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Pseudo-Allyl Complexes from Monoazadienes and $Co_2(CO)_8$ by Activation of Dihydrogen under Mild Conditions[1]

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The reaction of monoazadienes (MAD, **a**–**g**) with $Co_2(CO)_8$ under H_2 atmosphere, affording the new pseudo-(α-aminoallyl) complexes $Co(CO)_3\{RC(H)C(H)C(H)NHR'\}$ (**1a**–**g**), provides an example of activation of dihydrogen under mild conditions (293 K, 1.2 bar H_2). Complexes **1** have also been prepared by the reaction of $HCo(CO)_4$ with MAD, by the reaction of $Co_2(CO)_8$ with MAD in the presence of small amounts of water, and by the reaction of $Co_4(CO)_{12}$ with MAD under H_2. The electron-donating properties of the α-amino substituent in **1**, inducing an increase of electron density at Co and asymmetry in the allyl-bonding, has been studied by IR, ^1H, ^{13}C, and ^{59}Co NMR, and an X-ray crystal structure determination of **1a** (R, R′ = Me, *p*-Tol). Crystals of **1a** are monoclinic, spacegroup $P2_1/c$ with cell constants a = 9.304 (1) Å, b = 20.585 (3) Å, c = 7.613 (1) Å, β = 90.80 (2)°, Z = 4. A total of 1091 reflections have been used in the refinement, resulting in a final R value of 0.068. Concerning the mechanism of H_2 activation, a radical pathway is proposed by which the observed quantitative yields of **1a**/**b** (R′ = aryl) and the moderate yields of **1c**–**g** (R′ = alkyl) can be explained. Also α,β-unsaturated aldehydes appear to be suitable substrates in the H_2 activation reaction with $Co_2(CO)_8$, but the products are very unstable and could be characterized only partly.

Introduction

Transition-metal complexes of unsaturated organic molecules have been a subject of particular interest, mainly because of their role in many catalytic processes. An important catalytic reaction, in which a homogeneous metal carbonyl catalyst has been employed, concerns the hydroformylation of unsaturated molecules, using $Co_2(CO)_8$. Many substrates, such as alkenes,[2] dienes,[3] imines,[4] and enones[5,6] have been studied in both catalytic and stoichiometric reactions with $Co_2(CO)_8$ or $HCo(CO)_4$. Enimines or monoazadienes (MAD, RCH=CHCH=NR′[7]), however, have been rarely used in $Co_2(CO)_8$ chemistry. This unsaturated ligand is interesting for two main reasons. First, MAD offers the possibility of cyclometalation as has been found in reactions of MAD with $Ru_3(CO)_{12}$.[8] The resulting metallacyclic hydride complex displays a rich chemistry, involving aspects such as insertion, H migration, and dimerization (with loss of H_2 or CO). Second, MAD may exhibit a versatile coordination behavior, as it may bind to a metal via its lone pair on the hard nitrogen atom and/or via either or both of its softer π-bonds. Such a coordination behavior for example has been demonstrated in the reaction of MAD with $Fe_2(CO)_9$.[9–11] So, generally speaking, MAD can adjust its bonding mode to the electronic character of the metal.[8] It is very difficult to predict, a priori, which site of MAD will govern its reactivity toward $Co_2(CO)_8$. When MAD reacts as a diene, a substitution product might be obtained analogous to the product of the reaction of butadiene with $Co_2(CO)_8$, i.e. $Co_2(CO)_6(C_4H_6)$ and $Co_2(CO)_4(C_4H_6)_2$.[3,12] The intermetallic bond in the latter compound can be easily oxidized with $Ph_3C^+BF_4^-$ affording $[Co(CO)_3(\eta^4\text{-}C_4H_6)]^+BF_4^-$ in high yield.[13,14] Such a cationic species containing an η^4-coordinated MAD ligand would be very interesting in order to study nucleophilic addition reactions[15–18] and reactions with carbonylmetalates, which yield heteronuclear MAD complexes.[19]

Regarding MAD as a base, a completely different chemistry toward $Co_2(CO)_8$ might be expected. It is well-known that base-induced disproportionation of $Co_2(CO)_8$ results in a Hieber type Co(II)/Co(–I) salt.[20] Another aspect of $Co_2(CO)_8$ chemistry concerns the role of a base in the hydroformylation of alkenes. Small amounts of bases greatly accelerate the H_2 activation step.[21] Di-

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hydrogen activation by $Co_2(CO)_7$, derived from $Co_2(CO)_8$, is believed to be the rate-determining step in cobalt-catalyzed hydroformylation,[22] and severe reaction conditions, e.g. 80 °C and 95 bar CO/H_2, are required to generate the catalytically active species $HCo(CO)_4$ and $HCo(CO)_3$. Stoichiometric reactions between $HCo(CO)_4$ and olefins at room temperature and 0.5–3 bar CO affording the hydroformylation products[23] indicate that the elevated temperature and pressure in the catalytic reaction are only necessary to activate dihydrogen.

In the present paper we describe the H_2 activation reaction by $Co_2(CO)_8$, involving MAD as a base, yielding pseudo-(α-aminoallyl)$Co(CO)_3$ complexes as the reaction products. The influence of the α-amino substituent on the allyl-bonding type is examined by spectroscopy and by an X-ray analysis. For a better understanding of the product formation, we have extended our studies to reactions of MAD with $HCo(CO)_4$ and to reactions of α,β-unsaturated aldehydes with $Co_2(CO)_8$ under H_2 atmosphere.

Experimental Section

Materials and Apparatus. ^1H, ^{13}C, and ^{59}Co NMR spectra were recorded on Bruker AC 100 and WM 250 spectrometers. IR spectra were measured on a Nicolet 7199B FTIR interferometer (liquid nitrogen cooled, Hg, Cd, Te detector). Field desorption (FD) mass spectra were obtained with a Varian MAT711 double-focusing mass spectrometer with a combined EI/FI/FD source. Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, TNO Zeist, The Netherlands, or Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. All preparations, including the sampling of the crystal, were carried out under an atmosphere of purified nitrogen. Carefully dried and distilled solvents were used. Silica gel for column chromatography (Merck, 60 Mesh) was dried and activated before use. $Co_2(CO)_8$ was recrystallized at −80 °C from hexane before use. The monoazadienes $R^1R^2R^3R^4$ MAD **a**–**g**[24] and the complexes $HCo(CO)_4$, $Co(CO)_3(1\text{-Me-}\eta^3\text{-}C_3H_4)$, and $Co(CO)_2PPh_3(1\text{-Me-}\eta^3\text{-}C_3H_4)$ were prepared according to literature procedures.[25,33]

Reaction of $Co_2(CO)_8$ with $R^1R^2C{=}CR^3CH{=}NR^4$: I. Under N_2. To a solution of 0.34 g of $Co_2(CO)_8$ (1.0 mmol) in 20 mL of hexane was added 5.0 mmol of MAD. After stirring for about 3–6 h at 20 °C a dark brown/red oily precipitate was formed. The brown supernatant liquid contained small to significant amounts (5–40%) of $Co_4(CO)_{12}$.[26] The brown/red precipitate was soluble in CH_2Cl_2 and showed only one strong absorption band in IR at 1890 cm^{-1}. Anal. (oil; MAD e) Calcd for $[Co(MAD)_6][Co(CO)_4]_2\cdot CH_2Cl_2$ (M = 1152): C, 53.13; H, 6.94; N, 7.29; Co, 15.36. Found: C, 52.76; H, 6.96; N, 7.42; Co, 15.63.

II. Under N_2 in the Presence of Water. Synthesis of 1e. To a solution of 0.34 g of $Co_2(CO)_8$ (1.0 mmol) in 20 mL of hexane, containing about 0.05 mL of H_2O/D_2O, was added 5.0 mmol of CH_3,*i*Pr MAD. After stirring for 2 h at 20 °C an orange/red solution was formed above a dark brown precipitate. The volume of the solution was reduced to 2 mL and the residue purified by column chromatography on silica. Complex **1e** was eluted as an orange band with hexane/dichloromethane (20:1). Yield of the orange/red air sensitive oil: ca. 0.15 g (30%). FD-mass: m/e 255 (M = 255).

III. Under H_2. Synthesis of 1a–g. To a solution of 0.34 g of $Co_2(CO)_8$ (1.0 mmol) in 20 mL of THF, saturated with H_2, was added 3.0 mmol of MAD. After stirring under 1.2 bar H_2 for 24 h at 20 °C an orange/brown solution was obtained. The solution was evaporated to dryness. The complexes **1a–g**, except **1e**, could be purified by column chromatography on silica, using hexane/dichloromethane (20:1) as the eluent. The complexes were isolated as orange/red, air-sensitive oils (**1c–e**) or solids (**1a,b,f,g**). Spectral data are given in the Tables III–VI. Yield and analytical data for **1a**: yield 95%; C, 54.06 (55.48); H, 4.83 (4.62); N, 4.44 (4.62). Yield and analytical data for **1b**: yield 95%; FD-mass m/e 365 (M = 365); C, 62.04 (62.48); H, 4.32 (4.41); N, 3.79 (3.83). Yield and analytical data for **1c**: yield 70%; FD-mass m/e 317 (M = 317). Yield for **1d**: 60%. Yield for **1e**: 0%. Yield for **1f**: 30%. Yield and analytical data for **1g**: yield 30%; FD-mass m/e 283 (M = 283).

By using dichloromethane as the eluent, a dark brown/red fraction was obtained, which showed only one strong absorption at 1890 cm^{-1} in the IR spectrum. For ligand e this product was characterized by elemental analysis. Anal. Calcd for $[Co(MAD)_6][Co(CO)_{42}\cdot 1.5CH_2Cl_2$ (M = 1163): C, 51.73; H, 6.78; N, 7.03; Co, 14.82. Found: C, 51.58; H, 6.57; N, 6.62; Co, 15.84.

Reaction of $R^1R^2C{=}CR^3CH{=}NR^4$ with $HCo(CO)_4$: Alternative Synthesis of 1a–g. To a solution of about 0.17 g of $HCo(CO)_4$ (1.0 mmol) in 10 mL of hexane at −70 °C was added 2 equiv of MAD. A brown/orange precipitate was formed instantaneously. The supernatant was decanted, and the precipitate was washed with 10 mL of cold hexane. Then 20 mL of hexane was added and the reaction mixture was warmed to 20 °C. Upon warming, the precipitate gradually dissolved and complex **1a–g** could be isolated as described above in almost quantitative yields.

Reaction of $Co_4(CO)_{12}$ with PhCH=CHCH=N-*p*-Tol (b) under H_2: Synthesis of 1b. A solution of 0.57 g of $Co_4(CO)_{12}$ (1.0 mmol) and 0.88 g of PhCH=CHCH=N-*p*-Tol (4 equiv) in 50 mL of THF was stirred under 1.5 bar H_2 for 16 h at 20 °C. Then the reaction was stopped although some starting compounds were still present. The yield of **1b** after this limited reaction time was 0.22 g (60%).

Reaction of 1b with $CH_3CH{=}CHCH{=}N$-*i*Pr. To a solution of 0.15 g of **1b** (0.4 mmol) in 5 mL of CH_2Cl_2 was added 0.05 g of $CH_3CH{=}CHCH{=}N$-*i*Pr (0.4 mmol) in 20 mL of hexane. The solution was stirred for 20 h at 20 °C and quickly chromatographed on silica with hexane/$CHCl_2$ (5:1). The products were examined with ^1H NMR. Complex **1b** and **1e** appeared to be present in a ratio of 1:3.

Reactivity of 1a/b toward PR_3. A solution of 1.0 mmol of **1a**/**1b** and 1 equiv of PPh_3 (0.26 g, 1.0 mmol) or $P(OMe)_3$ (0.12 g, 1.0 mmol) in 50 mL of hexane was stirred for 3 h at 20 °C. No change in the IR spectrum was observed.

Reaction of RCH=CR′CH=O with $Co_2(CO)_8$ under H_2: Synthesis of 2a–c. To a solution of 0.34 g of $Co_2(CO)_8$ (1.0 mmol) in 20 mL of THF, saturated with H_2, 4.0 mmol of RCH=CR′CH=O was added. After stirring for 24 h under 1.2 bar H_2 at 20 °C an orange/brown solution was obtained. Yields of the $Co(CO)_3$ complexes **2** were estimated on the basis of the IR spectra of this THF solution (**2a**, R = Me, R′ = H, 70% yield; **2b**, R = Ph, R′ = H, 90% yield; **2c**, R = Ph, R′ = Me, 85% yield). After evaporation of the THF, the complexes **2b** and **2c** (together with unreacted ligand) were extracted with hexane. Upon evaporating the solvent of the solution of **2a** the complex decomposed to $Co_4(CO)_{12}$. Compound **2a** could be purified by adding 50 mL of hexane to precipitate the $Co(CO)_4$ anion containing species and by subsequent filtration.

Reaction of 2a with MAD b and e. To the hexane/THF solution of complex **2a**, obtained as described above, an (about 2-fold molar) excess of MAD was added at 20 °C. The color of the solution instantaneously changed from orange/brown to orange/red. After stirring for 5 min, complexes **1b** and **1e** were formed in 95% and 50% yields, respectively (based on IR). In the reaction with MAD e also a considerable amount of [Co-

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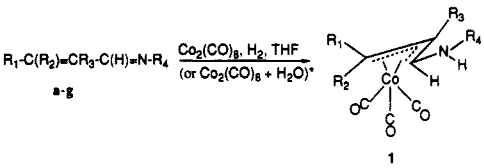


1

	R¹	R²	R³	R⁴
1a	Me	H	H	p-Tol
1b	Ph	H	H	p-Tol
1c	Ph	H	H	iPr
1d	Ph	H	Me	iPr
1e	Me	H	H	iPr
1f	Me	H	H	t-Bu
1g	Me	Me	H	t-Bu

* for the preparation of **1e**

Figure 1. Formation of complexes **1a–g**.

(MAD)$_6$][Co(CO)$_4$]$_2$ was detected, as indicated by an absorption at 1890 cm^{-1} in the IR spectrum.

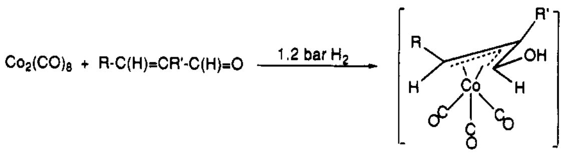
Crystal Structure Determination of Co(CO)$_3$(CH$_3$C(H)C(H)C(H)NH-*p*-Tol) (1a). A crystal with approximate dimensions 0.15 × 0.35 × 0.4 mm^3, grown from a saturated hexane solution at 193 K, was used for data collection on a ENRAF-NONIUS CAD4 diffractometer using graphite-monochromated Cu Kα radiation at room temperature (λ = 1.5418 Å; $2.5 \leq \theta \leq 70°$; $-11 \leq h \leq 11$; $0 \leq k \leq 25$; $0 \leq l \leq 9$). A total of 2854 unique intensities was measured of which 1763 were below the significance level of $2.5\sigma(I)$ and were treated as unobserved. Crystals of the title compound are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions a = 9.304 (1) Å, b = 20.585 (3) Å, c = 7.613 (1) Å, β = 90.80 (2)°, V = 1457.9 (4) Å^3, μ(Cu Kα) = 97.0 cm^{-1}, d_x = 1.38 g cm^{-3}. The structure was determined by standard heavy-atom atom techniques and refined by using block-diagonal least-squares refinement based on F with weights $w^{-1} = 10.64 + F_o + 0.0145F_o^2$. The position of the hydrogen atoms of the *p*-tolyl entity was calculated on the basis of standard geometry and kept fixed, the remaining hydrogen atoms were found in a ΔF synthesis. Anisotropic refinement for the non-H atoms and isotropic for the H atoms converged to R = 0.068 (R_w = 0.101, maximum Δ/σ = 0.43). A final difference synthesis revealed a residual electron density between −0.3 and 0.4 e Å^{-3}. The anomalous dispersion of Co was taken into account. An empirical absorption correction (DIFABS)[27] was applied with corrections in the range 0.66–1.65. The calculations were carried out with XRAY76.[28] The scattering factors were taken from the literature.[29]

Results

When an (ca. 5-fold molar) excess of MAD **b**, **c**, or **e** was added to a solution of Co$_2$(CO)$_8$ in hexane at 20 °C, gas evolution and formation of a brown/red precipitate occurred. After about 4–10 h all Co$_2$(CO)$_8$ had reacted and only Co$_4$(CO)$_{12}$ was detected by IR. A fast reaction and small amounts of Co$_4$(CO)$_{12}$ (5%) were observed for the most basic ligand, **e**, whereas in the slow reaction of ligand **b** large amounts of Co$_4$(CO)$_{12}$ (40%) were present.

The brown/red oily precipitate is soluble in CH$_2$Cl$_2$ and shows only one strong band at 1890 cm^{-1} in IR, which is assigned to an unperturbed Co(CO)$_4$- anion. The cation is free of CO but could unfortunately not be characterized by ^{1}H NMR due to line broadening, caused by a paramagnetic species.[30] Attempts to crystallize the salt failed. Elemental analysis of the oily product in the case of ligand **e** indicated that a Hieber type salt [Co(MAD)$_6$][Co(CO)$_4$]$_2$ had been obtained. As can be expected for an oily sample, about 1 equiv of solvent (CH$_2$Cl$_2$) was analyzed with the Co complex. When the reaction described above was not performed under strictly anhydrous conditions, small amounts of a new complex Co(CO)$_3$(R^{1}C(R^2)C(R^3)C(H)-NHR^4) (**1**) were found (Figure 1).

Before purification by column chromatography on silica, complex **1** is present in at least two different isomeric forms, indicated by two peaks for the A$_1$ vibration and in some cases also for the E vibration in the IR of the crude mixture. Complex **1** has been isolated as the syn,syn-isomer, which of course can be expected to be the most stable. Examination of complex **1** by NMR spectroscopy revealed the presence of an additional hydrogen atom on the nitrogen atom. The origin of this H atom became evident by reacting Co$_2$(CO)$_8$ with Me,iPr MAD (**e**) in the presence of D$_2$O. In this case complex **1e** was formed with 100% deuterium incorporation on the nitrogen atom.



2

2a. R = Me, R' = H
2b. R = Ph, R' = H
2c. R = Ph, R' = Me

Figure 2. Activation of H$_2$ in the reaction of Co$_2$(CO)$_8$ with α,β-unsaturated aldehydes and the proposed structure for compound **2**.

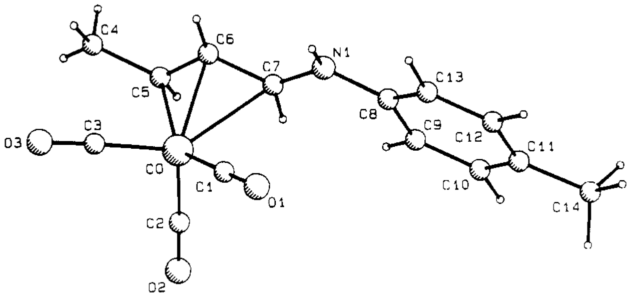


Figure 3. X-ray molecular structure of **1a**.

The formation of **1** can be readily explained by addition of HCo(CO)$_4$ to MAD. Upon performing this stoichiometric reaction, HCo(CO)$_4$ reacted already at −70 °C with MAD in hexane, yielding a precipitate. Upon warming, the precipitate, probably the salt (MAD+H)$^+$Co(CO)$_4^-$, dissolved and complex **1** could be detected.

Upon performing the reaction of MAD with Co$_2$(CO)$_8$ in THF under dihydrogen atmosphere, we found that dihydrogen was activated under very mild conditions and that complex **1** was formed in moderate to quantitative yields, depending on the specific substituents on MAD. The R^4 substituent on N appears to have the largest influence on the yield: for aromatic R^4 groups the yield is almost quantitative, while it drops to low values when alkyl groups are introduced on the C=CC=N skeleton. In the case of ligand **e** complex **1e** was not formed at all, only the disproportionation product [Co(MAD)$_6$][Co(CO)$_4$]$_2$ was isolated and characterized by elemental analysis. When the reaction of ligand **b** was carried out under D$_2$ atmosphere, complex **1b** was formed and the deuterium label was selectively incorporated on the nitrogen atom.

As the R^4 substituent appeared to influence this reaction to a large extent, it was deemed interesting to perform reactions of Co$_2$(CO)$_8$ with α,β-unsaturated aldehydes under the same conditions as the reactions with MAD (Figure 2).

The products, complexes **2a–c**, appeared to be very unstable. Complex **2a** decomposed during evaporation of the solvent. On the basis of IR spectroscopy, which showed the characteristic M(CO)$_3$ absorption pattern, it seems likely that the complexes **2** are analogues of the α-aminoallyl complexes **1**, as is shown in Figure 2. Due to the instability of **2a–c** this could not be confirmed by NMR spectroscopy. Further convincing evidence for the facile H$_2$ activation in the case of the α,β-unsaturated aldehydes was provided by the reaction of **2a** with MAD **b** and **e**, where the complexes **1b** and **1e** were formed instantaneously.

Molecular Structure of 1a. The molecular geometry of **1a** along with the adopted numbering scheme is given in Figure 3. Positional parameters and selected bond lengths and bond angles are listed in Tables I and II. As

Table I. Fractional Coordinates for the Non-Hydrogen Atoms and Equivalent Isotropic Parameters for 1a

	x	y	z	U_{eq}, Å^2
Co	0.0868 (2)	0.11750 (9)	0.4286 (2)	0.0463 (9)
C(1)	−0.101 (1)	0.1107 (6)	0.451 (2)	0.063 (8)
C(2)	0.132 (1)	0.2008 (6)	0.441 (2)	0.064 (8)
C(3)	0.145 (1)	0.0803 (7)	0.626 (2)	0.060 (8)
C(4)	0.391 (1)	0.0550 (8)	0.371 (2)	0.08 (1)
C(5)	0.269 (1)	0.0900 (6)	0.288 (2)	0.052 (7)
C(6)	0.147 (1)	0.0594 (5)	0.224 (2)	0.047 (7)
C(7)	0.043 (1)	0.0965 (6)	0.133 (1)	0.045 (6)
C(8)	−0.193 (1)	0.1070 (5)	−0.015 (1)	0.050 (7)
C(9)	−0.167 (1)	0.1692 (7)	−0.087 (2)	0.09 (1)
C(10)	−0.275 (2)	0.2032 (8)	−0.174 (2)	0.09 (1)
C(11)	−0.410 (1)	0.1777 (6)	−0.192 (2)	0.067 (9)
C(12)	−0.435 (1)	0.1178 (7)	−0.122 (2)	0.074 (9)
C(13)	−0.327 (1)	0.0836 (6)	−0.033 (2)	0.062 (8)
C(14)	−0.528 (2)	0.2130 (8)	−0.289 (2)	0.10 (1)
N(1)	−0.084 (1)	0.0719 (4)	0.070 (1)	0.050 (5)
O(1)	−0.225 (1)	0.1072 (6)	0.460 (1)	0.105 (8)
O(2)	0.159 (1)	0.2546 (4)	0.459 (2)	0.103 (8)
O(3)	0.188 (1)	0.0596 (5)	0.755 (1)	0.088 (7)

the *syn,syn*-η^3-allyl group acts as a bidentate ligand, the geometry around the Co center is approximately square pyramidal with C(1), C(3), C(5), and C(7) occupying the four basal positions and C(2) the axial position. From the angles {basal atom}–Co–C(2) only C(5)–Co–C(2) (95.5 (5)°) deviates significantly from 105°, which is the angle for the perfect square pyramid. The other angles are in the range 105–107°. The allylic moiety C(5)–C(6)–C(7) has a staggered orientation with respect to the $Co(CO)_3$ unit; the mouth of the allylic moiety faces the axial CO ligand, which has been shown by extended Hückel molecular orbital calculations to be the most stable orientation for 18-electron (η^3-allyl)ML_3 systems in general.[31] From the cobalt to allylic carbon bond distances it becomes clear that the coordination of the allyl group in this complex is not a standard one. The Co–C(5) bond (2.09 (1) Å) is comparable to other Co–allyl complexes (2.09–2.12 Å),[32-37] whereas the Co–C(6) bond (2.05 (1) Å) is slightly longer (2.00–2.02 Å) than normally observed. Strikingly anomalous is the Co–C(7) bond (2.32 (1) Å), which is extremely elongated compared to the other Co–allyl compounds (2.09–2.12 Å). When the Co–C(7) distance is not regarded as a bonding interaction, the ligand should consequently be formally positively charged and bonded to a formally negatively charged Co center via a η^2-C=C interaction. However, when taking the spectroscopic data into account, we have to consider complex 1 as a pseudo-allyl complex (vide infra).

The hybridization of the N atom in **1a** approximates sp^2-hybridization, as indicated by the C(7)–N–C(8) angle of 124.5 (8)°, which is close to the ideal value of 120°. The intraligand bonds C(5)–C(6), C(6)–C(7), C(7)–N, and even N–C(8) are all in the range of bond lengths observed for single and double bonds. This implies a large extent of conjugation through the ligand, which extends even to the aromatic substituent on the nitrogen atom. The plane of the *p*-tolyl group makes an angle of 20° with the plane defined by C(4)C(5)C(6)C(7)N. Such a flat ligand system provides the appropriate basis for an extended conjugation through strong π-overlap. There are two dihedral angles of some interest in allyl complexes, as has been pointed out in a theoretical study on $Co(CO)_3(\pi\text{-}C_3H_5)$, based on data for a gas-phase electron diffraction study.[38] First, the dihedral angle τ, defined as the angle between the plane of the allyl and the carbonyl carbon plane, is a measure for the amount of tilt of the allyl unit. Secondly, ϕ was defined as the angle between the plane through cobalt and the terminal allyl carbon atoms and the allyl plane. A τ value of 36° and ϕ value of 105° were found for $Co(CO)_3(\pi\text{-}C_3H_5)$ in the gas phase. These values are very different for **1a** being 19.1 and 79.3°, respectively. However, for $\{Co(CO)_3[(CH)_2CCH_2]\}_2$ values of the same order of magnitude as for **1a** (22.7 and 77.8°) have been reported.[37]

Spectroscopic Properties of 1a–g. The IR, ^1H NMR, $^{13}C\{^1H\}$ NMR, and ^{59}Co NMR data for the new α-aminoallyl cobalt complexes are given in the Tables III–VI. The IR spectra for **1a–g** generally show only two absorption bands; one sharp band between 2019 and 2041 cm^{-1} and a stronger, broader band between 1950 and 1983 cm^{-1}, which are indicative of a $M(CO)_3$ group with local C_{3v} symmetry. For **1b**, **1d**, and **1f** splitting of the E vibration has been observed, which must be due to lowering of the symmetry from C_{3v} to C_s. Among the complexes **1a–g** there are some differences. The wavenumbers for complex **1b**, having two aromatic substituents, are about 25 cm^{-1} higher than for **1g**, which is highly substituted by alkyl groups.

The coupling constants ^3J(H,H) in the proton NMR spectra of **1a–g** are all in the range 9.2–9.8 Hz, which are typical values for a trans coupling in allylic systems.[39,40] This means that all complexes are isolated in the syn,syn conformation. The chemical shift for protons at positions R^2 (2.38–3.34 ppm) and R^3 (3.72–4.58 ppm) agree very well with the chemical shifts of the corresponding protons in, e.g., $Co(CO)_3(C_3H_5)$, $Co(CO)_3$(*syn*-MeC_3H_4), and $Co(CO)_3$(*syn*-PhC_3H_4) (being for R^2 1.85, 2.72, and 3.67 ppm and for R^3 4.40, 4.26, and 5.06 ppm, respectively).[41]

In the latter complexes the resonance for the other terminal anti-proton has been observed in the range 1.64–1.85 ppm. For **1a–g** the value for H^5 has been found in the range 4.97–6.09 ppm. The proton H^5 is to be expected to resonate at higher frequency, because of the diamagnetic deshielding by the amino group. Such an effect has also been observed for the complex with R^4 = $-OSi(CH_3)_3$,[41] where H^5 resonates at 5.01 ppm.

A better insight into the electronic effects of substituents on the pseudo-allylic coordination in **1a–g** has been obtained from the ^{13}C NMR data (Table V). The values for C(5) (55.7–60.6 ppm) are comparable to those observed for terminal allyl carbon atoms in $\{(CO)_3Co[(CH)_2CCH_2]\}_2$ and $Co(CO)_2(PPh_3)(C_3H_5)$, being 52.6 and 47.2 ppm, respectively.[33,37] Compounds **1d** and **1g** (with C(5) at 73.1 and 71.3 ppm, respectively) fall outside this range, which is probably due to the higher degree of substitution at the allylic moiety. The central allylic carbon atom of **1a–g** resonates in the range 57.9–71.8 ppm, which is at a lower frequency than observed for $Co(CO)_2(PPh_3)(C_3H_5)$ (80.2 ppm). The other terminal allylic carbon atom C(7) in **1a–g** has shifted significantly toward higher frequency as compared to C(5). This influence of the amino group appears, moreover, to be dependent on the substituent on the nitrogen atom, R^4. For an aromatic R^4 group such as the

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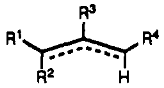
Table II. Selected Bond Distances (Å) and Bond Angles (deg) for 1a (with Esd's in Parentheses)

Co–C(1)	1.76 (1)	C(2)–O(2)	1.14 (2)	C(8)–C(13)	1.35 (2)
Co–C(2)	1.77 (1)	C(3)–O(3)	1.14 (2)	C(8)–N(1)	1.39 (1)
Co–C(3)	1.77 (1)	C(4)–C(5)	1.48 (2)	C(9)–C(10)	1.39 (2)
Co–C(5)	2.09 (1)	C(5)–C(6)	1.38 (2)	C(10)–C(11)	1.37 (2)
Co–C(6)	2.05 (1)	C(6)–C(7)	1.41 (2)	C(11)–C(12)	1.36 (2)
Co–C(7)	2.32 (1)	C(7)–N(1)	1.36 (1)	C(11)–C(14)	1.50 (2)
C(1)–O(1)	1.16 (2)	C(8)–C(9)	1.41 (2)	C(12)–C(13)	1.40 (2)
C(1)–Co–C(2)	108.0 (6)	C(1)–Co–C(3)	100.2 (6)	C(1)–Co–C(5)	146.9 (5)
C(1)–Co–C(6)	107.9 (5)	C(1)–Co–C(7)	85.2 (5)	C(2)–Co–C(3)	107.6 (6)
C(2)–Co–C(5)	95.5 (5)	C(2)–Co–C(6)	122.6 (6)	C(2)–Co–C(7)	105.8 (6)
C(3)–Co–C(5)	94.3 (5)	C(3)–Co–C(6)	108.2 (5)	C(3)–Co–C(7)	142.4 (5)
C(5)–Co–C(6)	38.9 (4)	C(5)–Co–C(7)	65.7 (4)	C(6)–Co–C(7)	36.9 (4)
Co–C(5)–C(4)	122.6 (9)	Co–C(5)–C(6)	68.9 (7)	Co–C(6)–C(5)	72.2 (7)
Co–C(6)–C(7)	82.2 (7)	Co–C(7)–C(6)	60.9 (6)	Co–C(7)–N(1)	123.6 (8)
Co–C(1)–O(1)	178 (1)	Co–C(2)–O(2)	176 (1)	Co–C(3)–O(3)	176 (1)
C(4)–C(5)–C(6)	124 (1)	C(5)–C(6)–C(7)	119 (1)	C(6)–C(7)–N(1)	124 (1)
C(7)–N(1)–C(8)	126.0 (9)				

Table III. IR Data for Co(CO)$_3$(R^{1}R^{2}CCR^{3}CHR^4)^a (1a–g) and for 2a–c



compd	R^1	R^2	R^3	R^4	ν(CO), cm$^{-1\,a}$	
1a	Me	H	H	NH-*p*-Tol	2038 (s)	1972 (vs)
1b	Ph	H	H	NH-*p*-Tol	2041 (s)	1983 (s), 1975 (s)
1c	Ph	H	H	NH*i*Pr	2024 (s)	1952 (vs)
1d	Ph	H	Me	NH*i*Pr	2033 (s)	1969 (s), 1959 (s)
1e	Me	H	H	NH*i*Pr	2030 (s)	1959 (vs)
1f	Me	H	H	NH*t*Bu	2029 (s)	1962 (s), 1955 (s)
1g	Me	Me	H	NH*t*Bu	2019 (s)	1950 (vs)
2a	Me	H	H	OH	2038 (s)^b	1965 (vs)^b
2b	Ph	H	H	OH	2050 (s) {2045 (s)}^{b}	1980 (vs) {1970 (vs)}^{b}
2c	Ph	H	Me	OH	2050 (s) {2042 (s)}^{b}	1980 (vs) {1970 (vs)}^{b}

[a] In hexane. [b] In THF.

p-tolyl group (**1a** and **1b**) C(7) resonates at 93 ppm, whereas alkyl substituents R^4 cause an extra high frequency shift of about 20 ppm, i.e. C(7) resonates at 110–116 ppm.

The ^{59}Co NMR spectra were measured in order to probe the relative electron density at the Co atom (Table VI). For comparison, also the ^{59}Co NMR spectra of Co(CO)$_3$(1-MeC$_3$H$_4$) and Co(CO)$_2$PPh$_3$(1-MeC$_3$H$_4$) have been recorded; resonances have been observed in the range −2700 to −3100 ppm.

Discussion

Influence of the α-Amino Substituent in the Complexes 1a–g. Comparison to Normal η^3-Allyl Complexes. It is clear from both the spectroscopic and crystallographic data that, due to the presence of the α-amino substituent, the character of the η^3-bonded allyl moiety

Table IV. ^{1}H NMR Data for Co(CO)$_3$(R^{1}R^{2}CCR^{3}CH^{5}NHR^4) (1a–g)

	δ (ppm)^a					
compd	R^1	R^2	R^3	H^5	R^4	N-H
1a	1.41 (d, 6.3)	2.38 (dq, 9.3, 6.3)	4.00 (dd, 9.3, 9.3)	4.97 (dd, 9.3, 12.2)	2.05 (s) 6.83, 6.47 (d, 8.0)	4.47 (br d, 12.2)
1b	7.31–6.99 (m)	3.28 (d, 9.6)	4.78 (dd, 9.2, 9.6)	5.14 (dd, 9.2, 12.2)	2.08 (s) 6.88, 6.57 (d, 8.3)	4.62 (br d, 12.2)
1c	7.26–6.91 (m)	3.34 (d, 9.5)	4.52 (dd, 9.5, 9.5)	5.19 (dd, 9.5, 10.5)	2.75 (sept, 6.4) 0.78/0.72 (d, 6.4)	2.77 (br d, 10.5)
1d	6.98–6.89 (m)	5.03 (s)	1.64 (s)	6.09 (d, 13.8)	2.59 (d sept, 6.0, 7.0) 0.81/0.74 (d, 6.3)	3.30 (br, dd, 13.8, 6.0)
1e	1.43 (d, 6.3)	2.39 (dq, 6.2, 9.2)	3.72 (dd, 9.2, 9.8)	5.03 (dd, 9.8, 10.2)	2.65 (sept, 6.3) 0.73/0.65 (d, 6.3)	2.59 (br d, 10.2)
1f	1.45 (d, 6.1)	2.46 (dq, 6.1, 9.4)	3.72 (dd, 9.5, 9.8)	5.20 (dd, 9.8, 14.0)	0.81 (s)	3.15 (br d, 14.0)
1g	1.60 (s)	1.12 (s)	3.89 (d, 10.4)	5.75 (dd, 10.4, 13.9)	0.87 (s)	3.14 (br d, 13.9)

[a] Measured at 100.1 MHz, toluene-d_8, 293 K, multiplicity and $J_{\mathrm{H,H}}$ (Hz) in parentheses; for the adopted labeling of the substituents see Table III and Figure 1.

Table V. ^{13}C NMR Data for Co(CO)$_3${R^{1}C^5(R^2)C^6(R^3)C^7(H)NHR^4} (1a–g)

	δ (ppm)^a							
compd	R^1	R^2	C^5	C^6	C^7	R^3	R^4	CO
1a	20.8		57.4	68.9	93.9		139.4, 131.1, 130.6 115.0, 20.6	206.3
1b	141.6, 129.3 127.1		60.6	63.9	93.6		139.5, 131.4, 130.7 115.2, 20.9	205.6
1c	142.5, 125.9 125.7		56.9	57.9	116.0		47.0, 21.5/21.3	n.o.
1d	144.2, 128.6 126.0		73.1	71.8	112.7	22.5	49.9, 21.5/21.3	n.o.
1e^b	22.6		55.0	62.1	115.5		47.1, 22.2/21.9	209.5
1f	21.3		55.7	63.3	114.4		51.9, 28.5	n.o.
1g	27.7	31.4	71.3	66.8	110.2		51.9, 28.6	n.o.

[a] Measured at 25.0 MHz, toluene-d_8, 263 K, ^{13}C-APT, unless stated otherwise; for the adopted labeling of the substituents see Table III and Figure 1. [b] Recorded at 273 K; n.o. = not observed.

Table VI. ^{59}Co NMR Data

compd	δ (ppm)[a]
$Co(CO)_3(1\text{-}MeC_3H_4)$	−2727 (10^4)
$Co(CO)_2(PPh_3)(1\text{-}MeC_3H_4)$	−3115 (73)
$Co(CO)_3(MeC_3H_3NH\text{-}p\text{-}Tol)$ (**1a**)	−3113 (303)
$Co(CO)_3(MeC_3H_3NHiPr)$ (**1e**)	−3118 (650)

[a] Measured at 23.7 MHz in C_6D_6/CH_2Cl_2 (2:3) at 293 K; the peak width at half-height (Hz) is given in parentheses.

Table VII. Comparison of IR Data for $Co(CO)_3(\eta^3\text{-allyl})$ Complexes[a]

	ν(CO), cm^{-1}		ref
$Co(CO)_3(C_3H_5)$	2068 (s)	2000 (vs)	59
$Co(CO)_3(1\text{-}MeC_3H_4)$	2064 (s)	1995 (vs)	60
$Co(CO)_3(1\text{-}ClC_3H_4)$	2077 (s)	2017 (vs), 2010 (vs)	60
$[Co(CO)_3\{(CH)_2CCH_2\}]_2$	2072 (s), 2020 (s)	1996 (vs), 1992 (vs)	37
$Co(CO)_3(MeC_3H_3NH\text{-}p\text{-}Tol)$ (**1a**)	2038 (s)	1972 (vs)	

[a] In hexane solution.

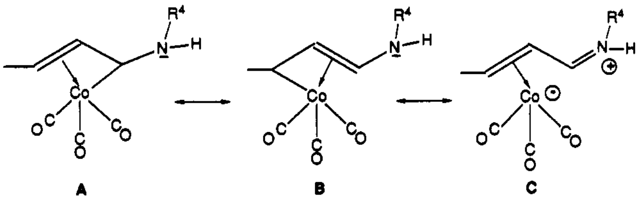


Figure 4. Resonance structures of compound 1.

in the complexes **1a–g** has significantly changed as compared to normal, unsubstituted η^3-allyl complexes.

Examining the crystallographic data, the effect of the amino group is most strikingly expressed by the extremely elongated Co–C(7) distance of 2.32 (1) Å (Figure 3). This value might imply that there is little bonding between Co and C(7), which may be represented by the resonance structures depicted in Figure 4.

The electron-donating properties of the amino substituent induce a charge separation, which is represented by resonance structure C. In order to obtain a closed valence shell for Co in structure C, no bond can be present between Co and C(7) and consequently Co is formally negatively charged and this extra electron density on Co should affect the bonding of the carbonyl ligands. From the lowering of the CO stretching frequencies compared to the other complexes in Table VII, it can be concluded that by the introduction of the α-amino group the electron density on Co has indeed increased, resulting in more π-back-donation to the CO ligands.

In the unsubstituted η^3-allyl complex $Co(CO)_3(\eta^3\text{-}C_3H_5)$ one CO ligand is particularly labile, which has been ascribed to the asymmetry of the $Co(CO)_3$ group, induced by the tilting of the allyl plane,[38] as expressed by a τ value of 36°. The labile CO ligand is easily substituted by PPh_3[33] in an instantaneous reaction, which is in contrast to complexes **1a** and **1b**, which do not react with PPh_3 or $P(OMe)_3$ even after 3-h reaction time. It would be an unwarranted simplification to attribute these observations to a difference in τ angle, as the smaller τ angle of 19° found in **1a** is comparable to the value reported for $\{(CO)_3Co[(CH)_2CCH_2]\}_2$ (τ = 22.7°)[37] and the latter complex reacts with $P(OMe)_3$ within 15 min to yield the phosphite-substituted complex, although the allyl plane in this complex exhibits a reduced tilting. The reason for the relative inertness of **1a**/**1b** toward phosphorus donor ligands probably originates from the high electron density on Co, visualized in resonance structure C (Figure 4) and the consequently stronger bonding of the CO ligands to the metal. This explanation is in agreement with the IR carbonyl stretching frequencies (see Table III and VII) and with the ^{59}Co NMR data (vide infra).

The ^{13}C NMR spectra of 1 show a high-frequency shift for the resonance of C(7) (at 93–116 ppm) as compared to conventional η^3-allyl groups, where it is found at about 60 ppm. A paramagnetic influence of the π electrons in the C–N bond, contributed by resonance structure C (Figure 4), accounts for this effect.

Comparison of the Pseudo-Allyl Complexes 1a–g. The contribution of resonance structure C (Figure 4) also enables the interpretation of the spectroscopic differences between the complexes **1a–g**. Electron-donating alkyl substituents R^4 favor resonance structure C (Figure 4) by stabilization of the formal positive charge on nitrogen. The consequently larger contribution of resonance structure C causes lower carbonyl stretching frequencies in the IR spectra and a high frequency shift of about 20 ppm for C(7) in the ^{13}C NMR spectra for **1c–g** as compared to **1a**/**b**. The same trend in the spectroscopic data was observed in the case of two Mn complexes,[42] which contain a similar ligand system as in 1. The data of Mn complexes, which are derived from nucleophilic attack of a secondary amine to (η^5-pentadienyl)$Mn(CO)_3$ were also interpreted as being a consequence of an increase of electron density at the metal due to reduced π-back-bonding to the aminoallyl fragment.

In the case of **1a** and **1e** the actual contribution of structure C with enhanced electron density on the metal has also been corroborated by ^{59}Co NMR spectroscopy. The ^{59}Co chemical shift is largely dependent on the oxidation state of the Co atom,[43–45] and generally, organo-Co(I) complexes cover a range roughly between −800 and −2800 ppm.[44] The ^{59}Co signals of the complexes in Table VI have been found at the low-frequency extreme of the Co(I) range. The most relevant parameter governing the ^{59}Co chemical shift is the paramagnetic shielding term σ_p, which in formula contains a radial factor r^{-3}, as well as the average electronic excitation energy, ΔE: $\sigma_p = -(\text{constant})(r^{-3})/\Delta E$. In closely related complexes, such as the complexes we measured, the contribution of the r^{-3} factor is probably negligible and σ_p will be inversely dependent on ΔE.[45] Comparing $Co(CO)_3(\eta^3\text{-}C_4H_7)$ with $Co(CO)_2(PPh_3)(\eta^3\text{-}C_4H_7)$, a low-frequency shift of 400 ppm, going from −2700 to −3100 ppm, is observed. This low-frequency shift, which is similar to that in other reports,[45] can be explained by the expected increase in the ligand field energy, ΔE, due to the introduction of the electron-releasing PPh_3 group. Comparing $Co(CO)_3(\eta^3\text{-}C_4H_7)$ with **1a** or **1e**, the electron density on Co in **1a**/**e** has increased, due to the contribution of mesomeric structure C (Figure 4). Consequently, the ΔE factor can be expected to increase, leading to the decrease of σ_p and δ, which is in agreement with the observed data.

Mechanism of H_2 Activation. The influence of base on the activation of H_2 by $Co_2(CO)_8$ has been known for a considerable time.[21,46] The mechanism, however, has not been completely clarified. Before going into more detail regarding the interaction of base with $Co_2(CO)_8$ under H_2 atmosphere, first the reaction of $Co_2(CO)_8$ with base in an inert atmosphere, which leads to the dispro-

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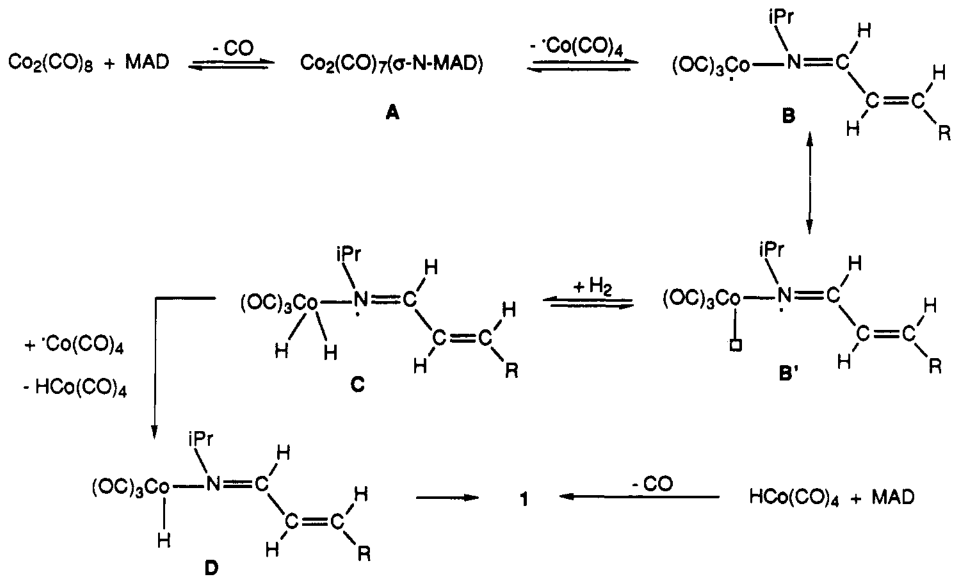
Scheme I. Proposed Mechanism for the H_2 Activation Reaction under Mild Conditions by the $Co_2(CO)_8$/MAD System, Yielding Compound 1



portionation of $Co_2(CO)_8$, will be discussed briefly.

Disproportionation of $Co_2(CO)_8$. Disproportionation reactions of $Co_2(CO)_8$ have been studied extensively. Factors determining the disproportionation equilibrium of $Co_2(CO)_8$ are the solvation energy of the ionic species in the solvent, the ability of the entering base to act as a ligand, and the change in reduction potential of the cobalt cation.[47] The specific type of disproportionation product is determined by the kind of base used. For hard bases like pyridine a Co(II) species with composition $[CoL_6][Co(CO)_4]_2$ has been obtained, which is generally called a Hieber salt. For softer bases like phosphines the product usually is a Co(I) salt of the composition $[Co(CO)_nL_{5-n}][Co(CO)_4]$, where $n = 1, 2$, or 3.[48] Several disproportionation mechanisms have been proposed, which can be roughly divided in two categories, viz. involving heterolytic or homolytic rupture of the Co–Co bond.

Heterolytic splitting of the Co–Co bond induced by addition of two molecules of base ligand, followed by substitution of CO by a third molecule of base ligand and subsequent disproportionation of the $Co_2(CO)_7L_3$ species, was proposed to occur when amines were employed as the base ligands.[49,50] In the case of a sterically hindered N base like Et_3N or in the case of alcohols such as MeOH, the first step probably is dissociative CO substitution, followed by disproportionation of $Co_2(CO)_7L$ into $Co(CO)_3L^+$ and $Co(CO)_4^-$.[47] In the case of homolysis of the intermetallic bond for soft bases such as phosphines and phosphites, a mechanism was proposed involving initial association of the Lewis base, followed directly by homolytic splitting of the Co–Co bond, affording radical intermediates.[51] In the reaction of MAD with $Co_2(CO)_8$, MAD obviously behaves as a base, so substitution of CO takes place and MAD binds to the metal via the lone pair on the nitrogen atom. The resulting disproportionation product in the case of ligand **e** has been characterized as a Hieber type salt of the composition $[Co(MAD)_6][Co(CO)_4]_2$. In the case of the ligands **a** and **b**, containing aromatic substituents, the disproportionation reaction proceeded very slowly, which is in agreement with the generally observed accelerating effect of increasing ligand basicity on the rate of disproportionation as mentioned before.

H_2 Activation. The central question in the disproportionation mechanism, viz. how molecules of base interact with $Co_2(CO)_8$, is also crucial for the mechanism of H_2 activation in the reaction of $Co_2(CO)_8$ with base under H_2 atmosphere and constitutes the key problem in the rate-accelerating effect of base in the hydroformylation reaction of alkenes by $Co_2(CO)_8$ as well. From the literature it is known that the largest effect was observed with some nitrogen heterocycles and tertiary phosphines.[21] At the same time the base/Co ratio leading to maximum $HCo(CO)_4$ concentration appeared to decrease with increasing basicity of the additives. We have found (vide supra) that the yield of the complexes **1a–g** in the reaction of $Co_2(CO)_8$ with MAD under H_2 is also correlated to the basicity of the ligands. The less basic ligands **a** and **b**, bearing aromatic substituents on nitrogen, give the highest yields. Moreover, the oxygen-containing compounds, RCH=CR′CH=O, being less basic as compared to nitrogen-containing compounds, also display suitable properties for catalyzing the H_2 activation by $Co_2(CO)_8$. As the ability to substitute CO will decrease when the basicity of the ligand is reduced, these results suggest that activation of H_2 may occur when a small number of base molecules have interacted with $Co_2(CO)_8$.

Fachinetti et al. studied the Hieber reaction in more detail, also in connection with the question of H_2 activation.[52-55] They distinguished three kinds of homonuclear ion pairs (HNIP) by IR, which are intermediates on the route to the Hieber complex $[Co(pyr)_6][Co(CO)_4]_2$, which is the final disproportionation product in the presence of a large excess of pyridine.

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These HNIP's effect the activation of H_2 under the same very mild conditions. The actual activation step has been ascribed to highly polarizing Co^{2+} ions in the HNIP's, which are capable of activating H_2.[53] By analogy with the work of Fachinetti the reaction of $Co_2(CO)_8$ with MAD under H_2 to yield 1 might also proceed via HNIP's as the reactive intermediates. The influence of H_2O on the reaction in absence of H_2 may be explained by those reactive HNIP's as well, as coordination of H_2O to an unsaturated Co^{2+} atom in a HNIP may result in the formation of Co-hydroxide and a hydride, the latter being responsible for the formation of 1. Water may also accelerate the disproportionation reaction. This mechanism, however, does not explain the observed differences in yields of **1a**–**1g** as a function of the substituents of the MAD ligand.

Alternatively, a radical mechanism may be involved, as has been suggested by other authors as well.[51,56,57] In analogy, we propose the mechanism shown in Scheme I, which accounts for the formation and yields of the compounds **1a**–**g**. In this view, intermediate **B** is stabilized by the resonance structure **B′** featuring the radical delocalized in the LUMO of the monoazadiene system. Structure **B′** can be rationalized by reports on ESR data of similar metal–imine compounds.[58] From this stage, activation of H_2 and formation of the products is straightforward. In the case of MAD ligands containing aromatic substituents, intermediate **B′** is stabilized by delocalization, thus increasing its lifetime. In the case of aliphatic substituents the lifetime of **B′** is too short for H_2 activation to take place; recombination of radicals and disproportionation will occur instead.

Compounds with large substituents at the nitrogen atom, such as in **f** and **g**, will cause an increased lifetime of **B**/**B′**, as the recombination reaction of the radicals is hampered on steric grounds. In the case of ligand **e**, containing neither an aromatic substituent nor a large group on the nitrogen atom, disproportionation to a Hieber-type product takes place, as could be inferred from the elemental analysis of the product salt. Unfortunately, we have not been able to obtain direct evidence to support the proposed radical mechanism; i.e. the reaction of $Co_2(CO)_8$ with **b** under H_2 was not influenced by the presence of radical traps, such as phenanthrenequinone or styrene.

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Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters for the non-hydrogen atoms, and all bond distances and angles (4 pages). Ordering information is given on any current masthead page.

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