2 (2)

Table VII. Fractional Atomic Coordinates (Esd) of $(OC)_3\overline{CoPPh_2CH_2}$ (3a)

atom	*x*	*y*	*z*
Co	0.25744 (5)	0.18760 (8)	0.94116 (3)
P	0.3055 (1)	0.2347 (1)	0.83628 (5)
O(1)	0.2960 (4)	-0.1857 (5)	0.9552 (2)
O(2)	-0.0192 (3)	0.2206 (6)	0.9455 (2)
O(3)	0.4185 (3)	0.3228 (5)	1.0683 (2)
C(1)	0.2792 (4)	-0.0391 (6)	0.9502 (2)
C(2)	0.0884 (4)	0.2105 (6)	0.9428 (2)
C(3)	0.3555 (4)	0.2666 (6)	1.0190 (2)
C(4)	0.2884 (4)	0.4163 (6)	0.8879 (2)
C(11)	0.1916 (4)	0.2235 (5)	0.7545 (2)
C(12)	0.2147 (4)	0.1204 (5)	0.6973 (2)
C(13)	0.1255 (4)	0.1142 (6)	0.6350 (2)
C(14)	0.0134 (4)	0.2108 (6)	0.6299 (2)
C(15)	-0.0110 (4)	0.3107 (7)	0.6871 (2)
C(16)	0.0762 (4)	0.3161 (7)	0.7499 (2)
C(21)	0.4668 (4)	0.2055 (5)	0.8154 (2)
C(22)	0.5587 (4)	0.1320 (6)	0.8675 (2)
C(23)	0.6850 (4)	0.1130 (6)	0.8546 (2)
C(24)	0.7181 (4)	0.1636 (6)	0.7896 (2)
C(25)	0.6275 (4)	0.2332 (6)	0.7376 (2)
C(26)	0.5012 (4)	0.2578 (5)	0.7502 (2)
H(1)	0.368 (4)	0.465 (6)	0.909 (2)
H(2)	0.211 (4)	0.475 (6)	0.879 (2)

Table VIII. Fractional Atomic Coordinates (Esd) of $(OC)_3\overline{CoP(C_6H_{11})_2(CH_2)_3}$ (4b)

atom	*x*	*y*	*z*
Co	0.37963 (3)	0.66210 (3)	0.19485 (4)
P	0.31354 (6)	0.70313 (5)	0.42977 (7)
O(1)	0.1839 (3)	0.6300 (2)	-0.1355 (3)
O(2)	0.5837 (2)	0.5491 (2)	0.2117 (3)
O(3)	0.6037 (2)	0.8993 (2)	0.2428 (3)
C(1)	0.2632 (3)	0.6463 (2)	-0.0040 (3)
C(2)	0.5067 (3)	0.5959 (2)	0.2081 (3)
C(3)	0.5146 (3)	0.8065 (2)	0.2269 (3)
C(4)	0.2146 (3)	0.4933 (2)	0.1577 (3)
C(5)	0.2202 (3)	0.4668 (2)	0.3259 (3)
C(6)	0.1970 (3)	0.5586 (2)	0.4484 (3)
C(11)	0.1956 (2)	0.7845 (2)	0.4375 (3)
C(12)	0.0576 (3)	0.7298 (2)	0.2776 (3)
C(13)	-0.0381 (3)	0.7983 (2)	0.2817 (4)
C(14)	-0.0885 (3)	0.8064 (2)	0.4411 (4)
C(15)	0.0469 (3)	0.8626 (2)	0.6009 (4)
C(16)	0.1462 (3)	0.7970 (2)	0.5999 (3)
C(21)	0.4626 (2)	0.7795 (2)	0.6378 (3)
C(22)	0.5570 (3)	0.9107 (2)	0.6670 (3)
C(23)	0.6669 (3)	0.9705 (2)	0.8475 (4)
C(24)	0.7704 (3)	0.9113 (3)	0.8827 (4)
C(25)	0.6807 (3)	0.7797 (2)	0.8453 (4)
C(26)	0.5681 (3)	0.7203 (2)	0.6668 (3)
H(41)	0.232 (3)	0.440 (2)	0.078 (4)
H(42)	0.115 (3)	0.493 (2)	0.112 (4)
H(51)	0.317 (3)	0.469 (2)	0.374 (3)
H(52)	0.134 (3)	0.383 (2)	0.295 (3)
H(61)	0.227 (3)	0.563 (2)	0.565 (3)
H(62)	0.092 (3)	0.545 (2)	0.409 (3)

in Figure 1 while **4b** is shown in Figure 2. Final atomic positional parameters for **3a** and **4b** are listed in Tables VII and VIII, respectively. Table V contains selected interatomic distances for both complexes, and Table VI contains selected interatomic angles. A common structural feature of three-membered $\overline{M-C-P}$ rings is the short P–C bond.[6f,g,8] Indeed the X-ray structure determination of **3a** reveals a short P—C(4) linkage of 1.725 (5) Å that can be considered a P═C double bond elongated upon coordination. This is in accord with a description of the $\overline{Co-C-P}$ ring in **3a** as a phosphorus ylide with complexed ylidic C(4) atom, while **4b** is essentially a puckered cobaltacyclopentane with a P–C(6) single bond (torsional angle C(4)–Co–P–C(6) = 12.2°). Because of the particular geometric requirements of the small-membered heterocycle, **3a** adopts a distorted trigonal-bipyramidal geometry. For example, the C(1)–Co–C(4) angle is 149.2 (2)° rather than the expected 180°, and the P–Co–C(1) angle is 102 (1)° rather than the expected 90°. The minor distortion of the trigonal bipyramid of **4b** results from tilting the atoms C(1), C(2), and P in the direction of C(4). The double bond P═C(4) in **3a** is roughly oriented in such a way as to bisect the angle C(2)–Co–C(3). The Co–P distance in **4b** compares well with those reported for tertiary phosphane cobalt complexes,[34] whereas it is noteworthy that the Co–P distance in **3a** is significantly shorter. The Co–CH_2 bonds have the average length of 2.079 Å and are increased as compared to those reported for similar Co(III) compounds.[34,35]

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Registry No. **1a**, 103817-23-8; **2a**, 103817-24-9; **2b**, 103817-25-0; **3a**, 103817-26-1; **4a**, 103817-27-2; **4b**, 103817-28-3; **5a**, 103817-29-4; **5b**, 103817-30-7; **6a**, 103817-31-8; **7b**, 103817-32-9; Ph_2PCH_2Cl, 57137-53-8; $HPPh_2$, 829-85-6; $Co_2(CO)_8$, 10210-68-1; $Ph_2P(CH_2)_3Cl$, 57137-55-0; $Cy_2P(CH_2)_3Cl$, 71734-57-1.

Supplementary Material Available: Tables of least-squares planes, final positional and anisotropic thermal parameters, interatomic distances and angles, and torsional angles for **3a** and **4b** (24 pages); listings of observed and calculated structure factors for **3a** and **4b** (37 pages). Ordering information is given on any current masthead page.

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