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# Cobalt Diazenides of Main-Group I–III (1–3[†]) Metals: X-ray Structure of a Grignard Compound Containing (Dinitrogen)(trimethylphosphane)cobaltate Anions

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Dinitrogen cobaltates $(Me_3P)_3CoN_2A$ [A = K (**1a**), Na (**1b**), Li (**1c**)] have been synthesized by metal reduction of $CoCl_2$ in the presence of trimethylphosphane and olefin ligands at ambient temperature under 1 bar of $N_2$. By reaction of **1a** with organomagnesium halides dimeric $(Me_3P)_3CoN_2MgR(OEt_2)$ compounds [R = $CH_3$ (**2a**), $CH_2CH(CH_3)_2$ (**2b**), $C(CH_3)_3$ (**2c**), $C_6H_5$ (**2d**)] are formed, while dimethylaluminum chloride yields dimeric $(Me_3P)_3CoN_2AlMe_2$ (**4**). X-ray structural data for **2c** show a four-membered ring, $N_2Mg_2$, which is almost square and contains sp$^2$-nitrogen atoms (terminal) of two $(Me_3P)_3CoN_2$ groups, thereby closely resembling the structure of isoelectronic **4**. Bond distances N–N (**1a**, 1.17 (3) Å; **2c**, 1.211 (4) Å; **4**, 1.252 (6) Å) reflect heterobimetallic activation of dinitrogen via push–pull action of an electron-rich cobalt center and acceptor-type main-group substituents, while Co–N bonding increases accordingly (**1a**, 1.70 (2) Å; **2c**, 1.672 (3) Å; **4**, 1.642 (4) Å). In tetrahydrofuran Schlenk-type equilibria of **2a–d** are shown to give $[(Me_3P)_3CoN_2]_2Mg(THF)_4$ (**3**).

## Introduction

One of the extensively studied nitrogen-fixing systems involves a transition-metal halide and a strongly reducing agent like organolithium, Grignard, or alkylaluminum compounds.[1] In some cases the electropositive metals eventually become part of the dinitrogen complex that is finally isolated; examples are $Co(N_2)L_3M$ (L = $P(CH)_3)_3$, M = K,[2] $^1/_2Mg(THF)_4$;[3] L = $P(C_6H_5)_3$, M = Na,[4] $Li(OR_2)_3$, $^1/_2Mg(THF)_4$[5]), $[(C_5H_5)Ti]_2N_2MgCl$,[6] $([(C_6H_5Li)_3Ni]_2N_2{\cdot}2OEt_2)_2$,[7] and $[\{C_6H_5(NaOEt_2)_2[(C_6H_5)_2Ni]_2N_2NaLi_6(OEt)_4{\cdot}OEt_2\}_2]$.[8]

Structural investigations of such heterobimetallic dinitrogen activation so far invariably show contacts between main-group elements and the dinitrogen ligands to be directional, involving either a linear arrangement M–N–N–M′ (M′ = Co, M = $^1/_2$ $Mg(THF)_4$,[3] $Li(OR_2)_3$[5]) or cluster-type structures showing additional polarization of the $N_2$ ligands by neighboring metal atoms in one or two directions perpendicular to the NN axis as in $[Co(PMe_3)_3N_2K]_6$[3] or in nickel dinitrogen cluster structures.[7,8]

In particular, an increase of covalent bonding along the NN vector will lengthen the NN bond distance, which becomes a diazenide double bond (*d*(NN) = 1.25 (6) Å) in $[(PMe_3)_3CoN_2AlMe_2]_2$[9] with each terminal nitrogen atom a member of a square $Al_2N_2$ ring. The question arises whether magnesium substituents of the type MgR could create an intermediate situation, B, between alkali-metal and $AlR_2$ substituents on the nigrogen, A and C.

$(Me_3P)_3CoN_2A$ (A = Li, Na, K)
A

$(Me_3P)_3CoN_2MgR$
B

$(Me_3P)_3CoN_2AlR_2$
C

Grignard compounds are used as reductants in the synthesis of ammonia from dinitrogen in Ziegler–Natta-type systems like $Cp_2TiR_2$[10] or in the synthesis of $CoH(N_2)(PPh_3)_3$.[11] Intermediates containing magnesium–nitrogen bonds have been postulated, but there are very few well-characterized compounds of this type. Yamamoto et al. obtained $[CoN_2(PPh)_3)_3]_2Mg(THF)_4$[5] from $CoH(N_2)(PPh_3)_3$ and $MgEt_2$ with a supposedly similar molecular structure as in $[Co(N_2)(PMe_3)_3]_2Mg(THF)_4$.[3] Infrared data and the poor solubility in nonpolar solvents suggest a marked ionic character that is assisted by THF solvation. However, with elements of main-group I or III (1 or 3) compounds such as the $KN_2Co(PMe_3)_3$ hexamer[2] and the $Me_2AlN_2Co(PMe_3)_3$ dimer[9] are found to be soluble in pentane. Specific effects of ether solvents were part of the study because Schlenk-type equilibria (eq 1) were expected to be sensitive to ligand properties of the O-donor molecules.[12]

$$2L_3CoN_2MgR \rightleftharpoons (L_3CoN_2)_2Mg + MgR_2 \qquad (1)$$

## Experimental Section

**General Procedures and Materials.** Standard vacuum techniques were used in manipulations of volatile and air-sensitive material.[13] Microanalyses (C, H by combustion; metals by AAS) were carried out by W. Barth, U. Graf, and *G. Schuller* in the Garching microanalytical laboratory.

Trimethylphosphane was prepared from triphenyl phosphite and methylmagnesium chloride.[14] Other chemicals (Merck-

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[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Schuchardt) were used as purchased.

Infrared spectra were recorded on a Perkin-Elmer, Type 297, spectrophotometer; $^1$H NMR spectra were obtained from a JEOL C-60 HL (60 MHz) spectrometer equipped with a low-temperature unit that was calibrated with a standard methanol sample. Melting points as determined in capillaries sealed under argon are uncorrected.

**Preparations. Improved Synthesis of $(Me_3P)_3CoN_2K^2$ (1a)** $Co(c\text{-}C_5H_8)(PMe_3)_3$ (1.6 g, 4.6 mmol) was dissolved in 50 mL of pentane containing 1% THF and the mixture reduced with 0.2 g (5.5 mmol) of freshly cut pieces of potassium metal with stirring (1 bar of $N_2$, 12 h, 20 °C). The volatiles were removed in vacuo, and the orange residue was extracted with 30 mL of ether. Crystallization over dry ice afforded 1.5 g of orange crystals (92%).

**Synthesis of $(Me_3P)_3CoN_2Na$ (1b).** Sodium powder (170 mg), freshly prepared from a paraffin dispersion by extraction with pentane, was used in a similar synthesis as for **1a**. $Co(c\text{-}C_5H_8)(PMe_3)_3$ (1.34 g, 3.8 mmol) under 1 bar of $N_2$ after 4 days at 20 °C gave 1.0 g of orange powder, $(Me_3P)_3CoN_2Na$, which was recrystallized from 20 mL of ether. Anal. Calcd for $C_9H_{27}CoN_2NaP_3$: C, 31.93; H, 8.00; Co, 17.45. Found: C, 31.98; H, 7.88; Co, 17.3.

**Synthesis of $(Me_3P)_3CoN_2Li^{15}$ (1c).** $Co(c\text{-}C_5H_8)(PMe_3)_3$ (830 mg, 2.34 mmol) in 50 mL of pentane containing 1% THF was reduced with 16 mg of lithium sand (1 bar of $N_2$, 48 h, 20 °C). The volatiles were removed in vacuo, and the residue was extracted with 30 mL of THF. Crystallization at −78 °C yielded orange, microcrystalline $(Me_3P)_3CoN_2Li$ (85%), decomp pt >142 °C. Anal. Calcd for $C_9H_{27}CoLiN_2P_3$: C, 33.56; H, 8.45; Co, 18.3; Li, 2.15. Found: C, 33.68; H, 8.07; Co, 17.2; Li, 2.1.

**Synthesis of Grignard Compounds 2a–d. General Procedure.** Halide (**2a**, $CH_3Br$; **2b**, $BrCH_2CH(CH_3)_2$; **2c**, $ClC(CH_3)_3$; **2d**, $C_6H_5I$) (10 mmol) in 40 mL of ether was added dropwise to 400 mg of magnesium turnings (excess). After 5 h at reflux the Grignard solution was filtered through a sintered disk and the magnesium content titrated with EDTA. To a solution of $KN_2Co(PMe_3)_3$ in 50 mL of ether was added an equimolar amount of Grignard solution at −78 °C, and the mixture was reacted to completion at −20 °C for 1 h. The volatiles were removed in vacuo, and the residue was extracted with 40 mL of fresh ether through a sintered disk. Crystallization at dry ice temperature yielded crystalline compounds.

$(Me_3P)_3CoN_2MgCH_3(OEt_2)$ (**2a**): 0.20 g of red microcrystals, 59% yield with respect to 0.30 g (0.85 mmol) of $KN_2Co(PMe_3)_3$; decomp pt >0 °C.

$(Me_3P)_3CoN_2Mg(CH_2CHMe_2)(OEt_2)$ (**2b**): dark red solid, 27% yield with respect to 0.50 g (1.40 mmol) of $KN_2Co(PMe_3)_3$; decomp pt >0 °C.

$(Me_3P)_3CoN_2Mg(CMe_3)(OEt_2)$ (**2c**): red crystals, 66% yield with respect to 0.55 g (1.53 mmol) of $KN_2Co(PMe_3)_3$; decomp pt >20 °C. Anal. Calcd for $C_{34}H_{92}Co_2Mg_2N_4O_2P_6$ (941.5): C, 43.38; H, 9.85; Co, 12.52. Found: C, 44.16; H, 10.05; Co, 12.2.

$(Me_3P)_3CoN_2MgC_6H_5(OEt_2)$ (**2d**): red crystals, 61% yield with respect to 0.71 g (1.97 mmol) of $KN_2Co(PMe_3)_3$; decomp pt >20 °C. Anal. Calcd for $C_{38}H_{84}Co_2Mg_2N_4O_2P_6$ (981.5): C, 46.50; H, 8.63; Co, 12.0. Found: C, 45.23; H, 8.55; Co, 12.1.

$^1$H NMR (60 MHz, tetrahydrofuran-$d_8$, −30 °C, $Me_4Si$ external reference, $\delta$ 0): **2c**, $\delta(CMe_3)$ 1.6 (m br, 9 H), $\delta(PMe_3 + OCH_2CH_3)$ 1.3 (m br, 33 H), $\delta(OCH_2CH_3)$ 3.44 (q, 4 H, $^3J(HH)$ = 7.0 Hz); **2d**, $\delta(PMe_3 + OCH_2CH_3)$ 2.0 (m br, 33 H), $\delta(OCH_2CH_3)$ 4.8 (q, 4 H, $^3J(HH)$ = 7.0 Hz), $\delta(C_6H_5)$ 9.7 (m br, 2 H), 10.2 (m br, 2 H), 10.7 (m br, 1 H).

**Preparation of $Mg(THF)_4[Co(N_2)(PMe_3)_3]_2$.**[3] To anhydrous $CoCl_2$ (1.81 g, 13.9 mmol) and magnesium turnings (1.00 g, 41.1 mmol) was added 50 mL of THF-containing $PMe_3$ (5.3 mL, 55.8 mmol) (in vacuo at −78 °C). After warming, the mixture was stirred vigorously under 1 bar of $N_2$ for 3 days at room temperature. The orange solution was evaporated to dryness and the residue extracted with 75 mL of pentane. This solution was reduced to 45 mL in vacuo and cooled to −78 °C. Orange-red crystals of **3** (4.48 g, 70%) were isolated by decantation and carefully dried in vacuo at −20 °C; decomp pt >82 °C (1 bar of Ar). Anal. Calcd for $C_{34}H_{86}Co_2N_4O_4P_6Mg$: C, 43.30; H, 9.20; Co, 12.49. Found: C, 43.17; H, 8.95; Co, 11.88.

**Syntheses of the Diorganoaluminium Diazenide 4.** To 1.7 g (4.8 mmol) of **1a** in 50 mL of ether was added dropwise at −78 °C 3.8 mL of a 1.2 M $AlClMe_2$ solution in ether. After 1 h at −20 °C the volatiles were evaporated and the residue was extracted with 50 mL of pentane. Crytallization over dry ice afforded 1.1 g of red-brown crystals (62%) that slowly decomposed on standing at 20 °C. Anal. Calcd for $C_{22}H_{66}Al_2Co_2N_4P_6$ (744.5): C, 35.49; H, 8.94; Co, 15.8. Found: C, 35.11; H, 8.96; Co, 15.1.

**Attempted Reactions of 2c and 4 with Hydrogen or Carbon Monoxide.** In four test reactions 2-mmol portions of **2a** or **4** were dissolved in 40 mL of ether and the mixture was kept under 1 bar of CO or $H_2$, respectively, for 5 h at −20 °C. No change of color was observed. Crystallization over dry ice gave virtually quantitative yields of **2a** and **4** (IR).

**Attempted Reactions of 4 with Cyclopentadiene or Anthracene.** **4** (2 mmol) was dissolved in 40 mL of pentane containing 2 mmol of freshly distilled cyclopentadiene or 2 mmol of anthracene, respectively, and the mixture kept at −20 °C for 3 h. As no change in color was observed, the mixtures were allowed to warm up to room temperature for 1 h. A dark brownish tinge of the solutions was then observed. Over dry ice brown crystalline solids were obtained that consisted of starting material **4** together with some decomposition product (ca. 10% $[(Me_3P)_2Co(PMe_2)]_2$) (IR) and white crystals of anthracene.

**Reaction of 1a with Benzyl Bromide.** To a solution of **1a** (1.35 g, 1.45 mmol) in 25 mL of ether that was vigorously stirred at −78 °C was added $C_6H_5CH_2Br$ (0.34 mL, 2.90 mmol) in 25 mL of ether over a period of 30 min. After the evolution of gas had ceased, the dark brown mixture was warmed to −20 °C. After 3 h, the volatiles were removed in vacuo and the residue was extracted with 20 mL of pentane at −20 °C. Reducing the volume to 5 mL and cooling to −78 °C gave dark brown needles of $Co(CH_2C_6H_5)(PMe_3)_3$: 0.47 g, 43% decomp pt >35 °C. Anal. Calcd for $C_{16}H_{34}CoP_3$: C, 50.79; H, 9.06. Found: C, 50.31; H, 9.08. $^1$H NMR (60 MHz, toluene-$d_8$, 30 °C, $Me_4Si$ external reference, $\delta$ 0): $\delta(C_6H_5)$ 6.8–5.3 m, $\delta(PCH_3)$ 0.9 (center of multiplet), $\delta(CoCH_2)$ −0.3 (q, $^3J(PH)$ = 10 Hz). $^{31}P\{^1H\}$ NMR (36.43 MHz, toluene-$d_8$, −100 °C, $H_3PO_4$ external reference, $\delta$ 0): $\delta(P_{ax})$ 7.28 (t), $\delta(P_{eq})$ 1.10 (d, $^2J(PP)$ = 12.2 Hz).

**X-ray Crystal Measurements.** Single crystals of **2c** were sealed in a glass capillary under nitrogen and held at −50 °C in a stream of nitrogen. Cell dimensions were obtained from a specimen (0.35 × 0.4 × 0.5 mm) on a Syntex $P2_1$ four-circle diffractometer using axial fotos (10 reflections) and were refined by using 15 reflections with $17° < 2\theta < 22°$ (XTL-software): $C_{34}H_{92}Co_2Mg_2N_4O_2P_6$, $M_n$ 941.5, triclinic, $P\bar{1}$, $Z = 1$; $a$ = 12.910 (3) Å, $b$ = 9.254 (2) Å, $c$ = 12.302 (3) Å, $\alpha$ = 105.18 (2)°, $\beta$ = 90.17 (2)°, $\gamma$ = 100.43 (2)°, $V$ = 1393 Å$^3$; $d$(calcd) = 1.12 g cm$^{-3}$. A total of 4381 independent reflections were collected ($\omega$ scan, $\Delta\omega$ = 1°, scan rate = 1.1–29.3° min$^{-1}$, $2° \leq 2\theta \leq 48°$); after polarization and Lorentz corrections 3667 reflections were observed with $I > 1.96\sigma(I)$. No absorption corrections were included (Mo K$\alpha$ radiation; $\lambda$ = 71.069 pm; graphite monochromator, $\mu$ = 8.4 cm$^{-1}$).

**Solution and Refinement of Structure.** The structure was successfully solved by using Patterson methods (Syntex XTL). Anisotropic refinement and subsequent difference Fourier maps gave the positions of all non-hydrogen atoms and some of the hydrogen atoms.

The positions of the remaining hydrogen atoms were calculated according to ideal geometry. With all hydrogen atoms in fixed positions refinement (FMLS) based on 3667 reflections with $F_0 > 3.92\sigma(F_o)$ using 226 parameters converged to $R$ = 0.041 and $R_w$ = 0.044. A final difference map exhibited maximum residuals of 0.54 e Å$^{-3}$ ($\Delta/\sigma$ < 0.05).

## Results and Discussion

As a convenient starting material $Co(PMe_3)_3(c\text{-}C_5H_8)$ is prepared by reduction of $CoCl_2$ with magnesium in the presence of the ligands. Under mild conditions (20 °C, 1 bar of $N_2$) dinitrogen is coordinated upon further reduction[2] (eq 2). In a pure hydrocarbon medium this reaction is complete after 4 days. However, with catalytic amounts

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$$Co(PMe_3)_3(C_5H_8) + K + N_2 \xrightarrow[\text{THF}]{\text{pentane}} KN_2CoL_3 + C_5H_8 \quad (2)$$

of tetrahydrofuran high yields are obtained in less than 6 h. Diethyl ether affords dark brown products containing potassium ethene cobaltates[16] as impurities, while the reported synthesis in tetrahydrofuran solution[2] gives lower yields. Quite essential is the presence of auxiliary ligands like olefin that form tetracoordinate cobalt(0) and cobalt(I–) intermediates. In a reduction of chlorotris(trimethylphosphane)cobalt[13] with alkali metal according to eq 3 dinitrogen is not coordinated.[21] However, in the presence of cyclopentene (excess or as little as 0.3 equiv good yields of **1a** are obtained.

$$CoCl(PMe_3)_3 + K \xrightarrow{\text{1 bar of } N_2} {}^3/_4Co(PMe_3)_4 + {}^1/_4Co + KCl \quad (3)$$

A $Co(PMe_3)_3$ fragment once generated in tetrahydrofuran solution decomposes to give elemental cobalt and tetrakis(trimethylphosphane)cobalt that may be further reduced with excess potassium to yield $KCo(PMe_3)_4$.[17] Similar observations have been made with sodium and lithium metals.

A high-yield synthesis of sodium and lithium compounds from (cyclopentene)tris(trimethylphosphane)cobalt and -sodium powder at 20 °C slowly proceeds in pentane and with lithium may be accelerated by a trace of tetrahydrofuran (eq 4). We note that in (dinitrogen)cobaltates

$$Co(C_5H_8)(PMe_3)_3 + A \xrightarrow{\text{1 bar of } N_2} AN_2Co(PMe_3)_3 \quad (4)$$
$$\textbf{1b}, A = Na$$
$$\textbf{1c}, A = Li$$

containing trimethylphosphane ligands the alkali-metal counterions $A^+$ tend to lose their solvation shells of ether molecules. This is likely due to enhanced donor properties of the coordinated dinitrogen as compared with the corresponding triphenylphosphane system.[5] We expect contacts between dinitrogen and Li or Na to be similar to those found in the structure of the $KN_2Co(PMe_3)_3$ hexamer.[2] Thus far, crystals suitable for X-ray work could not be obtained with **1b** and **1c**.

$KN_2Co(PMe_3)_3$ in ether at –78 °C reacts with Grignard solutions made from bromomethane, bromo-2-methylpropane, chlorodimethylethane, or iodobenzene (eq 5).

$$2KN_2Co(PMe_3)_3 + 2RMgHal \xrightarrow{Et_2O} [(Et_2O)RMgN_2Co(PMe_3)_3]_2 + 2KHal \quad (5)$$
$$\textbf{2a}, R = CH_3$$
$$\textbf{2b}, R = CH_2CH(CH_3)_2$$
$$\textbf{2c}, R = C(CH_3)_3$$
$$\textbf{2d}, R = C_6H_5$$

Compounds **2a–d** are crystallized from ether or pentane in the cold and after being dried in vacuo still contain ether that is recognized from infrared absorptions at 1030–1045 cm$^{-1}$ ($\nu$ CO) and is shown by $^1H$ NMR to be reproducibly associated with the RMg moiety.

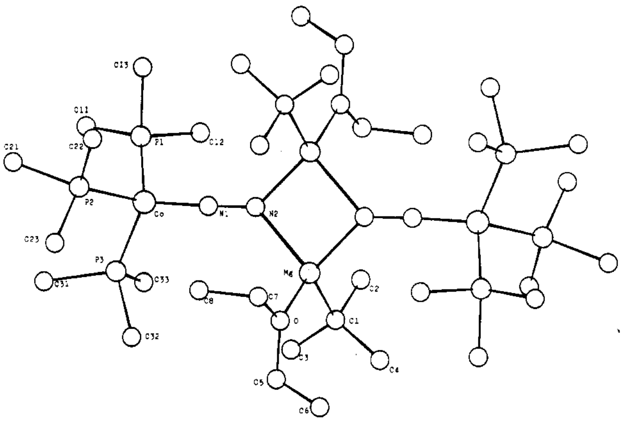


**Figure 1.** Perspective view of a molecule of **2c**.

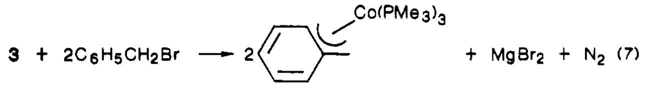
**2a** and **2b** have not been characterized by NMR due to paramagnetic byproducts that broaden the conspicuous $PCH_3$ resonances at $\delta$ 2.0 and 1.9. While more stable, **2c** and **2d** each clearly exhibit the $CH_2$ quartet of ether at 4.9 and 4.8 ppm, respectively. These compounds cannot be obtained in the presence of tetrahydrofuran. From a THF solution of **2a** diluted with pentane $(THF)_4Mg[N_2Co(PMe_3)_3]_2$ (**3**) is obtained through a Schlenk-type equilibrium (eq 6). Compounds **2a** and **2b** at 20 °C under argon

$$2CH_3MgX \rightleftharpoons MgX_2 + (CH_3)_2Mg \quad X = N_2Co(PMe_3)_3 \quad (6)$$

undergo a fast thermal decomposition giving dark colored solids containing cobalt, while **2c** and **2d** under same conditions remain as stable crystals for some hours. Progress of decomposition may be monitored by typical infrared bands at 677 and 867 cm$^{-1}$ that are due to $[(Me_3P)_2CoPMe_2]_2$.[18]

**2c** and **2d** are freely soluble in pentane with a bright red color and on slow cooling grow as brown violet columns. Apart from being sensitive to oxygen, chemical reactions expected of low-valent cobalt are slow. No ligand is replaced by carbon monoxide or hydrogen (1 bar, 20 °C). Infrared spectra contain very intense bands ranging from 1560 to 1663 cm$^{-1}$ that are probably due to $\nu$(NN) vibrations. There is no indication of cobaltate anions $[CoN_2(PMe_3)_3]^-$ as in the solution spectra of $(THF)_4Mg[N_2Co(PMe_3)_3]_2$ ($\nu$(NN) 2053 cm$^{-1}$). Thus bands at low frequencies appear to be associated with bridging diazenide units as present in the crystal structure of **2c** (Figure 1). All attempted reactions of **2a–d** in ether proceeding with complete loss of dinitrogen proved to be similar to those of **3** but gave lower yields. Under the reaction conditions exchange of anionic groups according to eq 1 must be occurring, and this can cause side reactions with a dialkylmagnesium intermediate (which was not found in the residue).

Similar observations were made with an oxidative addition of benzyl bromide where **3** gave higher yields (30%) of ($\eta^3$-benzyl)tris(trimethylphosphane)cobalt than **2a** (eq 7). This compound is better obtained from **1a** and benzyl



bromide (see Experimental Section). An $\eta^3$-benzyl coordination is indicated by a high field shift of ortho phenyl protons ($\delta(C_6H_5(ortho))$ 5.3.[23]

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**Table I. Infrared Bands (Nujol Solution, 2100–1500 cm$^{-1}$) of Diazenides 1–4**

| $(Me_3P)_3CoN_2M$ | $\nu$(NN), cm$^{-1}$ | $(Me_3P)_3CoN_2M$ | $\nu$(NN), cm$^{-1}$ |
|---|---|---|---|
| **1a**[a] | 1795 vs (br) | **2a** | 1560 vs (br) |
|  | 1753 m | **2b** | 1630 vs (br) |
| **1a** ($^{15}N_2$)[a] | 1735 vs (br) | **2c** | 1660 vs (br) |
|  | 1697 m | **2d** | 1663 vs (br) |
| **1b**[a] | 1850 m | 3 | 2058 m[b] |
|  | 1770 vs (br) |  | 1825 vs (br) |
| **1c**[a] | 1735 vs (br) | 4 | 1570 s |
|  | 1715 vs |  | 1525 vs |

[a] In THF solution: **1a**, 1867 vs, 1834 s cm$^{-1}$; **1a** ($^{15}N_2$), 1800 vs, 1769 s cm$^{-1}$; **1b**, 1960 w, 1850 vs (br) cm$^{-1}$; **1c**, 1960 s, 1860 vs cm$^{-1}$. [b] Sharp band (in a spectrum obtained from a thick mull) that increases with dilution at the expense of the broad band.

**Table II. Positional Parameters for Non-Hydrogen Atoms**

| atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Co | 0.26166 (3) | 0.20267 (5) | 0.23948 (3) |
| P(1) | 0.37022 (7) | 0.34409 (11) | 0.16044 (8) |
| P(2) | 0.35626 (7) | 0.06669 (11) | 0.30043 (8) |
| P(3) | 0.22388 (7) | 0.35637 (11) | 0.39194 (8) |
| C(11) | 0.4739 (3) | 0.5019 (5) | 0.2364 (4) |
| C(12) | 0.3039 (4) | 0.4424 (6) | 0.0776 (4) |
| C(13) | 0.4478 (4) | 0.2455 (6) | 0.0507 (4) |
| C(21) | 0.4890 (3) | 0.1505 (5) | 0.3645 (4) |
| C(22) | 0.3858 (5) | −0.1001 (6) | 0.1975 (5) |
| C(23) | 0.3052 (4) | −0.0266 (6) | 0.4083 (5) |
| C(31) | 0.3173 (4) | 0.4317 (6) | 0.5155 (4) |
| C(32) | 0.1071 (4) | 0.2833 (6) | 0.4587 (4) |
| C(33) | 0.1899 (4) | 0.5359 (5) | 0.3826 (4) |
| N(1) | 0.1597 (2) | 0.1183 (3) | 0.1469 (2) |
| N(2) | 0.0876 (2) | 0.0671 (3) | 0.0762 (2) |
| Mg | −0.07459 (8) | 0.06183 (12) | 0.09269 (9) |
| C(1) | −0.1520 (3) | 0.2549 (4) | 0.1394 (3) |
| C(2) | −0.1228 (4) | 0.3424 (5) | 0.0523 (4) |
| C(3) | −0.1194 (4) | 0.3653 (5) | 0.2544 (4) |
| C(4) | −0.2704 (4) | 0.2066 (7) | 0.1300 (5) |
| O | −0.1129 (2) | −0.0841 (3) | 0.1922 (2) |
| C(5) | −0.1834 (3) | −0.0611 (5) | 0.2835 (3) |
| C(6) | −0.2894 (4) | −0.1604 (7) | 0.2542 (4) |
| C(7) | −0.0659 (4) | −0.2174 (5) | 0.1788 (4) |
| C(8) | 0.0279 (4) | −0.1906 (6) | 0.2569 (4) |

As seen by dynamic $^{31}P$ NMR spectroscopy, this 18-electron complex is a fluxional molecule. At −100 °C rotation of ligands is slow enough to place the unique phosphane in trans position to the benzyl $CH_2$ group (see Experimental Section). Most oxidation and ligand substitution reactions reported here resemble those of other (trimethylphosphane)cobaltate anions.[2,17] In ether solution **1a** smoothly reacts with dimethylaluminum chloride to give the diazenide 4 (eq 8). From fairly concentrated

$$2(Me_3P)_3CoN_2K + 2ClAlMe_2 \xrightarrow[-2KCl]{Et_2O} \underset{\mathbf{4}}{[(Me_3P)_3CoN_2AlMe_2]_2} \tag{8}$$

red-brown solutions dark red crystals of 4 are obtained at −78 °C. The compound is readily soluble in pentane or ether and tends to decompose on standing at 20 °C.[24] Like the Grignard diazenides **2a–d** it is sensitive to oxygen or moisture but is otherwise surprisingly unreactive. **2a** and 4 were compared in some test reactions. Simple ligand substitution reactions that are typical for low-valent cobalt compounds, e.g., carbonylation under ambient conditions or introduction of anthracene as a diene ligand,[20] were not observed prior to decomposition of **2a** or 4. No metal-assisted hydrogenation of the activated dinitrogen groups was feasible under 1 bar of $H_2$. And finally neither the cobalt center nor any $CH_3Al$ groups of 4 were attacked by cyclopentadiene.

In Table I infrared absorption are listed that are believed to be associated with dinitrogen stretching modes. Without complete isotopic labeling this assignment rests on the fact that in the observed region (2100–1500 cm$^{-1}$) no other vibrations are expected and none are found, with **2d** as only exception ($\nu$(C=C) = 1550 m cm$^{-1}$).

Furthermore, change of NN bond lengths, e.g., **2c** vs. **4**, are nicely reflected by a bathochromic shift of about 100 wavenumbers. A $\nu$(NN) difference of the same order is observed between families of compounds **2a–d** and **1a–c**. While the actual crystal structures may be anticipated to be different even within each family, a close resemblance of molecular structures in solution is expected from the infrared spectra.

**Molecular Structure of $[(Me_3P)_3CoN_2Mg(CMe_3)(OEt_2)]_2$ (2c).** Figure 1 gives a perspective view of the molecule **2c**. In Tables II and III atomic parameters and bond distances and angles are listed. The central element of the dimer molecule is a $Mg_2N_2$ ring which is almost square [*d*(MgN(2)) = *d*(MgN(2′)) = 2.097 (3) Å; MgN2Mg′

**Table III. Distances (Å) and Angles (deg) in 2c**[a]

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| Bond Distances |  |  |  |  |  |
| Co–P(1) | 2.152 (1) | P(2)–C(22) | 1.823 (6) | Mg–O | 2.047 (3) |
| Co–P(2) | 2.164 (1) | P(2)–C(23) | 1.828 (6) | C(1)–C(2) | 1.514 (6) |
| Co–P(3) | 2.154 (1) | P(3)–C(31) | 1.839 (5) | C(1)–C(3) | 1.519 (6) |
| Co–N(1) | 1.672 (3) | P(3)–C(32) | 1.826 (5) | C(1)–C(4) | 1.508 (6) |
| P(1)–C(11) | 1.835 (5) | P(3)–C(33) | 1.825 (5) | O–C(5) | 1.445 (5) |
| P(1)–C(12) | 1.833 (5) | N(1)–N(2) | 1.211 (4) | O–C(7) | 1.444 (5) |
| P(1)–C(13) | 1.831 (5) | N(2)–Mg | 2.097 (3) | C(5)–C(6) | 1.489 (7) |
| P(2)–C(21) | 1.831 (5) | N(2)–Mg* | 2.097 (3) | C(7)–C(8) | 1.486 (7) |
| Bond Angles |  |  |  |  |  |
| P(1)CoP(2) | 105.08 (4) | C(22)P(2)C(21) | 99.21 (24) | N(2)MgN(2′) | 84.24 (12) |
| P(1)CoP(3) | 104.76 (4) | C(23)P(2)Co | 119.05 (18) | OMgN(2′) | 102.49 (12) |
| P(2)CoP(3) | 103.30 (4) | C(23)P(2)C(21) | 98.39 (23) | OMgN(2) | 108.35 (12) |
| P(1)CoN(1) | 107.08 (10) | C(23)P(2)C(22) | 98.25 (25) | C(1)MgO | 112.19 (14) |
| P(2)CoN(1) | 120.26 (10) | C(31)P(3)Co | 121.89 (16) | C(1)MgN(2) | 126.84 (14) |
| P(3)CoN(1) | 114.98 (10) | C(32)P(3)Co | 115.27 (17) | C(1)MgN(2′) | 118.79 (14) |
| C(11)P(1)Co | 124.58 (16) | C(32)P(3)C(31) | 99.95 (23) | C(5)OMg | 124.34 (24) |
| C(12)P(1)Co | 112.90 (16) | C(33)P(3)Co | 118.09 (17) | C(7)OMg | 121.33 (24) |
| C(12)P(1)C(11) | 100.12 (2) | C(33)P(3)C(31) | 98.42 (23) | C(7)OC(5) | 114.27 (31) |
| C(13)P(1)Co | 116.44 (17) | C(33)P(3)C(32) | 99.21 (23) | C(6)C(5)O | 113.00 (37) |
| C(13)P(1)C(11) | 99.52 (23) | N(2)N(1)Co | 174.77 (26) | C(8)C(7)O | 112.87 (38) |
| C(13)P(1)C(12) | 99.28 (23) | MgN(2)N(1) | 129.54 (23) | C(3)C(1)C(2) | 107.07 (36) |
| C(21)P(2)Co | 120.82 (16) | Mg′N(2)N(1) | 134.42 (23) | C(4)C(1)C(2) | 106.99 (38) |
| C(22)P(2)Co | 116.77 (19) | Mg′N(2)Mg | 95.76 (12) | C(4)C(1)C(3) | 108.93 (38) |

[a] An asterisk represents the symmetry operation −*x*, −*y*, −*z*.

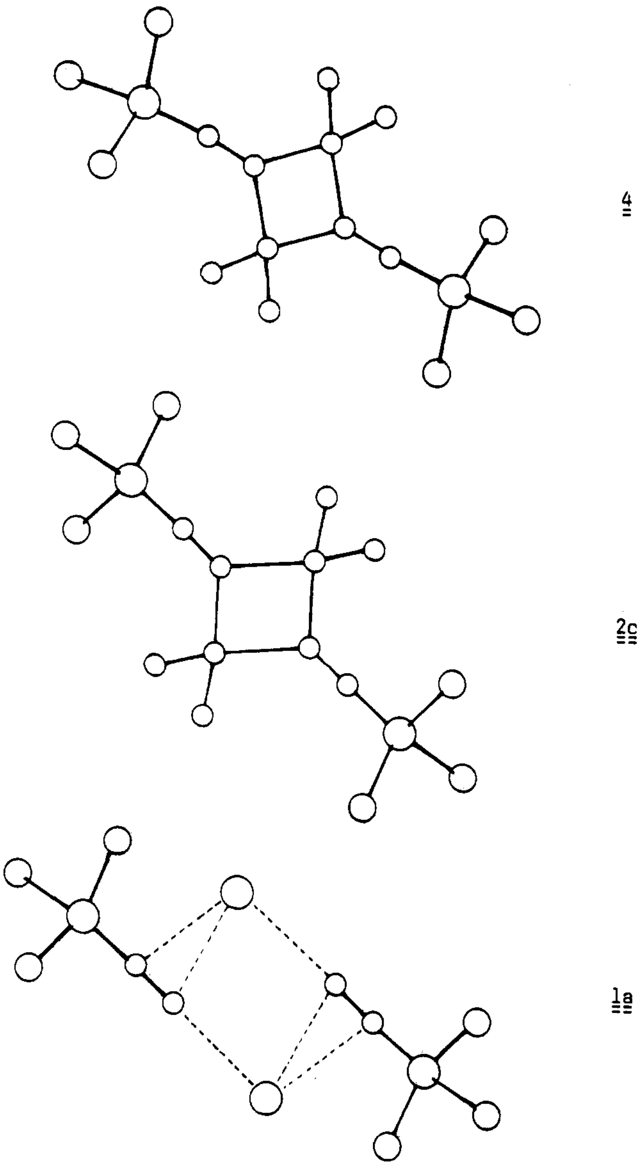


**Figure 2.** Bonding in heterobimetallic Diazenides: **4**, frame of atoms $(\mathrm{P_3CoN_2AlC_2})_2$; **2c**, frame of atoms $(\mathrm{P_3CoN_2MgCO})_2$; **1a**, frame of atoms $(\mathrm{P_3CoN_2K})_2$.

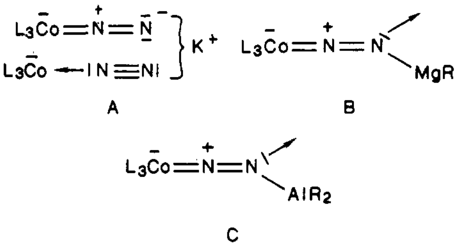
= 95.76 (12)°, N(2)MgN(2′) = 84.24 (12)°] and contains a center of symmetry. The $\mathrm{Co(PMe_3)_3}$ moieties are attached to this ring by dinitrogen bridges involving only minor out-of-plane bending. The angle between normals of the planes 1 [N(1)N(2)MgMg′N(2′)N(1′)] and 2 [N(1)N(2)MgMg′] is 3°. The coordination geometry of magnesium is tetrahedral with an angle between normals of the planes 1 and 3 [MgMg′C(10)] of 94°.

**Table IV. Characteristic Bond Distances (Å) and Angles (deg) for $(\mathrm{Me_3P})_3\mathrm{CoN_2K}$ (1a),[2] $[(\mathrm{Me_3P})_3\mathrm{CoN_2MgCMe_3(OEt_2)}]_2$ (2c) (This Work), and $[(\mathrm{Me_3P})_3\mathrm{CoN_2AlMe_2}]_2$ (4)[9]**

| | *d*(NN) | *d*(CoN) | *d*(MN) | CoNN | NNM | NMN′ |
|---|---|---|---|---|---|---|
| **1a** | 1.17 (3) | 1.70 (2) | 2.94 (2) | 178 (2) | 178 (2) | 85 (2) |
| **2c** | 1.211 (4) | 1.672 (3) | 2.097 (3) | 174.8 (3) | 134.4 (2)<br>129.5 (2) | 84.92 (1) |
| 4 | 1.252 (6) | 1.642 (4) | 1.931 (4) | 171.5 (4) | 130.6 (4)<br>130.3 (4) | 81.7 (2) |

In spite of different crystal data the molecular structure of **2c** very closely resembles that of $[(\mathrm{Me_3P})_3\mathrm{CoN_2AlMe_2}]_2$.[9] Table IV gives the pertinent bond lengths, and Figure 2 gives a geometrical impression of structural similarities. Together with a comparable section out of the structure of hexameric **1a**[2] emerges a consistent picture of push–pull type dinitrogen activation. As the acceptor strength of the main-group element increases (K < MgR < $\mathrm{AlR_2}$), the NN distances go up to attain values close to or slightly below a formal bond order or 2 ($\mathrm{CH_3N{=}NCH_3}$, *d*(NN) = 1.23 Å[19]) while CoN bond lengths decrease.

Bonding in Grignard diazenides **2a–d** appears to link the dominant ionic interactions in $[\mathrm{KN_2Co(PMe_3)_3}]_6$ with the covalently dimerized diorganoaluminum diazenide in accordance with simple valence bond representations A, B, and C.



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**Registry No.** **1a**, 63181-09-9; **1b**, 108009-02-5; **1c**, 108009-03-6; **2a**, 108009-04-7; **2b**, 108009-05-8; **2c**, 108034-78-2; **2d**, 108009-06-9; **4**, 87962-15-0; $\mathrm{Co(c\text{-}C_5H_8)(PMe_3)_3}$, 73557-03-6; MeMgBr, 75-16-1; $\mathrm{Me_2CHCH_2MgBr}$, 926-62-5; $\mathrm{Me_3CMgBr}$, 2259-30-5; PhMgI, 16002-63-4; $\mathrm{CoCl_2}$, 7646-79-9; $\mathrm{Mg(THF)_4[Co(N_2)(PMe_3)_3]_2}$, 60184-44-3; $\mathrm{AlClMe_3}$, 1184-58-3; $\mathrm{C_6H_5CH_2Br}$, 100-39-0; $\mathrm{Co(CH_2C_6H_5)(PMe_3)_3}$, 108009-07-0; cyclopentadiene, 542-92-7; anthracene, 120-12-7.

**Supplementary Material Available:** Complete lists of bond distances and angles including hydrogen atoms (Table V), anisotropic parameters for non-hydrogen atoms (Table VI), and hydrogen atom coordinates (Table VIII) (12 pages); a list of observed and calculated structure factors (Table VII) (20 pages). Ordering information is given on any current masthead page.

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(24) Using diethyl- and diisopropylaluminium chloride under same conditions gave similar diazenides ($\nu$(NN) at 1572 vs(br) and 1553 s (br) cm$^{-1}$, respectively) that have not been fully characterized due to an even faster decomposition in spite of bulkier substituents.