Cobalt-Catalyzed Carbonylation of *N*-Alkylbenzaldimines to '*N*-Alkylphthalimidines' (= 2,3-Dihydro-1*H*-isoindol-1-ones) *via* Tandem C–H Activation and Cyclocarbonylation

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

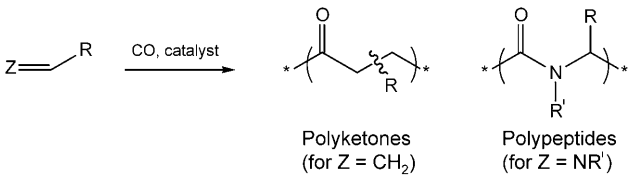
The reaction of *N*-alkylbenzaldimines with carbon monoxide (CO) in the presence of cobalt (Co) catalysts resulted in the formation of *N*-alkylphthalimidines (*Table 1*). Their formation is proposed to occur by C–H activation of the aryl ring, migratory insertion of the hydride species into the benzaldimine functionality, CO coordination, and insertion into the Co–C bond, followed by reductive elimination of the *N*-alkylphthalimidine and regeneration of the starting Co species (*Scheme 4*). Deuterium (^{2}H)-labeling NMR studies are consistent with this mechanism (*Scheme 5*).

Introduction. – The synthesis of 1,4-polyketones by the alternating copolymerization of alkenes and carbon monoxide (CO) by late-transition-metal complexes has been extensively studied and is well-established within the field of carbonylation chemistry [1–4]. However, the extension of this chemistry from C=C bonds of alkenes to isoelectronic C=N bonds of aldimines for the formation of polypeptides, as shown in *Scheme 1*, has proven to be much less successful.

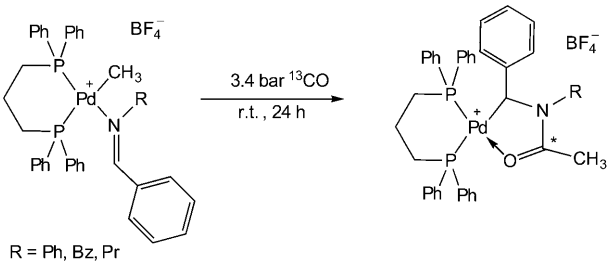
Previous work in our laboratory [5], as well as by others [6–10], has shown that cationic Pd^{II} complexes used in the successful copolymerization of alkenes and CO undergo sequential insertion of CO, followed by benzaldimine, into a Pd–alkyl bond. However, the CO group of the resultant amide functionality coordinates much more strongly to the Pd center than the corresponding ketone from alkene/CO copolymerization, prohibiting the subsequent insertion of CO and, thereby, terminating the reaction (*Scheme 2*) [5].

Related to the copolymerization of aldimines and CO, *Jia* and co-workers [11–14], and others [15] have shown that cobalt (Co) complexes can successfully copolymerize

Scheme 1. *Alternating Copolymerization of Isoelectronic Olefins and Imines with CO to Form Polyketones and Polypeptides, Respectively*



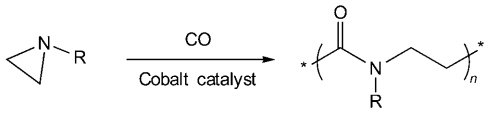
Scheme 2. *Sequential Insertion of CO and Benzaldimine to Form a Stable Pd^{II} Chelate Structure Prohibiting Further Reaction*

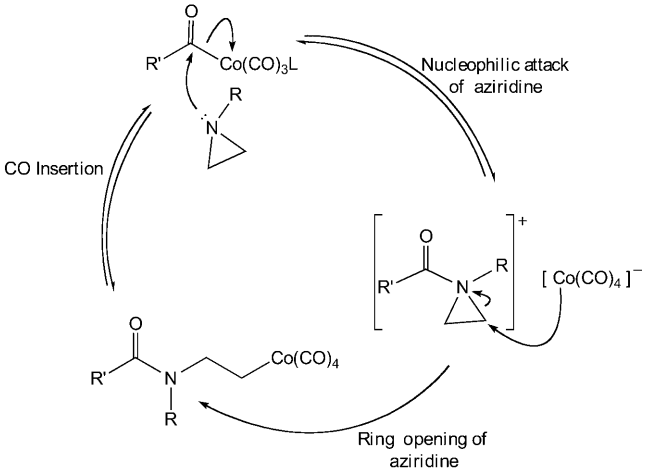


N-alkylaziridines and CO for the synthesis of poly-β-peptides (*Scheme 3*). The mechanism of this transformation has recently been investigated in detail (*Scheme 3*) [16].

Encouraged by these results, and based on previous results from our own laboratory for the Co-catalyzed synthesis of ε-caprolactam and polycaprolactam [17], we thought that the above system could also be used for the alternating copolymerization of benzaldimines and CO by an analogous mechanism. Herein, we report our initial results in this area.

Scheme 3. *Copolymerization of* N-*Alkylaziridines with CO to Form Poly-β-peptides, and Proposed Mechanism*





Results and Discussion. – 1. *Reaction of* N-*Alkylaldimines with CO.* The catalyst [Co($^{13}CH_3C(O)$)$(CO)_3(P(o\text{-tol})_3)$][1]) in deuterated 1,4-dioxane was found to produce not the expected polypeptide, but rather '*N*-alkylphthalimides' (=2,3-dihydro-1*H*-isoindol-1-ones) as the main products (*Table 1*). No reaction was observed when either the Co compound or CO was absent (*Entries 5* and *6*, resp.). For the reaction involving PhCH=NEt, ^{1}H-NMR analysis showed the disappearance of the benzaldimine peak at δ(H) 8.29, and the appearance of a new signal at δ(H) 4.36 (*s*). Furthermore, ^{13}C-NMR spectra taken before and after the reaction also showed the disappearance of the benzaldimine signals at δ(C) 160.4 (N=CH) and 56.3 (NCH_2), and the appearance of new resonances at δ(C) 167.7 and 49.5, respectively. The use of ^{13}CO resulted in a large enhancement of the amide resonance at δ(C) 167.7.

Table 1. *Reaction of Benzaldimines with CO to Phthalimidines in the presence of the Catalysts [Co($^{13}CH_3C(O)$)$(CO)_3(P(o\text{-tol})_3]$* (**A**) *or* $[Co_2(CO)_8]$ (**B**). All reactions were run in 2 ml of (D_8)-1,4-dioxane, unless noted otherwise.

Entry	Benzaldimine	Conditions	Yield [%][a])
1	PhCH=NMe	**A** (0.02 mmol), aldimine (19 equiv.), 1000 psi CO, 200°, 2 d	71
2	PhCH=NEt	**A** (0.02 mmol), aldimine (20 equiv.), 1000 psi CO, 200°, 2 d	71
3	PhCH=NEt	**A** (0.02 mmol), aldimine (19 equiv.), 300 psi ^{13}CO, 200°, 2 d	65
4[b])	PhCH=NEt	**B** (0.06 mmol), aldimine (20 equiv.), 1000 psi CO, 200°, 6 h	92
5	PhCH=NEt	No catalyst, aldimine (1 mmol), 2 ml (1000 psi CO, 200°, 1 d	n.r.[c])
6	PhCH=NMe	**A** (0.02 mmol), aldimine (19 equiv.), 1000 psi N_2, 200°, 1 d	n.r.
7	PhCH=NPr	**A** (0.02 mmol), aldimine (21 equiv.), 1000 psi CO, 200°, 1 d	62
8	2,6-$Me_2C_6H_3$CH=NEt	**A** (0.02 mmol), aldimine (23 equiv.), 1000 psi CO, 200°, 3 d	n.r.
9	2,6-$F_2C_6H_3$CH=NMe	**A** (0.02 mmol), aldimine (33 equiv.), 1000 psi CO, 200°, 3 d	n.r.

[a]) Yields were determined by ^{1}H-NMR spectroscopy rel. to an external standard of 1,3,5-trioxane in $CDCl_3$. [b]) In 2 ml of C_6D_6. [c]) No reaction.

At first glance, these new signals are consistent with the formation of an alternating benzaldimine/CO copolymer. However, further analysis revealed that they were not due to the copolymer. The HMQC spectrum of the product revealed that the signal at δ(C) 49.5 was correlated with δ(H) 4.36. Furthermore, DEPT-135 revealed that the resonance at δ(C) 49.5 was actually derived from a methylene ($-CH_2-$) species, consistent only with the formation of an *N*-alkylphthalimidine, as corroborated by

[1]) Abbreviation: '*o*-tol' refers to *ortho*-tolyl (=2-methylphenyl).

IR analysis. IR Spectra taken before and after the reaction showed the disappearance of the benzaldimine C=N absorption at 1646 cm^{-1}, and the appearance of a C=O absorption at 1694 cm^{-1}, corresponding to the formation of a five-membered lactam ring. An acyclic amide would be expected to resonate at *ca.* 1645 cm^{-1}. The observed isotopic shift of the product incorporating a ^{13}C=O group (1652 cm^{-1}) was in close agreement with the calculated value (1657 cm^{-1}).

Finally, X-ray crystallography of *N*-methylphthalimidine (*Figure*), the product obtained from the reaction of *N*-(1-phenylmethylidene)methanamine (PhC(H)=NMe) with CO, complemented the above analyses. Details of the structure determination and refinement are given in *Table 2* and in the *Exper. Part*.

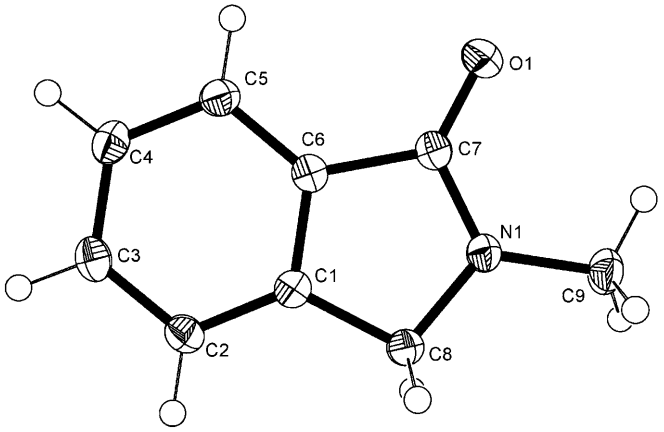


Figure. *X-Ray crystal structure* (ORTEP representation) *of* N-*methylphthalimidine formed in the reaction of* N-*(1-phenylmethylidene)methanamine with CO in the presence of a cobalt catalyst*

2. *Mechanistic Considerations.* A proposed mechanism for the formation of *N*-alkylphthalimidines in the presence of the Co complex is shown in *Scheme 4*. Analogous to that proposed by *Jia* and co-workers [16], the initial step of the reaction is likely to be nucleophilic attack of the benzaldimine on the Co–acyl functionality to generate a cobaltate species. In the case of *Jia*'s copolymerization of *N*-alkylaziridines with CO, ring opening of *N*-alkylaziridine relieves steric strain and leads to a new Co–alkyl species and eventual copolymer formation (see *Scheme 3* above). In our system, the nucleophilic attack of the cobaltate anion on the benzaldiminium species is apparently not as favorable. Instead, the cobaltate anion coordinates to another benzaldimine and undergoes oxidative addition of the aryl C–H bond of the benzaldimine, followed by migratory insertion of the C=N bond. This cobalt–amine species then inserts a CO molecule to form a Co–acyl species that reductively eliminates the *N*-alkylphthalimidines to regenerate the starting cobaltate anion.

In support of this mechanism, it has previously been shown that the cobaltate anion generated *in situ* in benzene from $[Co_2(CO)_8]$ is a very effective catalyst for the synthesis of *N*-alkylphthalimidines [18–20]. Indeed, using $[Co_2(CO)_8]$ as catalyst precursor in benzene also resulted in the formation of *N*-alkylphthalimidines (*Table 1*, *Entry 4*). To probe this mechanism, the deuterated benzaldimines $C_6D_5C(H)=NCH_3$ and C_6D_5-

Table 2. *Crystallographic Data for* N-*Methylphthalimidine* (see *Figure*)

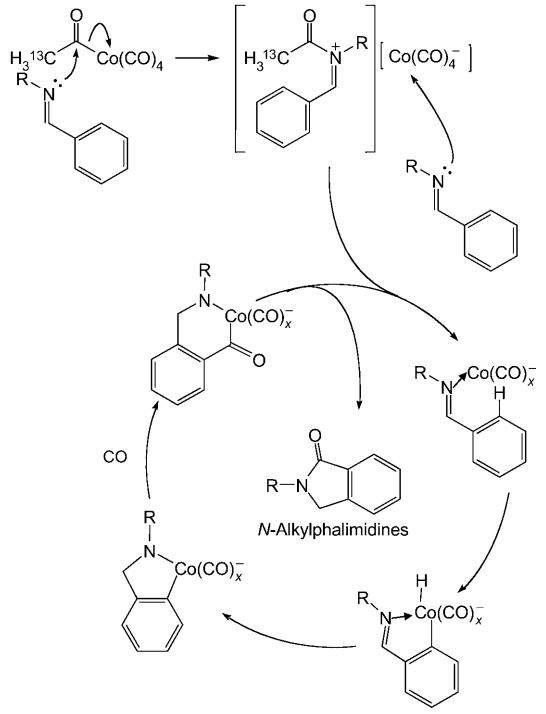
Empirical formula	C_9H_9NO
Formula weight [g/mol]	147.17
Temperature [K]	108(2)
Wavelength [Å]	0.71073
Crystal size [mm]	$0.50\times0.25\times0.20$
Crystal habit	yellow brick
Crystal system	monoclinic
Space group	$P\,2_1/c$
Unit-cell dimensions:	$a=9.1655(12)$ Å $\alpha=90^\circ$
	$b=9.0746(12)$ Å $\beta=114.445(2)^\circ$
	$c=9.6316(12)$ Å $\gamma=90^\circ$
V [Å^3]	729.28(16)
Z	4
D_{calc} [g/cm^3]	1.340
Absorption coefficient [mm^{-1}]	0.088
F(000)	312
Diffractometer	CCD area detector
Radiation source	fine-focus sealed tube, MoK_α
Generator power	1600 W (50 kV, 32 mA)
Detector distance	5.8 cm
Data collection method	ϕ and ω scans
θ Range for data collection	2.44–28.30°
Index ranges	$-12\le h\le11$, $-12\le k\le11$, $-12\le l\le7$

C(D)=NCH$_3$ were used as substrates. Because the use of [Co$_2$(CO)$_8$] resulted in the formation of *N*-alkylphthalimidines in higher yields, all reactions were run with this catalyst in C$_6$D$_6$. Analysis of the product from the reaction of C$_6$D$_5$C(H)=NCH$_3$ with CO by ^{13}C-NMR and GC/MS showed that 80% of the product had a CHD methylene unit, while 20% possessed a CH$_2$ unit (*Scheme 5*). In the case of the reaction of C$_6$D$_5$-C(D)=NCH$_3$ with CO, a similar analysis showed that 70% of the product contained a CD$_2$ unit, whereas 30% showed a CHD unit. In both cases, there was no evidence for H/D scrambling in the aromatic ring or the Me group. Together, these studies provide evidence in support of the proposed mechanism, where a Co–H species generated by C–H activation of the aromatic ring inserts into the C=N bond of the benzaldimine.

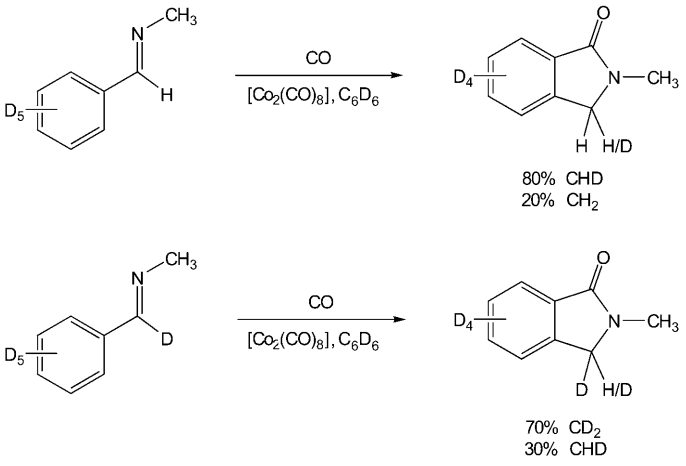
3. *Modified Aldimines for the Attempted Copolymerization with CO.* Since the copolymerization of benzaldimines with CO did not occur because of the alternative reaction pathway involving the activation of a ring C–H bond *ortho* to the aldimine functionality, two modified benzaldimines with two blocked *ortho*-positions were tested. The use of *N*-[(2,6-dimethylphenyl)methylidene]ethanamine (2,6-Me$_2$C$_6$H$_3$-C(H)=NEt) resulted in no reaction (*Table 1*, *Entry 8*). To further eliminate that this was due to the steric bulk of the two Me groups preventing the approach of the cobaltate anion to the imine functionality, we also tested the corresponding smaller difluoro congener. However, there was no reaction in this case either (*Entry 9*).

Conclusions. – The reaction of *N*-alkylbenzaldimines with CO in the presence of Co catalysts results not in the expected formation of the desired alternating copolymer, but in *N*-alkylphthalimidines arising from C–H activation of the aromatic ring of the benz-

Scheme 4. *Proposed Mechanism for the Formation of* N-*Alkylphthalimidines from Benzaldimines and CO in the Presence of* $[Co(^{13}CH_3C(O))(CO)_3(P(o\text{-}tol)_3)]$[1])



Scheme 5. *Deuterium Distribution in the Reaction of Isotopically-Substituted Benzaldimines with CO in the presence of* $[Co_2(CO)_8]$



aldimine. Attempts to copolymerize *N*-alkylbenzaldimines with CO by blocking the *ortho*-positions of the benzaldimine resulted in no reaction. Interestingly, although C–H activation was not observed in the attempted copolymerization of benzaldimines with CO using Pd compounds [5–7], there are numerous examples for C–H activation of benzaldimines in the literature [21–29].

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Experimental Part

General. (D_8)-1,4-Dioxane (*Aldrich*) and C_6D_6 (*Aldrich*) were dried over molecular sieves (*Aldrich*) [30]. The complex [Co($^{13}CH_3C(O)$)$(CO)_3$(P(*o*-tol)$_3$)][1]) was synthesized from [$NaCo(CO)_4$], tris(*o*-tolyl)-phosphine (P(*o*-tol)$_3$; *Strem*), and $^{13}CH_3I$ (*Aldrich*) according to literature procedures [16]. The aldimines were synthesized according to published procedures [31] by condensation of the appropriate aldehydes and amines, dried over CaH_2 (*Acros*) and purified by solvent removal (when necessary), followed by distillation. The aldimines were then degassed (three freeze/pump/thaw cycles) prior to use. [$Co_2(CO)_8$] (*Strem*) was used as received. CH_2Cl_2 (*EMS*) and EtOH (200 proof; *Pharmco*) were used as received. GC Analyses were performed on an *Agilent 5890 Series II* apparatus with an *RTX-5* split capillary column (*Restek*) connected to an FID detector. IR Spectra were recorded on a *Bruker* IR spectrometer in 0.05-mm CaF_2 liquid cells (resolution: 0.5 cm^{-1}). ^{1}H- (300 MHz) and ^{13}C-NMR (75 MHz) Spectra were recorded at r.t. on a *Bruker DPX-300* spectrometer; δ in ppm, J in Hz. All work involving air- and/or moisture-sensitive compounds was carried out in a dry box under N_2 atmosphere.

General Procedure (*GP 1*): N-*(1-Phenylmethylidene)methanamine* ($C_6H_5C(H)$=NMe). In a 100-ml round-bottom flask, benzaldehyde (5.0 g, 47 mmol; *Aldrich*) and excess 2.0M $MeNH_2$ in THF were reacted until the aldehyde was consumed (GC analysis). The soln. was then dried by careful addition of CaH_2, the solvent (THF) was removed, and the product was purified by distillation. ^{1}H-NMR ($CDCl_3$): 3.51 (*s*, Me); 7.40 (3 arom. H); 7.71 (2 arom. H); 8.25 (*s*, N=CH). ^{13}C-NMR ($CDCl_3$): 48.6 (Me); 128.3, 128.6, 130.9, 136.7 (Ph); 162.8 (N=CH).

General Procedure (*GP 2*): N-*(1-Phenylmethylidene)ethanamine* ($C_6H_5C(H)$=NEt). In a 100-ml round-bottom flask, benzaldehyde (5.0 g, 47 mmol) and excess $EtNH_2$ (*Aldrich*) were reacted until the aldehyde was consumed (GC analysis). The soln. was then dried by careful addition of CaH_2, and the product was purified by distillation. ^{1}H-NMR ($CDCl_3$): 1.31 (*t*, J=7.3, Me); 3.66 (*qd*, J=7.3, 1.3, NCH_2); 7.41 (3 arom. H); 7.75 (2 arom. H); 8.29 (*s*, N=CH). ^{13}C-NMR ($CDCl_3$): 16.8 (Me); 56.3 (CH_2); 128.4, 129.0, 130.9, 136.8 (Ph); 160.8 (N=CH).

N-*(1-Phenylmethylidene)propanamine* ($C_6H_5C(H)$=NPr). Prepared from benzaldehyde and $PrNH_2$ (*Aldrich*) according to *GP 2*. ^{1}H-NMR ($CDCl_3$): 0.99 (*t*, J=7.3, Me); 1.77 (*m*, J=7.2, NCH_2CH_2); 3.59 (*td*, J=6.9, 0.9, NCH_2); 7.39 (3 arom. H); 7.75 (2 arom. H); 8.26 (*s*, N=CH). ^{13}C-NMR ($CDCl_3$): 12.3 (Me); 24.5 (NCH_2CH_2); 63.9 (NCH_2); 128.5, 128.9, 130.8, 136.8 (Ph); 161.1 (N=CH).

N-*[(2,6-Dimethylphenyl)methylidene]ethanamine* (2,6-$Me_2C_6H_3C(H)$=NEt). Prepared from 2,6-dimethylbenzaldehyde (*Aldrich*) and $EtNH_2$ according to *GP 2*. ^{1}H-NMR ($CDCl_3$): 1.38 (*t*, J=7.3, MeN); 2.43 (*s*, 2 Me); 3.73 (*qd*, J=7.3, 1.2, NCH_2); 7.07, 7.17 (3 arom. H); 8.61 (*s*, N=CH). ^{13}C-NMR ($CDCl_3$): 17.1 (CH_2Me); 20.8 (2 Me); 57.3 (NCH_2); 128.7, 129.0, 134.9, 137.4 (C_6H_3); 160.9 (N=CH).

N-*[(2,6-Difluorophenyl)methylidene]methanamine* (2,6-$F_2C_6H_3C(H)$=NMe). Prepared from 2,6-difluorobenzaldehyde (*Aldrich*) and $MeNH_2$ according to *GP 1*. ^{1}H-NMR ($CDCl_3$): 3.58 (*s*, Me); 6.91 (*t*, J(H,F)=8.5, 2 arom. H); 7.30 (1, arom. H); 8.48 (*d*, J(H,F)=1.5, N=CH). ^{13}C-NMR ($CDCl_3$): 50.4 (Me); 112.2 (*dd*, J(C,F)=23.3, 2.4, arom. C); 112.2 (*dd*, J(C,F)=18.5, 7.2, arom. C); 114.1 (*t*, J(C,F)=12.9, arom. C); 131.8 (*t*, J(C,F)=10.9, arom. C); 153.6 (*s*, N=CH); 162.1 (*dd*, J(C,F)=256.3, 6.4, arom. C).

N-*{[(2,3,4,5,6-$^2H_5$)Phenyl]methylidene}methanamine* ($C_6D_5C(H)$=NMe). Prepared from 2,3,4,5,6-pentadeuterobenzaldehyde (*Cambridge Isotopes*) and $MeNH_2$ according to *GP 1*. ^{1}H-NMR ($CDCl_3$):

3.52 (*s*, Me); 8.19 (*s*, N=CH). ^{13}C-NMR ($CDCl_3$): 48.6 (Me); 127.9 (1:1:1 *t*, *J*(C,D) = 22.7, arom. C); 128.5 (1:1:1 *t*, *J*(C,D) = 24.1, arom. C); 130.4 (1:1:1 *t*, *J*(C,D) = 24.5, arom. C); 136.5 (*s*, arom. C); 162.8 (N=CH).

N-*{[(2,3,4,5,6-$^2H_5$)Phenyl](*^{2}*H)methylidene}methanamine* ($C_6D_5C(D)$=NMe). Prepared from (D_6)benzaldehyde (*Aldrich*) according to *GP 1*. ^{1}H-NMR ($CDCl_3$): 3.53 (*s*, Me). ^{13}C-NMR ($CDCl_3$): 48.6 (Me); 127.8 (1:1:1 *t*, *J*(C,D) = 24.3, arom. C); 128.5 (1:1:1 *t*, *J*(C,D) = 24.8, arom. C); 130.4 (1:1:1 *t*, *J*(C,D) = 24.5, arom. C); 136.4 (*s*, arom. C); 162.6 (1:1:1 *t*, *J*(C,D) = 24.0, N=CD).

General Procedure (*GP 3*) *for the Reaction of Benzaldimines with CO.* Into a thin-necked glass liner was added [Co($^{13}CH_3C(O)$)$(CO)_3$(P(*o*-tol)$_3$)] (20 mg, 0.04 mmol), benzaldimine (20 equiv.), and (D_8)-1,4-dioxane (2 ml). The mixture was then placed into a 125-ml *Parr* high-pressure reactor, which was sealed and charged with 1000 psi of CO. The reaction was run at 200° (oil-bath temp.) for the indicated amount of time (see *Table 1*). After cooling down and releasing the pressure, the mixture was analyzed by ^{1}H- and ^{13}C-NMR spectroscopy. The formation of the *N*-alkylphthalimidine main product was confirmed by ^{1}H-, ^{13}C- (DEPT135), and HMQC-NMR spectroscopy, as well as by X-ray crystallography in the case of *N*-methylphthalimidine (*Figure*).

N-*Methylphthalimidine* (=*2,3-Dihydro-2-methyl-1*H-*isoindol-1-one*). [Co($^{13}CH_3C(O)$)$(CO)_3$(P(*o*-tol)$_3$)] (20 mg), PhCH=NMe (0.19 g), and (D_8)-1,4-dioxane (2 ml) were reacted as described in *GP 3* at 200° for 7 d. The product mixture was concentrated under vacuum, and the Co species were removed by liq./liq. extraction with H_2O/CH_2Cl_2. The org. phase was evaporated, and crystals were grown from a conc. EtOH solution at −10°. ^{1}H-NMR ($CDCl_3$): 3.20 (*s*, Me); 4.37 (*s*, PhCH_2); 7.34 (*t*, *J* = 7.4, arom. H); 7.49 (*q*, *J* = 7.3, H, 2 arom. H); 7.83 (*d*, *J* = 7.6, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 29.8 (Me); 52.4 (CH_2N); 123.0, 123.9, 128.4, 131.5, 133.3, 141.4 (C_6H_4); 169.0 (C=O).

Reaction of N-*(1-Phenylmethylidene)ethanamine with ^{13}CO.* In a thin-necked glass liner was added [Co($^{13}CH_3C(O)$)$(CO)_3$(P(*o*-tol)$_3$)] (20 mg), PhC(H)=NEt (24 equiv.), and (D_8)-1,4-dioxane (2 ml). The mixture was placed in a 30-ml *Parr* high-pressure reactor, sealed, sequentially cooled (acetone/dry ice, then liq. N_2), and then exposed to *ca.* 300 psi of ^{13}CO. The mixture was warmed to r.t., and then heated at 200° for 48 h. Then, the reactor was cooled down, degassed, and the product mixture was subjected to IR, ^{1}H- and ^{13}C-NMR analyses.

General Procedure (*GP 4*) *for the Reaction of* N-*(1-Phenylmethylidene)alkanamines with CO Catalyzed by [$Co_2(CO)_8$].* In a thin-necked glass liner was added [$Co_2(CO)_8$] (20 mg), the imine (*ca.* 20 equiv.), and C_6D_6 (2 ml). The mixture was placed into a 125-ml *Parr* high-pressure reactor, which was sealed and charged with 1000 psi of CO. The reaction was run at 200° for 6 h. The reactor was cooled down, degassed, and the solvent was evaporated under a stream of air. The products were dissolved in CH_2Cl_2, and the Co species were removed by extraction with 1% aq. HCl (2 × 10 ml). The org. layer was dried (Na_2SO_4) and concentrated under a stream of air. The resulting product was recrystallized from EtOH at −10°, and the crystals were dried under vacuum and then subjected to GC/MS, ^{1}H-NMR, and ^{13}C-NMR analyses.

X-Ray Crystal Structure of N-*Methylphthalimidine* (=*2,3-Dihydro-2-methyl-1*H-*isoindol-1-one*)[2]). A yellow brick-shaped crystal (*ca.* 0.20 × 0.25 × 0.50 mm) of *N*-methylphthalimidine, was used for the X-ray crystallographic analysis. Intensities were recorded at a temp. of 108(2) K (*Rigaku-MSC X-Stream 2000* cooler) on a *Bruker SMART APEX CCD* area-detector system equipped with a graphite monochromator and an MoK_α fine-focus sealed tube (λ = 0.71073 Å) operated at 1600 W (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal. A total of 1,850 frames were collected, with a scan width of 0.3° in ω and an exposure time of 5 s/frame; the total data-collection time was *ca.* 5 h. The frames were integrated with the *Bruker* SAINT software package using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 4,636 reflections to a maximum θ angle of 28.30° (0.90-Å resolution), of which 1,758 were independent (completeness: 96.7%, R_{int} = 0.0216,

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[2]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication number CCDC-612554. Copies of the data can be obtained, free of charge, *via* the internet (http://www.ccdc.cam.ac.uk/data_request/cif), by e-mail (data_request@ccdc.cam.ac.uk), or fax (+44-1223-336033).

$R_{sig}=0.0252$), 1,610 reflections being greater than $2\sigma(I)$. Final cell constants: $a=9.1655(12)$, $b=9.0746(12)$, $c=9.6316(12)$ Å, $\alpha=90$, $\beta=114.445(2)$, $\gamma=90°$; $V=729.28(16)$ Å^3. The data are based on refinement of the *XYZ* centroids of 2,787 reflections $>20\sigma(I)$, with $2.441° < \theta < 28.298°$. Analysis of the data showed negligible decay during data collection. The data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.875721. The structure was solved and refined with the *Bruker* SHELXTL (vers. 6.1) software package, using the space group $P2_1/c$, with $Z=4$ for the formula unit (C_9H_9NO). The final anisotropic full-matrix least-squares refinement on F^2 with 101 variables converged at $R1=4.07\%$ (obs. data) and $wR2=10.71\%$ (all data). The goodness-of-fit was 1.040. The largest peak on the final difference map was 0.301 e$^-$/Å^3, and the largest hole was -0.251 e$^-$/Å^3. Based on the final model, the calculated density of the crystal was 1.340 g/cm^3, and $F(000)$ amounts to 312 electrons.

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