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Novel Structures and Pauson−Khand Activities of N-Heterocyclic Carbene Dicobalt Complexes

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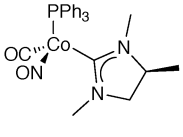
Summary: N-Heterocyclic carbene derivatives of dicobalt octacarbonyl have been synthesized for the first time and tested in the Pauson−Khand reaction. Two complexes with both NHC and PPh$_3$ ligands represent the only examples of structurally characterized dicobalt hexacarbonyl complexes with two different non-CO ligands.

Interest in N-heterocyclic carbene (NHC) ligands has continued to grow given the beneficial effects they often have on homogeneous catalysis.[1] As a result of their electronic properties, NHCs have been considered as alternatives to phosphines, and substitution of a phosphine ligand with an NHC can lead to dramatic increases in catalytic activity and stability.[1c−f,2] Our interest in the Pauson−Khand reaction (PKR), the cyclization of an alkyne, alkene, and carbon monoxide to form a cyclopentenone,[3] and, in particular, in the use of (PPh$_3$)Co$_2$(CO)$_7$ as a PKR catalyst,[4] led us to question whether NHC derivatives of dicobalt octacarbonyl could be synthesized and whether these complexes would promote the PKR. Success in this endeavor would pave the way to new approaches to the catalytic asymmetric PKR.

Cobalt complexes containing NHC ligands have been known for some time. The earliest examples were reported by Lappert[5] and are tetrahedral Co(−1) complexes with one or two NHC ligands. A representative example, **1**,[5b,c] was characterized by single-crystal structure analysis, although the locations of the NO and CO ligands could not be distinguished. Later examples[6] include a number of cyclopentadienyl derivatives ranging from complex **2**,[6a] a Co(I) precursor to Co(III) and paramagnetic Co(II) cyclopentadienyl NHC complexes, to complex **3**,[6d] where the NHC unexpectedly displaced the tethered phosphine rather than the ethene ligand. Finally, Fehlhammer[7] has looked at synthesizing NHCs directly from cyano Co complexes[7a] and has also coordinated triscarbene versions of the well-known hydrotris(pyrazolyl)borate ligand to Co(III) to make hexacarbene complexes (**4**).[7b] To the best of our knowledge, however, there are no examples of dicobalt NHC complexes.



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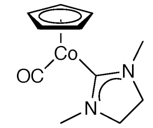

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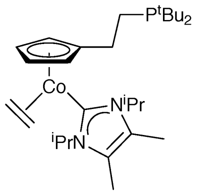

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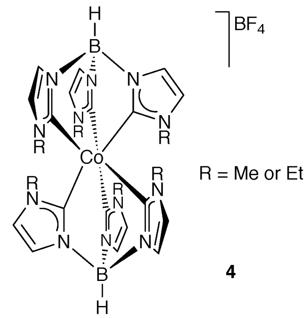

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Generation of the free carbene in situ from imidazolium salt **5**, followed by addition of Co$_2$(CO)$_8$, gave complex **6** based on spectroscopic data (eq 1). All attempts to crystallize the air- and moisture-sensitive complex led to decomposition. The strong electron-donating properties of NHCs often give their metal complexes increased stability,[1b−f] but we unexpectedly

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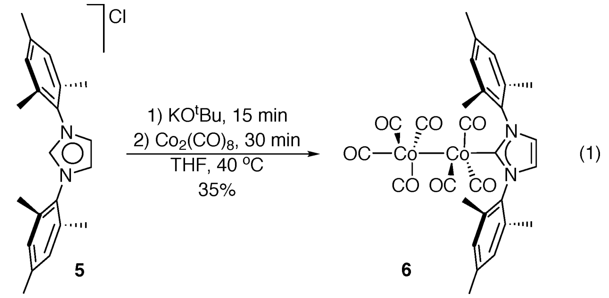
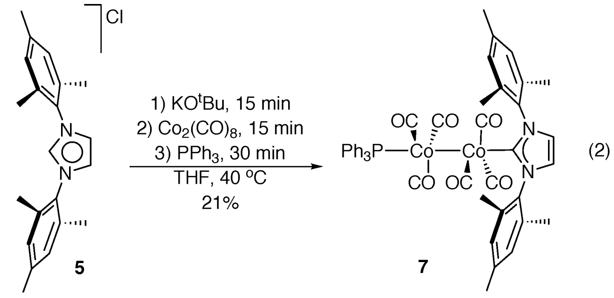
found **6** to be less stable than its triphenylphosphine analogue, $(PPh_3)Co_2(CO)_7$.



(1)

We next looked at the possibility of introducing a PPh_3 ligand into the dicobalt NHC system to see if this would lead to a complex with improved stability. Simple modification of the procedure used to synthesize **6** gave complex **7** (eq 2), which we were pleased to find could be crystallized and analyzed by X-ray diffraction (Figure 1).[8] It should also be stated that the same product is formed if $(PPh_3)Co_2(CO)_7$ is added as the Co source to the carbene solution.



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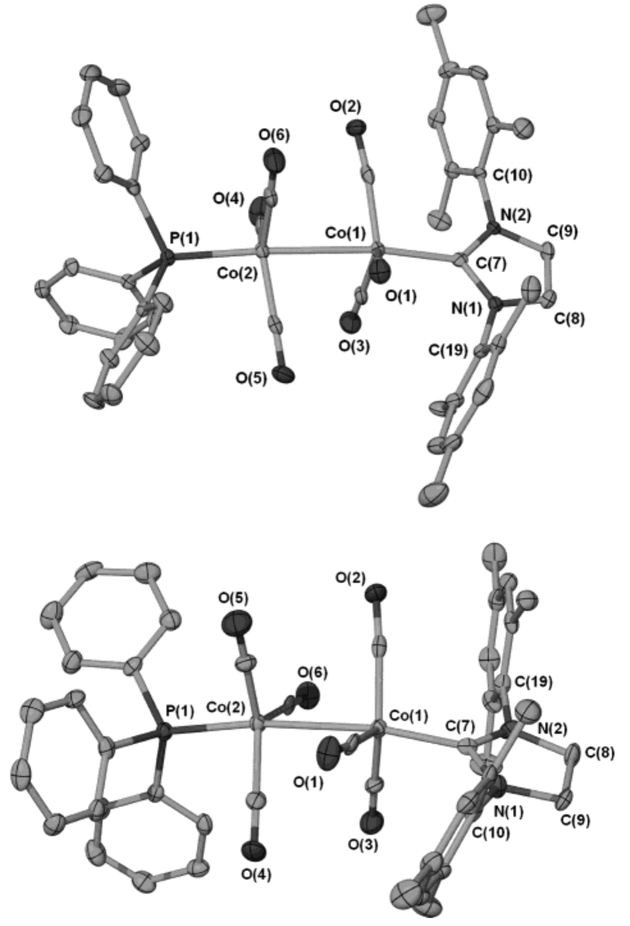

Figure 1. Molecular structures of **7** (top) and **9** (bottom). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 7 and 9

	7	**9**
Co(1)−Co(2)	2.6819(5)	2.6856(9)
Co(1)−C(7)	1.944(3)	1.941(5)
Co(2)−P(1)	2.1832(9)	2.1876(15)
C(8)−C(9)	1.341(4)	1.525(7)
C(7)−Co(1)−Co(2)	171.78(9)	167.35(15)
Co(1)−Co(2)−P(1)	175.20(3)	171.81(5)

The NHC and PPh_3 ligands occupy transoid positions in complex **7**, as was found for other dicobalt complexes containing two identical phosphine[9] or arsine[10] ligands. Interestingly, there is only one other report[11] of a dicobalt hexacarbonyl complex with two different non-CO ligands, and this species was not crystallographically characterized. The length of the Co−NHC carbon bond for Co(0) complex **7** (1.944(3) Å, Table 1) falls between the Co−NHC bond length reported for a Co(−1) NHC complex (1.974(15) Å)[5b,c] and the bond lengths reported for Co(I), Co (II), and Co(III) NHC complexes (1.888(3)−1.929(8) Å).[6a,b,d] The only exception is the hexacarbene Co(III) complex **4**,[7b] in which the Co−NHC bond lengths range from 1.943(4) to 1.959(5) Å. In this case, the fact that the high trans effect NHC ligands are trans to one another provides an explanation for the longer bond lengths. Except for one case,[9f] the C(7)−Co(1)−Co(2) and Co(1)−Co(2)−P(1) angles are smaller than previous reports. The Co−Co and Co−P bond lengths are, however, similar to those of other $Co_2(CO)_6(phosphine)_2$ complexes.[9]

We were also interested in synthesizing the analogue of complex **7** with a saturated NHC backbone, as use of

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(8) Crystal data: **7**: $C_{45}H_{39}Co_2N_2O_6P$, $M = 852.61$, red block ($0.40 \times 0.35 \times 0.20$ mm), monoclinic, space group $P2_1/c$ (No. 14), $a = 10.3815(3)$ Å, $b = 23.4351(7)$ Å, $c = 17.6562(6)$ Å, $\beta = 105.2150(10)°$, $V = 4145.0(2)$ Å^3, $Z = 4$, $D_c = 1.366$ g/cm^3, $F_{000} = 1760$, Nonius KappaCCD, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 55.0°$, 10 402 reflections collected, 6805 unique ($R_{int} = 0.0588$). Final GooF = 1.076, R1 = 0.0507, wR2 = 0.0813, R indices based on 4923 reflections with $I > 2\sigma(I)$ (refinement on F^2), 512 parameters, 0 restraints. *Lp* and absorption corrections applied, $\mu = 0.888$ mm^{-1}. **9**: $C_{45}H_{41}Co_2N_2O_6P$, $M = 854.63$, red block ($0.60 \times 0.30 \times 0.25$ mm), triclinic, space group $P\bar{1}$ (No. 2), $a = 9.2002(4)$ Å, $b = 12.6209(6)$ Å, $c = 18.5026(10)$ Å, $\alpha = 89.283(2)°$, $\beta = 85.545(2)°$, $\gamma = 74.202(2)°$, $V = 2060.95(17)$ Å^3, $Z = 2$, $D_c = 1.377$ g/cm^3, $F_{000} = 884$, Nonius KappaCCD, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 50.0°$, 11 979 reflections collected, 7191 unique ($R_{int} = 0.1026$). Final GooF = 1.136, R1 = 0.0722, wR2 = 0.1324, R indices based on 4818 reflections with $I > 2\sigma(I)$ (refinement on F^2), 512 parameters, 0 restraints. *Lp* and absorption corrections applied, $\mu = 0.894$ mm^{-1}.

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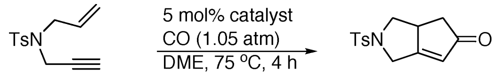
Table 2. PKR Employing Dicobalt Carbonyl Complexes

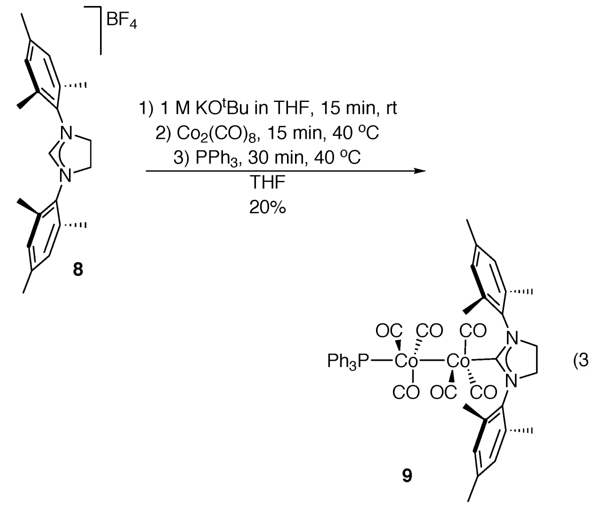


10 **11**

entry	catalyst	^{1}H NMR yield (%)[a]
1	**6**	73
2	**7**	40
3	**9**	49, 68
4	$(PPh_3)Co_2(CO)_7$	97,[4b] 96
5	$Co_2(CO)_8$	86, 87

[a] Isolated yields were recorded in five examples and were typically 12% below the ^{1}H NMR yield.

an NHC ligand with a saturated rather than an unsaturated backbone can give catalysts with improved activity.[2a,12] Modification[12a,13] of the procedure used to make **7** gave complex **9** with a nearly identical yield (eq 3). Crystals of **9** suitable for X-ray analysis could also be obtained (Figure 1).[8] The C(7)−Co(1)−Co(2) and Co(1)−Co(2)−P(1) angles found for **9** are even smaller than those found for **7**, and this bent geometry can be seen in Figure 1. Other bond lengths and angles are comparable to **7** with the obvious exception of the NHC backbone. Attempts to synthesize the saturated NHC analogue of **6** always gave a product too unstable to fully characterize.



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9

(3)

We next examined the activity of complexes **6**, **7**, and **9** in the PKR using a standard PKR substrate and our optimized reaction conditions for $(PPh_3)Co_2(CO)_7$.[4b] As these were the first attempts to catalyze a PKR using an NHC complex, we were pleased to note that all three complexes gave rise to catalytic activity (Table 2). It is interesting to compare the activity of complexes **6**, **7**, and **9** with the activities of $(PPh_3)Co_2(CO)_7$ and $Co_2(CO)_8$. In our experience, $Co_2(CO)_8$ and $(PPh_3)Co_2(CO)_7$ exhibit very similar levels of activity with intramolecular substrates such as **10**,[4b] although the triphenylphosphine derivative is a more practical precatalyst as it does not suffer from the instability and purification problems associated with $Co_2(CO)_8$.[14] Because of this, and because of the deactivating effect associated with phosphine substitution in stoichiometric PKRs,[15] we postulate that both precatalysts lead to the same active species, i.e. the phosphine-free carbonylcobalt(0) complex, $Co_2(CO)_7$. Turning to the NHC complexes, their slightly increased tendency to decompose may be responsible for their reduced activity. It is also possible, however, that the lower activity observed for these three complexes may be associated with persistent bonding between the NHC and the carbonylcobalt(0), i.e., that all three precatalysts lead to a catalytically active phosphine-free (NHC)carbonylcobalt(0) species, (NHC)-$Co_2(CO)_6$. This hypothesis is consistent with the accepted stronger bonding of NHCs to metals compared with phosphines[1c−f] and with the reduced activity associated with electron-donating species, which increase back-bonding to the carbonyl ligands, thereby hindering the creation of vacant coordination sites necessary for the catalytic cycle to proceed.[15b] If NHCs do indeed remain firmly bound to the catalytically active species in the PKR, then carefully designed NHC ligands may well provide a new entry into asymmetric catalytic versions of this attractive carbon−carbon bond-forming reaction.

Experimental Section

General Procedures. Syntheses were carried out under an atmosphere of nitrogen or argon in oven-dried glassware using standard Schlenk techniques. THF and 1,2-dimethoxyethane (DME) were distilled from sodium benzophenone ketyl. Dicobalt octacarbonyl and the imidazolium salts **5** and **8** were purchased from Strem Chemicals. The 1 M KO^{t}Bu in THF solution used in the synthesis of **9** was purchased from Aldrich. PKR substrate **10** was prepared according to literature procedures.[16] All other reagents are commercially available and were used as received. NMR spectra were recorded at room temperature on Bruker Avance 360, Bruker Avance 400, or Bruker DRX 500 instruments and referenced to residual undeuterated solvent (δ in ppm, J in Hz). Melting points were recorded in open capillaries on a Büchi 510 melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Mass spectra were recorded by the University of London School of Pharmacy Mass Spectrometry Facility on VG ZAB-SE or VG70-SE instruments. Elemental analyses were performed by the London Metropolitan University microanalytical service.

Synthesis of 6. In a Schlenk flask, 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride **5** (400 mg, 1.18 mmol) was suspended in anhydrous THF (5 mL) and kept under agitation at 40 °C for 15 min. KO^{t}Bu (95%, 150 mg, 1.26 mmol) was added, and stirring continued an additional 15 min. Dicobalt octacarbonyl (404 mg, 1.18 mmol) was added, and stirring continued in the dark at 40 °C for 30 min. The flask was allowed to cool, and neutral alumina (Grade II) was added before removing the solvent in vacuo. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane to remove unreacted dicobalt octacarbonyl and then with hexane−diethyl ether (8:2) to

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collect the title compound as a dark brown solid (255 mg, 35%). Mp: 170−172 °C (dec). IR ($CHCl_3$, cm^{-1}): ν_{CO} 2074 (m), 2022 (sh), 1988 (s), 1937 (m). ^1H NMR (500 MHz, THF-d_8): δ 2.14 (s, 12H, o-CH_3), 2.35 (s, 6H, p-CH_3), 7.08 (s, 4H, ArH), 7.48 (brs, 2H, NCHCHN). ^{13}C NMR (125 MHz, THF-d_8): δ 18.1 (o-CH_3), 21.0 (p-CH_3), 126.8 (NCHCHN), 130.1 (C_{meta}), 136.5 (C_{ortho}), 137.4 (C_{para}), 140.3 (C_{ipso}), 175.8 (NCN), 205.8 ($C\equiv O$). MS FAB: m/z (%) 618 (M^+, 1), 450 ($M^+ - 6CO$, 2), 422 ($M^+ - 7CO$, 2), 305 ($(C_9H_{11})_2C_3N_2H_3^+$, 100).

Synthesis of 7. In a Schlenk flask, 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, **5** (400 mg, 1.18 mmol), was suspended in anhydrous THF (10 mL) and kept under agitation at 40 °C for 15 min. KO^tBu (95%, 150 mg, 1.26 mmol) was added, and stirring continued an additional 15 min. After adding dicobalt octacarbonyl (404 mg, 1.18 mmol) and stirring in the dark at 40 °C for 15 min, triphenylphosphine (310 mg, 1.18 mmol) was added and stirring continued in the dark at 40 °C for an additional 30 min. The flask was allowed to cool, and neutral alumina (Grade II) was added before removing the solvent in vacuo. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane to remove unreacted dicobalt octacarbonyl and then with hexane−diethyl ether (7:3) to collect the title compound as a dark brown solid (211 mg, 21%). Analytically pure **7** suitable for a single-crystal structure determination was obtained by slow diffusion of pentane into a solution of **7** in THF at −20 °C. Mp: 160−165 °C (dec). IR ($CHCl_3$, cm^{-1}): ν_{CO} 1969 (sh), 1949 (s), 1922 (sh). ^1H NMR (400 MHz, THF-d_8): δ 2.11 (s, 12H, o-CH_3), 2.29 (s, 6H, p-CH_3), 7.01 (s, 4H, ArH), 7.35−7.63 (m, 17H, NCHCHN and ArH). ^{13}C NMR (100 MHz, THF-d_8): δ 17.8 (o-CH_3), 20.6 (p-CH_3), 125.5 (NCHCHN), 128.5 (d, $^3J_{CP} = 10$ Hz, PC_{meta}), 129.3 (C_{meta}), 130.3 (d, $^4J_{CP} = 2$ Hz, PC_{para}), 133.4 (d, $^2J_{CP} = 11$ Hz, PC_{ortho}), 135.7 (d, $^1J_{CP} = 44$ Hz, PC_{ipso}), 136.3 (C_{ortho}), 137.5 (C_{para}), 139.1 (C_{ipso}), 181.3 (NCN), 203.4 ($C\equiv O$). ^{31}P NMR (162 MHz, THF-d_8): δ 66.8 ($CoPPh_3$). MS FAB: m/z (%) 852 (M^+, 3), 712 ($M^+ - 5CO$, 9), 684 ($M^+ - 6CO$, 11), 305 ($(C_9H_{11})_2C_3N_2H_3^+$, 100). Anal. Calcd for $C_{45}H_{39}Co_2N_2O_6P$ (852.61): C, 63.39; H, 4.61; N, 3.29. Found: C, 63.43; H, 4.54; N, 3.24.

Synthesis of 9. In a Schlenk flask, 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolium tetrafluoroborate, **8** (300 mg, 0.76 mmol), was suspended in anhydrous THF (7 mL) and kept under agitation at room temperature for 15 min. KO^tBu (0.76 mmol, 1 M in THF) was added, and stirring continued an additional 15 min. Dicobalt octacarbonyl (260 mg, 0.76 mmol) was added, and the Schlenk flask was placed in a 40 °C oil bath. After stirring in the dark for 15 min, triphenylphosphine (200 mg, 0.76 mmol) was added and stirring continued in the dark for an additional 30 min. The flask was allowed to cool, and neutral alumina (Grade II) was added before removing the solvent in vacuo. The brown solid was charged onto a chromatography column of silica and eluted under nitrogen first with hexane to remove unreacted dicobalt octacarbonyl(0) and with hexane−diethyl ether (6:4) to collect the title compound as a dark brown solid (128 mg, 20%). Analytically pure **9** suitable for a single-crystal structure determination was obtained by slow diffusion of pentane into a solution of **9** in THF at −20 °C. Mp: 150−155 °C (dec). IR ($CHCl_3$, cm^{-1}): ν_{CO} 1969 (sh), 1949 (s), 1922 (sh). ^1H NMR (500 MHz, THF-d_8): δ 2.27 (s, 6H, p-CH_3), 2.37 (s, 12H, o-CH_3), 3.92 (s, 4H, NCH_2CH_2N), 6.94 (s, 4H, ArH), 7.2−7.5 (m, 15H, ArH). ^{13}C NMR (125 MHz, THF-d_8): δ 18.4 (o-CH_3), 21.1 (p-CH_3), 52.2 (NCH_2CH_2N), 129.0 (d, $^3J_{CP} = 10$ Hz, PC_{meta}), 130.1 (C_{meta}), 130.7 (PC_{para}), 133.9 (d, $^2J_{CP} = 11$ Hz, PC_{ortho}), 136.2 (d, $^1J_{CP} = 45$ Hz, PC_{ipso}), 137.6 (C_{ortho}), 138.5 (C_{para}), 138.6 (C_{ipso}), 203.9 ($C\equiv O$), 214.1 (NCN). ^{31}P NMR (162 MHz, THF-d_8): δ 67.0 ($CoPPh_3$). MS FAB: m/z (%) 686 ($M^+ - 6CO$, 2), 627 ($M^+ - 6CO - Co$, 6), 321 ($CoPPh_3^+$, 37), 307 ($(C_9H_{11})_2C_3N_2H_5^+$, 100). Anal. Calcd for $C_{45}H_{41}Co_2N_2O_6P$ (854.63): C, 63.24; H, 4.84; N, 3.28. Found: C, 63.32; H, 4.96; N, 3.16.

Typical PKR Procedure.[4b] Enyne **10** (125 mg, 0.5 mmol) and catalyst **9** (21.4 mg, 0.025 mmol) were dissolved at room temperature in CO-saturated DME (5 mL) under a carbon monoxide atmosphere (1.05 atm). The mixture was heated at 75 °C with vigorous stirring in the dark for 4 h. The resulting brown mixture was cooled, filtered through a short pad of Celite, and concentrated in vacuo. (^1H NMR spectroscopy at this stage revealed a 49% conversion.) Purification of the residue by flash column chromatography (SiO_2; hexane−EtOAc, 6:4) gave the known product **11**[17] as a white solid (51.1 mg, 37%). Mp: 147−149 °C (lit.[17a] 145−148 °C). IR ($CHCl_3$, cm^{-1}): $\nu_{C=O}$ 1714 (s), $\nu_{C=C}$ 1651 (m), $\nu_{C-C(Ar)}$ 1599 (w), ν_{NSO2} 1351, 1162 (s). ^1H NMR (360 MHz, $CDCl_3$): δ 2.06 (dd, 1H, $^3J_{HH} = 4$ Hz, $^2J_{HH} = 18$ Hz, CHHCO), 2.44 (s, 3H, CH_3), 2.56−2.64 (m, 2H, CHHCO and NCHHC=), 3.11−3.19 (m, 1H, CHCH$_2$CO), 4.00−4.05 (m, 2H, NCHHC= and NCHHCH), 4.34 (d, 1H, $^2J_{HH} = 17$ Hz, NCHHCH), 5.99 (s, 1H, C=CH), 7.35 (d, 2H, $^3J_{HH} = 8$ Hz, m-ArH), 7.73 (d, 2H, $^3J_{HH} = 8$ Hz, o-ArH). ^{13}C NMR (90 MHz, $CDCl_3$): δ 21.7 (CH_3), 39.9 (CH$_2$CO), 44.1 (CHCH$_2$CO), 47.8 (NCH$_2$CH), 52.6 (NCH$_2$C=), 126.3 (C=CH), 127.6 (C_{ortho}), 130.2 (C_{meta}), 133.6 (C_{para}), 144.3 (C_{ipso}), 178.9 (C=CH), 207.6 (C=O).

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Supporting Information Available: Crystallographic details for **7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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