Iminoacylcobalt Compounds as Starting Materials for the Synthesis of Alkynylcobalt Halfsandwiches and Cobaltaheterocycles[☆]

Helmut Werner*[a], Liu Xiaolan[a], Karl Peters[b], and Hans Georg von Schnering[b]

Institut für Anorganische Chemie der Universität Würzburg[a],
Am Hubland, D-97074 Würzburg, Germany

Max-Planck-Institut für Festkörperforschung[b],
Heisenbergstraße 1, D-70506 Stuttgart, Germany

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The iminoacylcobalt compound $[C_5H_5Co\{C(CH_3)=NCH_3\}(PMe_2Ph)]I$ (**3**) reacts with propargylic acid esters $HC\equiv CCO_2R$ (R = Me, Et) to give the alkynylcobalt halfsandwich-type complexes $[C_5H_5Co\{C(CH_3)=NHCH_3\}(C\equiv CCO_2R)(PMe_2Ph)]I$ (**5**, **6**). With $HC\equiv CCO_2Me$ as the substrate, besides **6** (R = Me) the five-membered cobaltaheterocycle $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_3)C(CH_3)CHC(CO_2Me)\}(PMe_2Ph)]I$ (**7**) is also obtained. The reactions of **3** and the analogous benzyl derivative **4** with terminal alkynes $HC\equiv CR'$ (R' = CH_2OH, CMe_2OH, $[CH_2]_2OH$, CH_2OMe, H, Me, *n*Bu, Ph) afford exclusively the heterocyclic complexes $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(R)C(CH_3)CHCR'\}(PMe_2Ph)]I$ (R = CH_3, CH_2Ph) (**8**–**18**) in 60–70% yield. The molecular structures of **5** (R = Et) and **16** (R = Me, R' = Ph) have been determined by X-ray crystallography.

In a series of papers we have recently shown that cationic cyclopentadienylcobalt complexes of the general composition $[C_5H_5Co\{C(CH_3)=NR\}(PMe_3)]^+$ behave as 1,3-dipoles and react with ketones, aldehydes, nitriles and isothiocyanates by [3 + 2] cycloaddition to form five-membered cobaltaheterocycles[1,2]. With the dimethylphenylphosphane compounds $[C_5H_5Co\{C(CH_3)=NR\}(PMe_2Ph)]I$ (R = Me, Ph, CH_2Ph) as starting materials and double- or triple-bonded systems such as $R'CH=O$, $Me_2C=O$, $Ph_2C=S$, $MeN=C=S$ and $R'C\equiv N$ as substrates related Co-containing heterocyclic products have been prepared[3]. A remarkable difference exists however, in the behavior of the analogous cations $[C_5H_5Co\{C(CH_3)=NCH_3\}(PMe_3)]^+$ and $[C_5H_5Co\{C(CH_3)=NCH_3\}(PMe_2Ph)]^+$ towards CS_2. Whereas the former yields a dicationic binuclear spirocyclic complex with the carbon atom of CS_2 as the spiro center[4], the latter gives a neutral mononuclear CoCNCS heterocycle from which on treatment with elemental sulfur a bicyclic organometallic product of unprecedented structure is formed[5].

It was this unexpected behavior of the cationic precursor with PMe_2Ph as a ligand that prompted us to study also the reactivity of $[C_5H_5Co\{C(CH_3)=NCH_3\}(PMe_2Ph)]I$ and $[C_5H_5Co\{C(CH_3)=NCH_2Ph\}(PMe_2Ph)]I$ towards terminal alkynes. Surprisingly, not only metallaheterocycles but also alkynyl halfsandwich-type complexes were obtained and characterized by spectroscopic techniques as well as X-ray crystallography.

Results

Reactions with CO_2R-Substituted Alkynes

The isocyanidecobalt(I) compounds $[C_5H_5Co(CNR)(PMe_2Ph)]$ (**1**, **2**), which have been prepared nearly quantitatively from $[C_5H_5Co(PMe_2Ph)_2]$ and CNR by ligand exchange[5], react with methyliodide in pentane at −30 °C to give a dark yellow precipitate **3**, **4** (Scheme 1). Conductivity measurements of **3** in nitromethane indicate[5], that iminoacylcobalt complexes, which are ionic in nature, are formed. We assume that the cation of **3** and **4** contains a coordinatively unsaturated metal center which would be in agreement with the behavior of the products towards nitriles, ketones etc.[3]

Treatment of a solution of the freshly prepared, extremely air-sensitive compound **3** in CH_2Cl_2 at −30 °C with a twofold excess of $HC\equiv CCO_2Et$ leads to a gradual change of color from brownish-yellow to orange. Upon warming to room temperature, removal of the solvent and chromatographic workup of the residue an orange-yellow solid of the composition $[C_5H_5Co\{C(CH_3)=NHCH_3\}(C\equiv CCO_2Et)(PMe_2Ph)]I$ (**5**) is isolated in 65% yield. In contrast to **3**, compound **5** is air-stable and can be stored under argon at room temperature for weeks. With regard to the mechanism of formation, we suppose that initially a protonation of the nitrogen atom of the imidoyl ligand by the acidic alkyne derivative takes place which is followed by the nucleophilic addition of the remaining alkynyl anion to the cobalt center. We note that the related iminoacylcobalt complex $[C_5H_5Co\{C(CH_3)=NPh\}(PMe_3)I]$ reacts with CF_3CO_2H to give also a cationic species containing a $CoC(CH_3)NHPh$ unit[10].

The result of the X-ray crystal-structural analysis of **5** is shown in Figure 1. The cation possesses the expected piano-stool configuration with bond angles P1−Co−C1, P1−Co−C4 and C1−Co−C4 of nearly 90°. The Co−C1−C2−C3 unit is almost linear with Co−C1 and C1−C2 distances which correspond to a Co−C single and a C−C triple bond. Although the hybridisation at C1 and

Scheme 1. L = PMe_2Ph

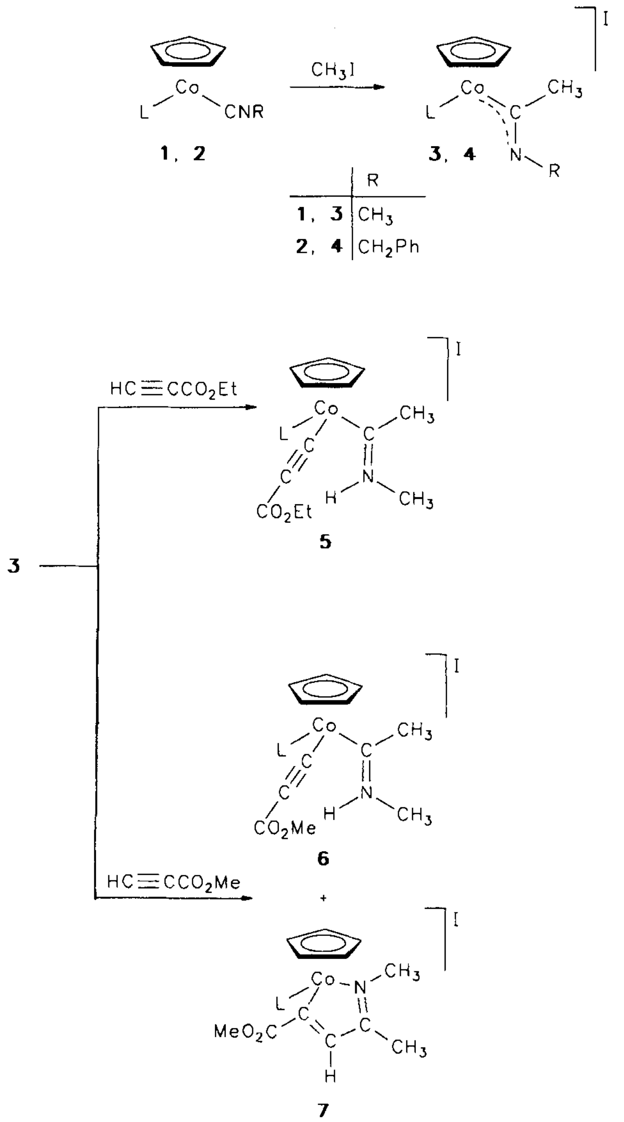
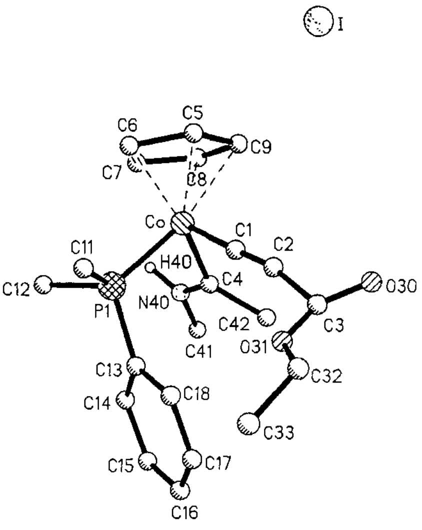


Figure 1. Molecular structure of 5[a]



[a] Selected bond lengths [Å] and angles [°]: Co−P1 2.171(3), Co−C1 1.876(12), Co−C4 1.882(8), Co−C5 2.05(2), Co−C6 2.07(1), Co−C7 2.04(1), Co−C8 2.04(1), Co−C9 2.09(3), C1−C2 1.20(2), C2−C3 1.43(2), C3−O30 1.14(3), C3−O31 1.33(2), C4−N40 1.31(2), C4−C42 1.50(2), N40−C41 1.47(1), N40−H40 1.03(1); P1−Co−C1 87.8(4), P1−Co−C4 90.9(3), C1−Co−C4 93.6(4), Co−C1−C2 179.1(6), C1−C2−C3 173.9(11), C2−C3−O30 127.3(13), C2−C3−O31 110.7(17), O30−C3−O31 122.0(15), Co−C4−N40 120.0(7), Co−C4−C42 124.0(9), C4−N40−C41 127.3(9), C4−N40−H40 129.1(8), N40−C4−C42 115.9(7), C41−N40−H40 101.9(9), Co−P1−C11 112.9(4), Co−P1−C12 114.8(3), Co−P1−C13 113.8(4).

C4 is different, the bond lengths Co−C1 and Co−C4 are virtually identical. This supports the assumption that the $C(CH_3)NHCH_3$ moiety is coordinated via a single and not via a double bond as would be anticipated for a carbene-type arrangement. The C4−N40 distance is 1.31(2) Å and thus only slightly longer than the average value for a C−N double bond[6]. The sum of the bond angles around C4 is 359.9° and around N40 358.8° which is in agreement with an sp^2 hybridization of these atoms. The bond lengths between the metal and the carbon atoms of the cyclopentadienyl ring differ only slightly which could be taken as an indication of a similar *trans* influence of the phosphane and the two C-bonded ligands.

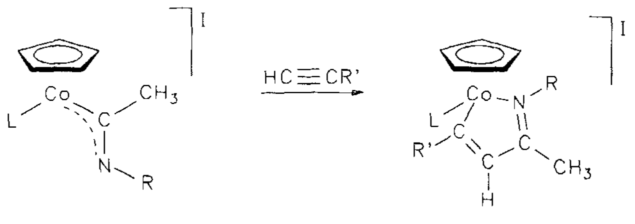
The reaction of **3** with $HC{\equiv}CCO_2Me$ affords two products **6** and **7** in a ratio of about 1:1. Compound **6** which is an orange solid probably is an analogue of the alkynyl complex **5**. The IR as well as the ^{1}H-NMR data of both compounds are quite similar and support the structural proposal shown in Scheme 1. The ^{13}C-NMR spectrum of **6** (in CD_3NO_2) displays besides the signals for the carbon atoms of the C_5H_5, CO_2Me and PMe_2Ph units one doublet at δ = 110.9 and one singlet at δ = 126.0 for the C-α and C-β atoms of the alkynyl ligand, a doublet at δ = 153.8 for the CoCN atom and two resonances δ = 37.6 and 36.3 for the carbon nuclei of the C- and N-bonded methyl groups.

The cation of the second product **7**, which is obtained from **3** and $HC{\equiv}CCO_2Me$ and which according to the elemental analysis is an isomer of **6**, presumably contains a five-membered metallaheterocycle. The IR spectrum (in KBr) shows two absorptions at $\tilde{\nu}$ = 1510 and 1590 cm^{-1}, corresponding to C=C and C=N stretching vibrations, but no signals at $\tilde{\nu} \approx$ 2100 and 3300 cm^{-1}, which could be assigned to $\nu(C{\equiv}C)$ and $\nu(NH)$ frequencies. Typical features of the ^{1}H-NMR spectrum of **7** (in CD_3NO_2) are the doublet for the proton of the C=C double bond at δ = 6.80 and the singlets for the CCH_3 and NCH_3 protons at δ = 1.52 and 2.29, of which the latter is significantly broadened. This broadening is certainly due to the quadrupole moments of the cobalt and nitrogen nuclei. The chemical shift of the signal for the =CH proton is quite similar to that of the =CH proton of the oxygen-containing nickelaheterocycle $[Ni\{\kappa^2(O,C)\text{-}OC(CH_3)CHCPh\}(PMe_3)_2Cl]$ (δ = 6.76, in C_6D_6), which has been prepared by Carmona et al. from the corresponding acetylnickel compound and phenylacetylene[7].

Cycloaddition Reactions of Terminal Alkynes

In order to find out whether the formation of the heterocyclic complex **7** is an exception or not, both iminoacylcobalt derivatives **3** and **4** have been treated with a variety of terminal alkynes HC≡CR′. Not only those with R′ = H, alkyl or aryl, but also those in which the substituent R′ contains an OH or OMe functionality have been used as substrates. The rate of the reaction of **3** and **4** with HC≡CR′ depends considerably on the unit R′ of the alkyne. Whilst for R′ = CH_2OH, CMe_2OH, $(CH_2)_2OH$ and CH_2OMe the starting material is consumed after 2 hours (in CH_2Cl_2 at room temperature), for R′ = H and CH_3 under the same conditions 4 hours and for R′ = Ph and *n*Bu two days are needed to complete the reaction. In all cases orange-yellow or orange-red solids are formed and after chromatographic workup isolated in 60–70% yield. Due to the elemental analyses and the spectroscopic data there is no doubt that the products **8–18** contain five-membered cobaltaheterocycles as is shown in Scheme 2. In analogy to the situation described for **7**, the ^{1}H-NMR spectra of **8–18** display a resonance for the =CH proton at δ = 6.0–6.8 with a P-H coupling constant of ca. 5 Hz, a doublet (for **16** and **18** a broadened singlet) for the methyl protons of the CoN(R)CC*H*$_3$ fragment at δ = 1.7–2.2, and a broadened signal for the NCH_3 or NC*H*$_2$Ph protons at δ = 3.1–3.4 or δ = 4.9–5.1, respectively. In the ^{13}C-NMR spectra of **15**, **16** and **17** a doublet for the metal-bonded carbon atom of the heterocycle appears at δ = 206–216 and a singlet for the neighboring C atom at δ = 146–151. The assignment of the latter signal has been confirmed by DEPT measurements.

Scheme 2. L = PMe_2Ph



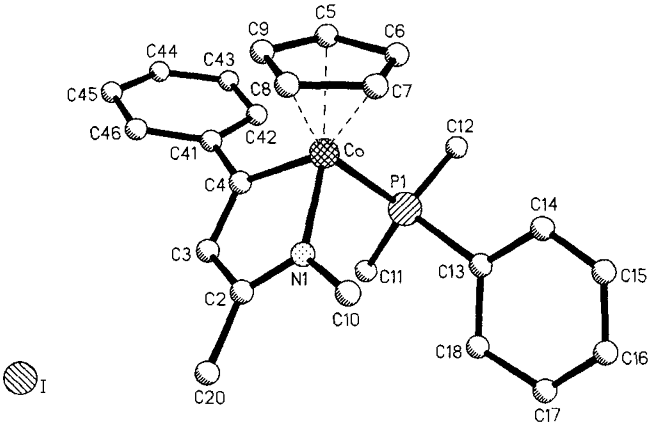
3, **4**

8-18

	R	R'		R	R'
8	CH_2Ph	CH_2OH	**13**	CH_2Ph	CH_3
9	CH_3	CMe_2OH	**14**	CH_3	H
10	CH_3	$(CH_2)_2OH$	**15**	CH_2Ph	H
11	CH_3	CH_2OMe	**16**	CH_3	Ph
12	CH_3	CH_3	**17**	CH_2Ph	Ph
			18	CH_3	*n*Bu

The structural proposal for **16** was confirmed by a single-crystal X-ray structure analysis. Figure 2 shows a plot of the cation with selected bond lengths and bond angles. The five-membered $CoNC_3$ ring is nearly coplanar with the largest deviation of the [Co, N1, C2, C3, C4] plane observed by Co (−0.02 Å) and N1 and C4 (both +0.02 Å). The three bonds of the N1–C2–C3–C4 unit show a short-long-short sequence, similar to the situation found in cobaltacyclopentadienes[8]. The distance Co–C4 is slightly longer than the cobalt–carbon distances of **5** but comparable to those in $[C_5H_5Co\{\kappa^2(C,C)\text{-}C_4(C_6F_5)_4\}(PPh_3)]$[8a], in $[(C_5H_4R)Co\{\kappa^2\text{-}(C,C)\text{-}C_4H_4\}(PPh_3)]$ (R = COMe, CO_2Me)[8c], and in the related ketenimine derivative $[C_5H_5Co\{\kappa^2(C,C)\text{-}RN{=}C{=}CR'_2\}(PMe_3)]$ [R = (*S*)-CH(Ph)CH_3; R′ = *p*-C_6H_4Cl][9]. The sum of the bond angles around N1, C2 and C4 are 359.9, 360.0 and 359.7°, respectively, which is in agreement with the planarity of the heterocycle.

Figure 2. Molecular structure of **16**[a]

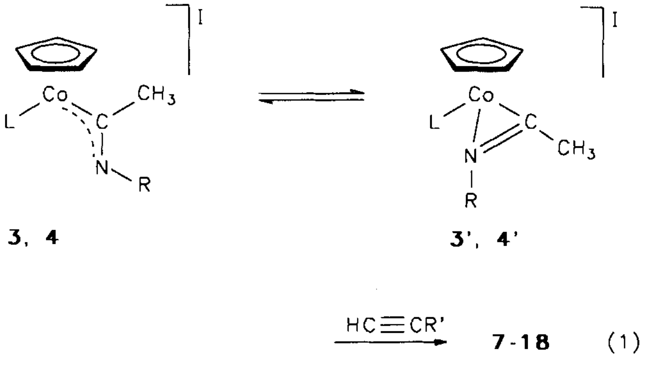


[a] Selected bond lengths [Å] and angles [°]: Co–P1 2.194(2), Co–N1 1.929(4), Co–C4 1.934(5), Co–C5 2.049(6), Co–C6 2.104(7), Co–C7 2.111(6), Co–C8 2.071(6), Co–C9 2.059(6), N1–C2 1.279(7), N1–C10 1.483(8), C2–C3 1.443(8), C2–C20 1.509(8), C3–C4 1.353(7), C4–C41 1.476(7); P1–Co–N1 90.5(1), P1–Co–C4 92.7(1), N1–Co–C4 82.9(2), Co–N1–C2 115.8(4), Co–N1–C10 124.0(4), C2–N1–C10 120.1(5), N1–C2–C3 113.7(5), N1–C2–C20 123.4(5), C3–C2–C20 122.9(5), C2–C3–C4 116.3(5), Co–C4–C3 111.1(4), Co–C4–C41 126.9(4), C3–C4–C41 121.7(5), Co–P1–C11 116.5(2), Co–P1–C12 116.6(2), Co–P1–C13 112.2(2).

Discussion

The present work has shown that imidoylcobalt complexes such as **3** and **4** readily undergo [3 + 2] cycloaddition reactions not only with nitriles, ketones etc. but also with terminal alkynes to give five-membered heterocycles. If esters of propargylic acid are used as substrates, an equally preferred pathway leads to alkynyl halfsandwich-type compounds, the formation of which is achieved by the transfer of the alkyne CH proton to the nitrogen atom of the iminoacyl unit. As far as the generation of the $CoNC_3$ cobaltaheterocycles is concerned, the most remarkable feature is the position of the nitrogen atom next to the metal center which would not be expected due to the structure of the starting material. A reasonable explanation for the stereochemistry of the $CoNC_3$ ring is that either an insertion of the alkyne into the Co-C bond, followed by coordination of the pendant NR group to the metal, takes place or an equilibrium as shown in eq. 1 is responsible for the formation of the products.

Although there is ample precedent for insertions of carbon nucleophiles into metalacyl or -iminoacyl bonds[11,12], the mechanistic scheme including the intermediates **3′** and **4′** should be definitely taken into consideration. For various transition metals, mainly of the Ti, V and Cr triads, η^2-iminoacyl structures are quite common[13], and even for co-



3, **4** **3'**, **4'**

$\xrightarrow{HC\equiv CR'}$ **7-18** (1)

L = PMe_2Ph

balt as the metal centre the coordination of an iminoacyl ligand via C and N has been proposed[10]. If in the present case an intermediate such as **3'** or **4'** is involved, the final step of the synthesis of **7**–**18** corresponds to the formation of cobaltacyclopentadienes $[C_5H_5Co\{\kappa^2(C,C)C_4R_4\}(PPh_3)]$ from $[C_5H_5Co(PPh_3)_2]$ and RC≡CR which proceeds via the alkyne complex $[C_5H_5Co(RC{\equiv}CR)(PPh_3)]$ as an intermediate[8b,14].

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Experimental Section

All operations were carried out under argon with the Schlenk technique. Compound **2** was prepared analogously as described for **1**[5], from $[C_5H_5Co(PMe_2Ph)_2]$ and $CNCH_2Ph$, and used without further purification for the synthesis of **4**. The alkynes were commercial products from Aldrich and ABCR or gifts from the group of Prof. *G. Erker*. – IR: Perkin-Elmer 1420. – NMR: Jeol FX 90 Q, Bruker AC 200 and AMX 400.

1. *Preparation of* $[C_5H_5Co\{C(CH_3)NHCH_3\}(C{\equiv}CCO_2Et)(PMe_2Ph)]I$ (**5**): A solution of 230 mg (0.52 mmol) of **3**[15] in 10 ml of CH_2Cl_2 was treated at −30 °C with 102 mg (1.04 mmol) of $HC{\equiv}CCO_2Et$. After the solution was warmed to room temp., it was stirred for 1 h, and then the solvent was removed. The residue was dissolved in 3 ml of CH_2Cl_2, and the solution was chromatographed on Al_2O_3 (neutral, acitivity grade V, length of column 7 cm). With CH_2Cl_2/CH_3NO_2 (1:8), an orange fraction was eluted which was brought to dryness in vacuo. Recrystallization of the residue from CH_2Cl_2/pentane gave orange-yellow air-stable crystals; yield 183 mg (65%). – IR (KBr): $\tilde{\nu}$ = 3310 cm^{-1} [ν(NH)], 2100 [ν(C≡C)], 1575 [ν(N=C)]. – ^{1}H NMR (90 MHz, CD_3NO_2): δ = 7.54 (m, 5H, C_6H_5), 5.29 [d, *J*(PH) = 0.4 Hz, 5H, C_5H_5], 3.97 [q, *J*(HH) = 6.8 Hz, 2H, CH_2CH_3], 2.98 [d, *J*(HH) = 4.3 Hz, 3H, $NHCH_3$], 2.26 (s, 3H, CCH_3), 2.16 [d, *J*(PH) = 11.1 Hz, 3H, PCH_3], 1.99 [d, *J*(PH) = 11.3 Hz, 3H, PCH_3], 1.75 [t, *J*(HH) = 6.8 Hz, 3H, CH_2CH_3]; signal of NH proton not exactly located. – $C_{21}H_{28}CoINO_2P$ (543.3): calcd. C 46.43, H 5.20, N 2.58; found C 46.72, H 5.21, N 2.74.

2. *Preparation of* $[C_5H_5Co\{C(CH_3)NHCH_3\}(C{\equiv}CCO_2Me)(PMe_2Ph)]I$ (**6**) *and* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_3)C(CH_3)CHC(CO_2Me)\}(PMe_2Ph)]I$ (**7**): A solution of 230 mg (0.52 mmol) of **3** in 10 ml of CH_2Cl_2 was treated at −30 °C with 88 mg (1.04 mmol) of $HC{\equiv}CCO_2Me$. The solution was warmed to room temp. and worked up as described for **5**. The residue, which was obtained after column chromatography, was dissolved in 2 ml of CH_2Cl_2, and ether was added dropwise to the solution. Orange air-stable crystals of **7** precipitated which were separated from the mother liquor, repeatedly washed with ether and dried; yield 104 mg (38%). The mother liquor was concentrated to ca. 1 ml in vacuo and after addition of pentane gave **6** as an orange-yellow air-stable solid; yield 82 mg (30%).

6: IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} [ν(NH)], 2100 [ν(C≡C)], 1580 [ν(N=C)]. – ^{1}H NMR (90 MHz, CD_3NO_2): δ = 7.52 (m, 5H, C_6H_5), 5.37 [d, *J*(PH) = 0.5 Hz, 5H, C_5H_5], 3.67 (s, 3H, CO_2CH_3), 3.15 [d, *J*(HH) = 4.5 Hz, 3H, $NHCH_3$], 2.62 (s, 3H, CCH_3), 2.09 [d, *J*(PH) = 11.2 Hz, 3H, PCH_3], 2.06 [d, *J*(PH) = 11.2 Hz, 3H, PCH_3]; signal of NH proton not exactly located. – ^{13}C NMR (22.5 MHz, CD_3NO_2): δ = 164.2 (s, CO_2CH_3), 153.8 [d, *J*(PC) = 1.5 Hz, $CoCCH_3$], 135.6 [d, *J*(PC) = 51.3 Hz, *ipso*-C of PC_6H_5], 132.3 [d, *J*(PC) = 3.7 Hz, *para*-C of PC_6H_5], 131.4 [d, *J*(PC) = 8.8 Hz, *meta*-C of PC_6H_5], 130.0 [d, *J*(PC) = 10.3 Hz, *ortho*-C of PC_6H_5], 126.0 (s, CoC≡*C*), 110.9 [d, *J*(PC) = 2.7 Hz, Co*C*≡C], 92.1 [d, *J*(PC) = 1.4 Hz, C_5H_5], 52.7 (s, OCH_3), 37.6 [d, *J*(PC) = 1.5 Hz, $CoCCH_3$], 36.3 (s, br., NCH_3), 17.6 [d, *J*(PC) = 11.4 Hz, PCH_3], 17.4 [d, *J*(PC) = 10.9 Hz, PCH_3]. – $C_{20}H_{26}CoINO_2P$ (529.2): calcd. C 45.39, H 4.95, N 2.65; found C 45.28, H 4.81, N 2.39.

7: IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1} [ν(N=C)], 1510 [ν(C=C)]. – ^{1}H NMR (90 MHz, CD_3NO_2): δ = 7.55 (m, 5H, C_6H_5), 6.80 [d, *J*(PH) = 4.8 Hz, 1H, =CH], 5.29 [d, *J*(PH) = 0.5 Hz, 5H, C_5H_5], 3.80 (s, 3H, OCH_3), 2.29 (s, br., 3H, NCH_3), 2.19 [d, *J*(PH) = 11.0 Hz, 3H, PCH_3], 1.86 [d, *J*(PH) = 11.2 Hz, 3H, PCH_3], 1.52 (s, 3H, CCH_3). – $C_{20}H_{26}CoINO_2P$ (529.2): calcd. C 45.39, H 4.95, N 2.65; found C 45.60, H 5.12, N 2.77.

3. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_2Ph)C(CH_3)CHC(CH_2OH)\}(PMe_2Ph)]I$ (**8**): A solution of **2**, prepared from 200 mg (0.50 mmol) of $[C_5H_5Co(PMe_2Ph)_2]$ and an equimolar amount of $CNCH_2Ph$ in 10 ml of pentane, was treated with 62 μl (1.00 mmol) of methyl iodide at room temp. A yellow precipitate of **4** was formed, which was separated from the mother liquor, washed with pentane (−30 °C) and dried; yield 217 mg (80%). The freshly prepared sample of **4**[15] was dissolved in 10 ml of CH_2Cl_2 and treated with 23 mg (0.40 mmol) of $HC{\equiv}CCH_2OH$ at room temp. After the solution was stirred for 2 h, the solvent was removed. The residue was dissolved in 3 ml of CH_2Cl_2, and the solution was chromatographed on Al_2O_3 (neutral, acitivity grade V, height of column 5 cm). With CH_2Cl_2/CH_3NO_2 (1:1), an orange fraction was eluted which was concentrated to ca. 3 ml in vacuo. Addition of 15 ml of ether led to the formation of an orange-yellow precipitate, which was separated from the mother liquor and recrystallized from CH_2Cl_2/OEt_2 (1:10); yield 139 mg (60%); m.p. 142 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 1580 cm^{-1} [ν(N=C)], 1520 [ν(C=C). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 12.0 (s, br., 1H, OH), 7.62 (m, 5H, C_6H_5), 6.60 [d, *J*(PH) = 4.8 Hz, 1H, =CH], 5.15–4.60 (m, br., 4H, NCH_2 and OCH_2), 5.10 [d, *J*(PH) = 0.7 Hz, 5H, C_5H_5], 2.12 [d, *J*(PH) = 10.7 Hz, 3H, PCH_3], 1.89 [d, *J*(PH) = 11.1 Hz, 3H, PCH_3] 1.82 [d, *J*(PH) = 2.4 Hz, 3H, CCH_3]. – $C_{25}H_{30}CoINOP$ (577.1): calcd. C 51.99, H 5.24, N 2.43; found C 51.80, H 5.31, N 2.53.

4. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_3)C(CH_3)CHCR'\}(PMe_2Ph)]I$ (**9**–**11**): A solution of 446 mg (1.00 mmol) of **3** in 15 ml of CH_2Cl_2 was treated with an equimolar amount of the alkyne HC≡CR' (R' = CMe_2OH, $[CH_2]_2OH$, CH_2OMe). After the solution was stirred for 2 h at room temp., it was worked up analogously as described for **8**. Recrystallization from CH_2Cl_2/OEt_2 (1:10) gave red (**9**) or orange-yellow crystals (**10**, **11**).

9: Yield 327 mg (62%); m.p. 134°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 11.7 (s, br., 1 H, OH), 7.55 (m, 5 H, C_6H_5), 6.34 [d, *J*(PH) = 5.4 Hz, 1 H, =CH], 5.52 [d, *J*(PH) = 0.7 Hz, 5 H, C_5H_5], 3.35 (s, br., 3 H, NCH_3), 2.34 [d, *J*(PH) = 11.0 Hz, 3 H, PCH_3], 2.17 [d, *J*(PH) = 2.3 Hz, 3 H, CCH_3], 1.89 and 1.87 [2 s, 3 H each, $C(CH_3)_2OH$], 1.74 [d, *J*(PH) = 11.2 Hz, 3 H, PCH_3]. – $C_{21}H_{30}CoINOP$ (529.1): calcd. C 47.63, H 5.72, N 2.65; found C 47.76, H 5.67, N 2.51.

10: Yield 350 mg (68%); m.p. 152°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.67 (m, 5 H, C_6H_5), 6.20 [d, *J*(PH) = 4.9 Hz, 1 H, =CH], 5.23 [d, *J*(PH) = 0.7 Hz, 5 H, C_5H_5], 3.90 [t, *J*(HH) = 2.0 Hz, 2 H, CH_2OH], 3.32 (s, br., 3 H, NCH_3), 2.96 [t, *J*(HH) = 2.0 Hz, 2 H, CCH_2], 2.00 [d, *J*(PH) = 10.7 Hz, 3 H, PCH_3], 1.84 [d, *J*(PH) = 2.9 Hz, 3 H, CCH_3], 1.80 [d, *J*(PH) = 10.7 Hz, 3 H, PCH_3]; signal of OH proton not exactly located. – $C_{20}H_{28}CoINOP$ (515.0): calcd. C 46.60, H 5.48, N 2.72; found C 46.80, H 5.54, N 2.75.

11: Yield 334 mg (65%); m.p. 171°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.60 (m, 5 H, C_6H_5), 6.24 [d, *J*(PH) = 4.8 Hz, 1 H, =CH], 5.26 [d, *J*(PH) = 0.7 Hz, 5 H, C_5H_5], 4.46 (s, br., 2 H, CH_2O), 3.42 (s, 3 H, OCH_3), 3.31 (s, br., 3 H, NCH_3), 2.00 [d, *J*(PH) = 10.6 Hz, 3 H, PCH_3], 1.82 [d, *J*(PH) = 10.8 Hz, 3 H, PCH_3], 1.76 (partial overlap with signal at δ = 1.82; CCH_3). – $C_{20}H_{28}CoINOP$ (515.0): calcd. C 46.60, H 5.48, N 2.72; found C 46.86, H 5.50, N 2.67.

5. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_3)C(CH_3)CHC(CH_3)\}(PMe_2Ph)]I$ (**12**): A slow stream of propyne was passed through a solution of 230 mg (0.52 mmol) of **3** in 10 ml of CH_2Cl_2 for 20 min at 0°C. After the solution was warmed to room temp., it was stirred for 4 h, and then worked up analogously as described for **8**. Recrystallization from CH_2Cl_2/OEt_2 (1:10) gave orange-yellow, air-stable crystals; yield 146 mg (58%); m.p. 111°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.35 (m, 5 H, C_6H_5), 6.01 [dq, *J*(PH) = 4.8, *J*(HH) = 1.7 Hz, 1 H, =CH], 5.16 [d, *J*(PH) = 0.7 Hz, 5 H, C_5H_5], 3.28 (s, br., 3 H, NCH_3], 2.51 (s, br., 3 H, $CoCCH_3$), 1.95 [d, *J*(PH) = 10.3 Hz, 3 H, PCH_3], 1.77 [d, *J*(PH) = 10.5 Hz, 3 H, PCH_3], 1.71 [d, *J*(PH) = 1.7 Hz, 3 H, CCH_3]. – $C_{19}H_{26}CoINP$ (485.0): calcd. C 47.01, H 5.40, N 2.84; found C 47.10, H 5.48, N 2.90.

6. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_2Ph)C(CH_3)CHC(CH_3)\}(PMe_2Ph)]I$ (**13**): Compound **13** was prepared analogously to **12** by using 260 mg (0.50 mmol) of **4** and propyne as starting materials; orange-yellow air-stable crystals; yield 160 mg (57%); m.p. 123°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.2–7.6 (m, 10 H, C_6H_5), 6.43 [dq, *J*(PH) = 4.8, *J*(HH) = 1.5 Hz, 1 H, =CH], 5.28 [d, *J*(PH) = 0.6 Hz, 5 H, C_5H_5], 5.12 (s, br., 2 H, NCH_2), 2.47 [d, *J*(PH) = 10.3 Hz, 3 H, PCH_3], 2.19 [d, *J*(PH) = 10.6 Hz, 3 H, PCH_3], 1.90 [d, *J*(PH) = 1.5 Hz, 3 H, CCH_3]. – $C_{25}H_{30}CoINP$ (561.1): calcd. C 53.47, H 5.39, N 2.50; found C 53.50, H 5.42, N 2.52.

7. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_3)C(CH_3)CHCH\}(PMe_2Ph)]I$ (**14**): A slow stream of acetylene was passed through a solution of 230 mg (0.52 mmol) of **3** in 10 ml of CH_2Cl_2 for 20 min at 0°C. After the solution was warmed up to room temp., it was stirred for 3 h and worked up as described for **12**. Orange-yellow air-stable crystals; yield 147 mg (60%); m.p. 134°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 9.84 [dd, *J*(PH) = 3.4, *J*(HH) = 6.2 Hz, 1 H, CoCH], 7.45 (m, 5 H, C_6H_5), 6.95 [dd, *J*(PH) = 5.3, *J*(HH) = 6.2 Hz, 1 H, CoCH=C*H*], 5.23 [d, *J*(PH) = 0.5 Hz, 5 H, C_5H_5], 3.38 (s, br., 3 H, NCH_3), 1.97 [d, *J*(PH) = 10.6 Hz, 3 H, PCH_3], 1.77 [d, *J*(PH) = 10.7 Hz, 3 H, PCH_3], 1.75 [d, *J*(PH) = 2.4 Hz, 3 H, CCH_3]. – $C_{18}H_{24}CoINP$ (471.0): calcd. C 45.86, H 5.14, N 2.97; found C 45.78, H 5.20, N 3.00.

8. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_2Ph)C(CH_3)CHCH\}(PMe_2Ph)]I$ (**15**): Compound **15** was prepared analogously to **14** by using 260 mg (0.50 mmol) of **4** and acetylene as starting materials; orange-yellow air-stable crystals; yield 170 mg (62%); m.p. 165°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 10.25 [dd, *J*(PH) = 2.8, *J*(HH) = 6.2 Hz, 1 H, CoCH], 7.3–7.7 (m, 10 H, C_6H_5), 6.8 [dd, *J*(PH) = 5.4, *J*(HH) = 6.2 Hz, 1 H CoCH=C*H*], 5.29 [d, *J*(PH) = 0.5 Hz, 5 H, C_5H_5], 5.04 (s, br., 2 H, NCH_2), 2.43 [d, *J*(PH) = 10.7 Hz, 3 H, PCH_3], 2.06 [d, *J*(PH) = 10.6 Hz, 3 H, PCH_3], 1.84 [d, *J*(PH) = 2.4 Hz, 3 H, CCH_3]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 212.9 [d, *J*(PC) = 31.1 Hz, CoCH], 198.3 (s, N*C*CH_3), 151.0 (s, CoCH=*C*H), 143.0 (s, C_6H_5), 137.1 [d, *J*(PC) = 51.0 Hz, *ipso*-C of PC_6H_5), 136.9, 135.2 (2 s, C_6H_5), 134.7 [d, *J*(PC) = 10.1 Hz, *ortho*-C of PC_6H_5), 133.6, 132.1 (2 s, C_6H_5), 89.4 (s, C_5H_5), 60.6 (s, br., NCH_2), 11.7 [d, *J*(PC) = 31.8 Hz, PCH_3], 11.1 [d, *J*(PC) = 36.1 Hz, PCH_3], 10.8 (s, C*C*H_3). – $C_{24}H_{28}CoINP$ (547.1): calcd. C 52.65, H 5.16, N 2.56; found C 52.70, H 5.16, N 2.65.

9. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_3)C(CH_3)CHC(Ph)\}(PMe_2Ph)]I$ (**16**): A solution of 446 mg (1.00 mmol) of **3** in 15 ml of CH_2Cl_2 was treated with 154 mg (1.50 mmol) of HC≡CPh and stirred for 48 h at room temp. After the solvent was removed, the residue was worked up as described for **8**. Orange-yellow air-stable crystals; yield 328 mg (60%); m.p. 144°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.2–7.8 (m, 10 H, C_6H_5), 6.21 [d, *J*(PH) = 4.9 Hz, 1 H, =CH], 5.05 (s, 5 H, C_5H_5), 3.10 (s, br., 3 H, NCH_3), 1.95 [d, *J*(PH) = 10.2 Hz, 3 H, PCH_3], 1.78 (s, 3 H, CCH_3), 1.72 [d, *J*(PH) = 10.5 Hz, 3 H, PCH_3]. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 206.3 [d, *J*(PC) = 26.1 Hz, Co*C*(Ph)], 184.3 (s, *C*CH_3), 146.4 (s, =CH), 137.5 (s, C_6H_5), 132.1 [d, *J*(PC) = 48.4 Hz, *ipso*-C of PC_6H_5], 129.6 [d, *J*(PC) = 2.4 Hz, *para*-C of PC_6H_5], 129.5 (s, C_6H_5), 129.1 [d, *J*(PC) = 8.4 Hz, *meta*-C of PC_6H_5], 127.7 [d, *J*(PC) = 10.2 Hz, *ortho*-C of PC_6H_5], 127.6, 127.4, 127.2, 125.9 (4 s, C_6H_5), 88.6 (s, C_5H_5), 46.9 (s, br., NCH_3), 18.4 (s, C*C*H_3), 17.0 [d, *J*(PC) = 31.6 Hz, PCH_3], 16.1 [d, *J*(PC) = 32.9 Hz, PCH_3]. – $C_{24}H_{28}CoINP$ (547.1): calcd. C 52.65, H 5.16, N 2.56; found C 52.75, H 5.23, N 2.37.

10. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_2Ph)C(CH_3)CHC(Ph)\}(PMe_2Ph)]I$ (**17**): Compound **17** was prepared analogously to **16** by using 260 mg (0.50 mmol) of **4** and 75 mg (0.75 mmol) of HC≡CPh as starting materials; orange-yellow air-stable crystals; yield 190 mg (61%); m.p. 157°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.0–7.8 (m, 15 H, C_6H_5), 6.43 [d, *J*(PH) = 4.7 Hz, 1 H, =CH], 4.96 (s, 5 H, C_5H_5), 4.95 (s, br., 2 H, NCH_2), 2.19 [d, *J*(PH) = 10.3 Hz, 3 H, PCH_3], 1.96 [d, *J*(PH) = 10.5 Hz, 3 H, PCH_3], 1.74 [d, *J*(PH) = 2.6 Hz, 3 H, CCH_3]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 216.6 [d, *J*(PC) = 23.0 Hz, Co*C*(Ph)], 186.2 (s, *C*CH_3), 147.3 (s, =CH), 141.3, 138.2, 135.5 (3 s, C_6H_5), 133.2 [d, *J*(PC) = 48.2 Hz, *ipso*-C of PC_6H_5], 130.7 [d, *J*(PC) = 3.3 Hz, *para*-C of PC_6H_5], 130.3 [d, *J*(PC) = 8.3 Hz, *meta*-C of PC_6H_5], 128.8 [d, *J*(PC) = 13.7 Hz, *ortho*-C of PC_6H_5], 127.5, 127.0, 125.8 (all s, C_6H_5), 89.1 (s, C_5H_5), 62.1 (s, br., NCH_2), 19.2 (s, C*C*H_3), 18.5 [d, *J*(PC) = 24.9 Hz, PCH_3], 17.9 [d, *J*(PC) = 26.4 Hz, PCH_3]. – $C_{30}H_{32}CoINP$ (624.9): C 57.69, H 5.33, N 2.24; found C 57.76, H 5.30, N 2.34.

11. *Preparation of* $[C_5H_5Co\{\kappa^2(N,C)\text{-}N(CH_3)C(CH_3)CHC(nBu)\}(PMe_2Ph)]I$ (**18**): Compound **18** was prepared analogously to **16** by using 445 mg (1.00 mmol) of **3** and 124 mg (1.50 mmol) of $HC{\equiv}C(CH_2)_3CH_3$ as starting materials; orange-yellow air-stable crystals; yield 337 mg (64%); m.p. 138°C (dec.). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.52 (m, 5 H, C_6H_5), 5.96 [dt, *J*(PH) = 4.9, *J*(HH) = 1.8 Hz, 1 H, =CH], 5.10 [d, *J*(PH) = 0.4

Table 1. Crystallographic data for **5** and **16**

	5	**16**
Formula	$C_{21}H_{28}CoINO_2P$	$C_{24}H_{28}CoINP$
Mol.mass	543.27	548.31
Cryst. size [mm]	0.2 × 0.2 × 0.6	0.4 × 0.6 × 0.3
Cryst. system	monoclinic	monoclinic
Space group	*C2/c*	*Pa*
a [Å]	27.244(3)	16.780(5)
b [Å]	10.689(1)	8.953(3)
c [Å]	20.566(2)	7.974(2)
β [Å]	126.59(1)	95.26(2)
V [Å^3]	4809.4(4)	1192.8(6)
Z	8	2
$d_{calcd.}$ [g cm^{-1}]	1.500	1.526
Diffractometer	Stoe STADI 4	Siemens R3m/V
Radiation (graphit-monochromated)	Mo-K_α	Mo-K_α
T [K]	293 ± 1	293 ± 1
μ [cm^{-1}]	2.06	2.07
Transmission min./max.	0.9351/0.9655	0.103/0.068
h, k, l	–32/+26, 12, 24	21, 11, ±10
Scan method	Θ/Θ	ω
2Θ(max) [°]	50.0	55.0
Absorption correction	geometrical	Ψ-scan
Total no. of reflexions scanned	7484	3025
No. of unique reflexions	4273	2764
No. of observed reflexions [$F_o > 3\sigma(F_o)$]	3608	2738
No. of parameters refined		
R	0.058	0.0252
R_w	0.048	0.0248
Reflexions/parameter ratio	14.26	10.87
Residual electron density [eÅ^{-3}]	+1.14/–0.80	+0.36/–0.44

Hz, 5H, C_5H_5], 3.24 (s, br., 3H, NCH_3), 2.5–2.8 [m, 4H, $(CH_2)_2$], 1.87 [d, J(PH) = 11.4 Hz, 3H, PCH_3], 1.74 [d, J(PH) = 10.6 Hz, 3H, PCH_3], 1.72 (s, br., 3H, CCH_3), 1.6 (m, 2H, CH_2), 0.9 [t, br., J(HH) = 2 Hz, 3H, CH_2CH_3]. – $C_{22}H_{32}CoINP$ (527.1): calcd. C 50.09, H 6.12, N 2.66; found C 50.11, H 6.13, N 2.68.

12. *X-ray Structure Determination of Compounds* **5** *and* **16**[16]: Single crystals of **5** and **16** were grown by slow diffusion of ether to a solution of **5** or **16** in CH_2Cl_2 at room temp. Crystal-data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXTL PLUS). Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method. The positions of the hydrogen atoms were calculated according to the ideal geometry (C–H 0.95 Å) and were refined by the riding method with fixed isotropic U values. For other details see Table 1.

☆ Dedicated to Professor *Günter Schmid* on the occasion of his 60th birthday.

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[15] Spectroscopic data for **3**: IR (KBr): $\tilde{\nu}$ = 1640 cm^{-1} [(C=N)]. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58 (m, 5H, C_6H_5), [d, J(PH) = 0.5 Hz, 5H, C_5H_5], 3.30 [s, br., 3H, $NHCH_3$], 3.05 [d, J(PH) = 2.0 Hz, 3H, CCH_3], 2.15 [d, J(PH) = 10.6 Hz, 3H, PCH_3], 2.02 [d, J(PH) = 10.8 Hz, 3H, PCH_3]. For spectroscopic data of **4** see: H. Werner, L. Xiaolan, K. Peters, H. G. von Schnering, *Chem. Ber.*, submitted for publication.

[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100108. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: internat. +1223/336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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