

Reactions of vinylidene and allenylidene cymantrene derivatives with isonitriles

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Abstract

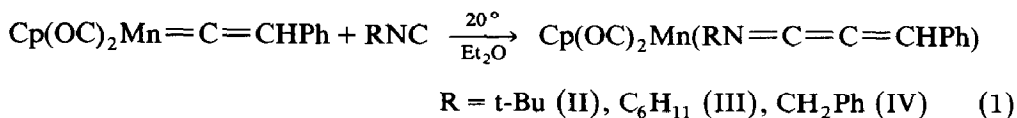
Isocyanides (RNC) insert into the M=C bond in $\text{Cp}(\text{OC})_2\text{Mn}=\text{C}=\text{CHPh}$ (I), to give the intermediates $\text{Cp}(\text{OC})_2\text{Mn}(\text{RN}=\text{C}=\text{C}=\text{CHPh})$, R = t-Bu (II), C_6H_{11} (III), CH_2Ph (IV). The reaction of II–IV with H_2O gives $\text{Cp}(\text{OC})_2\text{Mn}[\pi\text{-cis-Ph(H)C}=\text{C(H)C(O)NHR}]$, R = t-Bu (V), C_6H_{11} (VI), CH_2Ph (VII). Reaction of III with Et_2NH forms $\text{Cp}(\text{OC})_2\text{Mn}[\pi\text{-Ph(H)C}=\text{C}=\text{C(NEt}_2\text{)NHC}_6\text{H}_{11}]$, which upon reaction with H_2O yields VI. The possibility of eliminating π -olefin ligands from V or VII by reaction with n-donors (Py, PPh_3) is shown. Reaction of $\text{Cp}(\text{OC})_2\text{Mn}=\text{C}=\text{C}=\text{CPh}_2$ (VIII) with t-BuNC gives $\text{Cp}(\text{OC})_2\text{Mn}[\pi\text{-Ph}_2\text{C}=\text{C}=\text{CHC(O)NH-t-Bu}]$ (IX).

Introduction

The products of insertion of isocyanides into M=C bond in Fischer carbene complexes have found use as synthons in organometallic and organic synthesis in order to make different carbene complexes and N-containing heterocycles [1]. Fischer carbene complexes of cymantrene react with isocyanides to give n-donor complexes [2,3]. However the reactions of vinylidene and allenylidene complexes with isocyanides have not been investigated. We report here on our studies of the reactivity of the vinylidene and allenylidene cymantrene complexes $\text{Cp}(\text{OC})_2\text{Mn}=\text{C}=\text{CHPh}$ (I) and $\text{Cp}(\text{OC})_2\text{Mn}=\text{C}=\text{C}=\text{CPh}_2$ (VIII) in reactions with isocyanides with primary, secondary, and tertiary carbon substituents.

Results and discussion

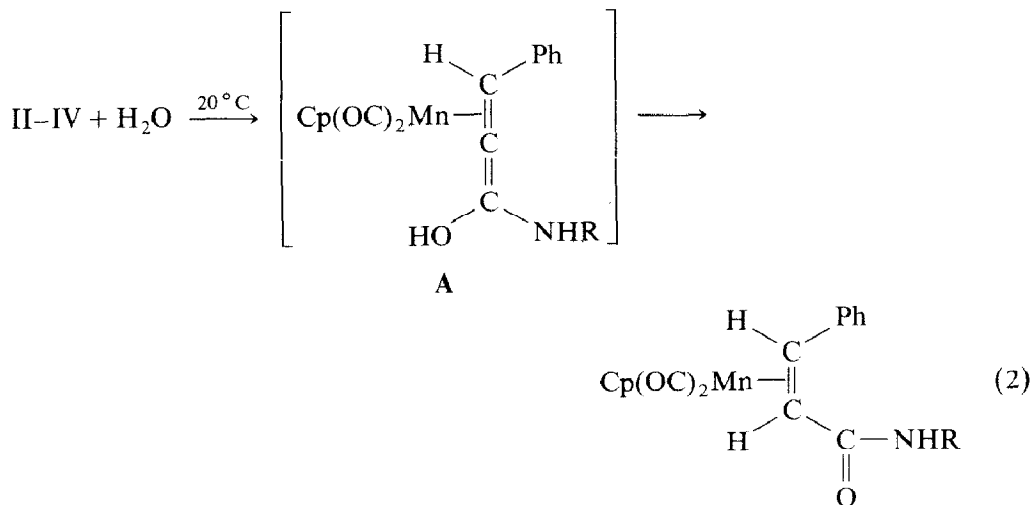
We have found that I reacts with RNC, to give products of the insertion of isonitriles into the M=C bond:



The keteneimine complexes II–IV were not isolated because of their high reactivity; they were characterized only from IR spectra showing $\nu(\text{C}\equiv\text{O})$ bands at ~ 1945 and $\sim 1895\text{ cm}^{-1}$.

Complexes II–IV react with water under mild conditions (chromatography in the presence of traces of moisture) to give the π -olefin derivatives V–VII containing the secondary amides of *cis*-cinnamic acid as ligands.

It was suggested that the addition of H_2O to the keteneimine ligand proceeds via intermediate A, which undergoes light rearrangement to the complexes V–VII:



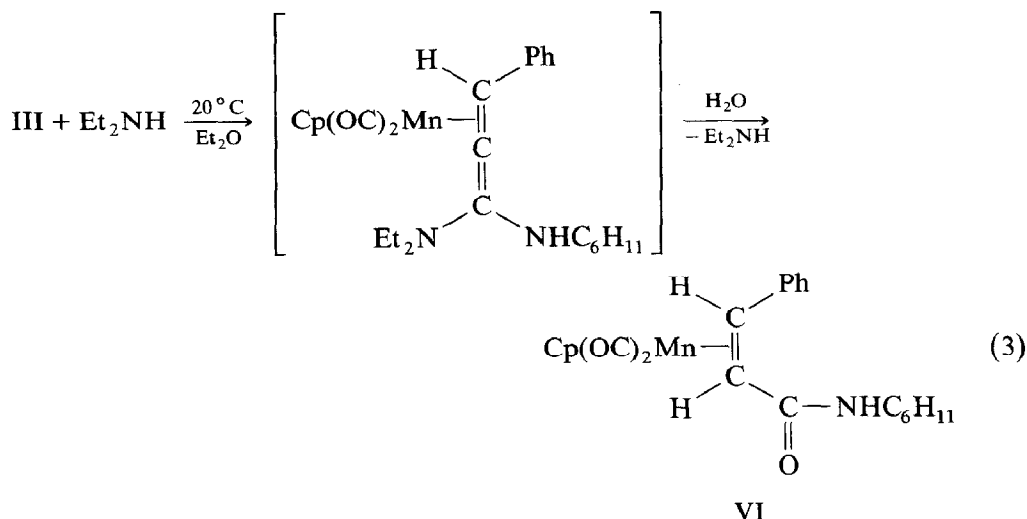
$\text{R} = t\text{-Bu (V)}, \text{C}_6\text{H}_{11} \text{ (VI)}, \text{CH}_2\text{Ph (VII)}$

Complexes V–VII were characterized by IR, ^1H NMR and mass spectroscopy. The IR spectra of V–VII show $\nu(\text{C}\equiv\text{O})$ bands at ~ 1990 and $\sim 1930\text{ cm}^{-1}$ and characteristic amide bands at ~ 1650 and $\sim 1590\text{ cm}^{-1}$. The ^1H NMR spectra containing two doublets of the olefin protons at δ 3.08–3.28 and 4.15–4.31 ppm with $^3J(\text{H,H}) \sim 10.3\text{ Hz}$ which points to a *cis*-configuration and the signals of the protons of the NH, Ph, Cp and corresponding alkyl groups.

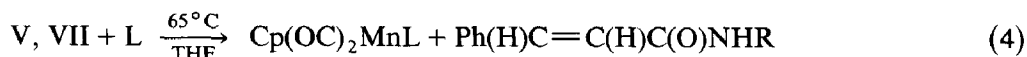
It is known [4–6] that the complexes $\text{L}_n\text{M}(\text{RN}=\text{C}=\text{C}(\text{X})\text{R})$ with n coordination of keteneimine ligands add nucleophiles NuH ($\text{Nu} = \text{OR}, \text{OH}, \text{NR}_2, \text{SR}$) to give the aminocarbene complexes $\text{L}_n\text{M}=\text{C}(\text{NHR})\text{C}(\text{X})(\text{R})\text{Nu}$. Formation of V–VII in the case of reactions of II–IV with H_2O may indirectly confirm the π -coordination of keteneimine ligands in these complexes.

It is noteworthy, that yields of V–VII fall in the order $t\text{-BuNC} > \text{C}_6\text{H}_{11}\text{NC} > \text{PhCH}_2\text{NC}$, which may have resulted in the decrease in the donor properties of the isonitrile carbon substituent.

It was of interest to investigate the action of nucleophiles (NuH) towards the complexes $\text{Cp}(\text{OC})_2\text{Mn}(\text{RN}=\text{C}=\text{C}=\text{CHPh})$. In order to elucidate this, the reaction of Et_2NH with $\text{Cp}(\text{OC})_2\text{Mn}(\text{C}_6\text{H}_{11}\text{N}=\text{C}=\text{C}=\text{CHPh})$ (III) was investigated. The reaction of III with Et_2NH usually proceeds via an allene intermediate, which is then hydrolysed to VI:



The insertion of isonitriles into $\text{M}=\text{C}$ bond of vinylidene complexes shows a general trend. Thus, the reactions of various vinylidene complexes and isonitrile give the secondary amides of unsaturated acids viz. $\text{R}^1\text{R}^2\text{C}=\text{CHC}(\text{O})\text{NHR}^3$, which are usually not readily accessible. We have found that the reaction of n -donors (Py , PPh_3) with V or VII results in the elimination of the π -olefin ligand. Furthermore, the $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NH-t-Bu}$ obtained by substitution is a mixture of *cis*- and *trans*-cinnamic acid amides in $\sim 1:1$ ratio in contrast to *cis*- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NHCH}_2\text{Ph}$:



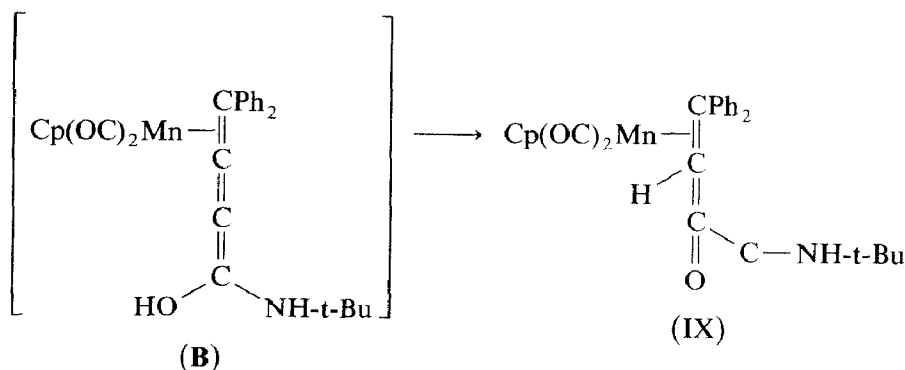
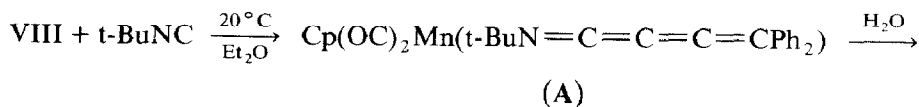
$\text{L} = \text{Py}$, PPh_3 , $\text{R} = \text{t-Bu}$, CH_2Ph

The ^1H MNR spectrum of *cis*- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NH-t-Bu}$ shows two doublets of olefin protons at 6.00 and 6.62 ppm ($^3J(\text{H},\text{H}) = 12.5$ Hz) since in the ^1H NMR spectrum of *trans*- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NH-t-Bu}$ the analogous doublet signals appear at 6.60 and 7.59 ppm ($^3J(\text{H},\text{H}) = 15.7$ Hz).

Prolonged exposure of isomeric cinnamic acid amides to sunlight or heating to 80°C has no effect on the isomeric ratio. The isomerisation of the ligand in V probably proceeds during its replacement by n -donors on heating.

Because the Fischer carbene complexes and vinylidene complexes show differing reactivity towards isonitriles we decided to study the reaction of isonitriles with unsaturated carbene complexes having more than two carbon atoms in the cumulene chain.

We studied the reactions of $\text{Cp(OC)}_2\text{Mn}=\text{C}=\text{C}=\text{CPh}_2$ (VIII) with t-BuNC , $\text{C}_6\text{H}_{11}\text{NC}$, and PhCH_2NC and found that VIII reacts with t-BuNC much more slowly than I, and scarcely reacts with $\text{C}_6\text{H}_{11}\text{NC}$ or PhCH_2NC . Reactions of VIII with t-BuNC also proceeds via the product (A) of insertion into the $\text{M}=\text{C}$ bond. A then reacts with H_2O to give the complex IX. Reaction of A with H_2O probably proceeds via the π -butatriene intermediate B:



Complex IX was characterized from its IR, mass and ^1H NMR spectra. The IR spectrum of IX shows $\nu(\text{C}=\text{O})$ bands at 2000 and 1940 cm^{-1} and characteristic amide bands at 1675 and 1600 cm^{-1} . The ^1H NMR spectrum shows signals of the protons of the allenic structure at 6.89 ppm and the signals from the protons of the NH, t-Bu, Cp, and Ph groups.

Experimental

All reactions were performed under argon, in argon-saturated, absolute solvents. Photochemical reactions were performed in a quartz Schlenk vessel in a water jacket under a PRK-7 mercury-quartz lamp (1000 W). Al_2O_3 (Brockmann II, Reanal, Hungary) and SiO_2 L 100/160 μ (Chemapol, Czechoslovakia) were used for the chromatography. Silufol (Czechoslovakia) thin-layer chromatography plates were also used. t-BuNC, $\text{C}_6\text{H}_{11}\text{NC}$, PhCH_2NC were prepared by published procedures [7], as were I and VIII [8,9]. IR spectra were recorded with a UR-20 Zeiss instrument, mass spectra were recorded with an MX-1303 mass spectrometer, and the ^1H NMR spectra were recorded with a Bruker WP 200 SY spectrometer (200.13 MHz).

Preparation of II and V

t-BuNC (0.083 g, 1.00 mmol) was added to a solution of I (0.278 g, 1 mmol) in 30 ml of absolute ether. The mixture was stirred for 15 min at 20°C (until disappearance of starting complex, monitored by TLC). The IR spectrum of the reaction mixture shows $\nu(\text{C}=\text{O})$ bands II at 1945, 1890 cm^{-1} (CH_2Cl_2). To the solution was added 0.02 ml (1 mmol) H_2O and the mixture was stirred for 3 h. The solvent was removed in vacuo, the residue was chromatographed on SiO_2 . A yellow band was eluted with ether/ CH_2Cl_2 (2/1). The solvent was removed in vacuo and the residue was recrystallized from hexane/ CH_2Cl_2 (1/1) to give 0.3 g (79%) of V as yellow crystals, m.p. 89–90°C. Found: C, 63.29; H, 6.33; N, 4.03; Mn, 14.08. $\text{C}_{21}\text{H}_{22}\text{NO}_3\text{Mn}$ calc.: C, 63.62; H, 5.80; N, 3.70; Mn, 14.51%. Mass spectrum (m/z): 204 $[\text{CpMn}(\text{CO})_3]^+$, 203 $[\text{L}]^+$, 176 $[\text{CpMn}(\text{CO})_2]^+$, 148 $[\text{CpMn}(\text{CO})]^+$, 146 $[\text{L}-\text{t-Bu}]^+$, 131 $[\text{L}-\text{NH-t-Bu}]^+$, 120 $[\text{CpMn}]^+$, 103 $[\text{L}-\text{C}(\text{O})\text{NH-t-Bu}]^+$, 77 $[\text{Ph}]^+$, 65 $[\text{Cp}]^+$, 57 $[\text{t-Bu}]^+$, 55 $[\text{Mn}]^+$. IR spectrum: $\nu(\text{C}=\text{O})$ 1990, 1930; $\nu(\text{C}=\text{O})$ 1650;

$\delta(\text{NH})$ 1590; $\nu(\text{C}=\text{C})$ 1440 cm^{-1} . ^1H NMR spectrum ($\text{THF}-d_8$, δ , ppm): 1.50 (s, 9 H, t-Bu), 3.28 (d, 1 H, $=\text{CHC}(\text{O})$, $^3J(\text{H},\text{H}) = 10.3$ Hz), 4.31 (d, 1 H, $=\text{CHPh}$), 3.64 (s, br., 1 H, NH), 4.66 (s, 5 H, Cp), 7.13–7.93 (m, 5 H, Ph).

Preparation of III and VI

$\text{C}_6\text{H}_{11}\text{NC}$ (0.109 g, 1.00 mmol) was added to a solution of I (0.278 g, 1 mmol) in 30 ml of absolute ether. The mixture was stirred for 30 min at 20 °C (until disappearance of starting complex, monitored by TLC). The IR spectrum of the reaction mixture shows $\nu(\text{C}\equiv\text{O})$ bands III at 1948, 1892 cm^{-1} (CH_2Cl_2). To the solution was added 0.02 ml (1 mmol) H_2O and the mixture was stirred for 4 h. The solvent was removed in vacuo, the residue was chromatographed on SiO_2 . A yellow zone was eluted with ether/ CH_2Cl_2 (2/1). The solvent was removed in vacuo and residue was recrystallized from hexane/ CH_2Cl_2 (1/1) to give 0.28 g (69%) of VI as yellow crystals, m.p. 114–115 °C. Found: C, 65.09; H, 5.91; N, 3.55; Mn, 13.42. $\text{C}_{23}\text{H}_{24}\text{NO}_3\text{Mn}$ calc.: C, 65.18; H, 5.92; N, 3.45; Mn, 13.58%. Mass spectrum (m/z): 349 [$M^+ - 2\text{CO}$], 307 [$M^+ - 2\text{CO}$, $\text{NHC}_6\text{H}_{11}$], 229 [L^+], 204 [$\text{CpMn}(\text{CO})_3^+$], 148 [$\text{CpMn}(\text{CO})^+$], 120 [CpMn^+], 103 [$L^+ - \text{C}(\text{O}) - \text{NHC}_6\text{H}_{11}$], 77 [Ph^+], 65 [Cp^+], 55 [Mn^+]. IR spectrum (KBr pellets): $\nu(\text{C}\equiv\text{O})$ 1985, 1928; $\nu(\text{C}=\text{O})$ 1650; $\delta(\text{NH})$ 1590; $\nu(\text{C}=\text{C})$ 1440 cm^{-1} . ^1H NMR spectrum ($\text{THF}-d_8$, δ , ppm): 1.50–2.1 (m, 11 H, $=\text{C}_6\text{H}_{11}$), 3.08 (d, 1 H, $=\text{CHC}(\text{O})$, $^3J(\text{H},\text{H}) = 10.3$ Hz), 4.15 (d, 1 H, $=\text{CHPh}$), 3.30 (s, br., 1 H, NH), 4.48 (s, 5 H, Cp), 6.95–7.95 (m, 5 H, Ph).

Preparation of IV and VII

PhCH_2NC (0.117 g, 1.00 mmol) was added to a solution of I (0.278 g, 1 mmol) in 30 ml of absolute ether. The mixture was stirred for 1 h (until disappearance of starting complex, monitored by TLC). IR spectrum of the reaction mixture shows $\nu(\text{C}\equiv\text{O})$ bands IV at 1950, 1895 cm^{-1} . To the solution was added 0.02 ml H_2O and the mixture was stirred for 8 h. The solvent was removed in vacuo, and the residue was chromatographed on SiO_2 . A yellow band was eluted with ether/ CH_2Cl_2 (3/1). The solvent was removed in vacuo and residue was recrystallized from hexane/ CH_2Cl_2 (1/1) to give 0.25 g (60.5%) of VII as yellow crystals, m.p. 109–110 °C. Found: C, 66.66; H, 4.75; N, 3.39; Mn, 13.34. $\text{C}_{23}\text{H}_{20}\text{NO}_3\text{Mn}$ calc.: C, 66.82; H, 4.84; N, 4.14; Mn, 13.32%. Mass spectrum (m/z): 357 [CpMnL^+], 237 [L^+], 204 [$\text{CpMn}(\text{CO})_3^+$], 131 [$L^+ - \text{NHCH}_2\text{Ph}$], 120 [CpMn^+], 106 [PhCH_2NH^+], 103 [$\text{PhCH}=\text{CH}^+$], 91 [PhCH_2^+], 77 [Ph^+], 65 [Cp^+], 55 [Mn^+]. IR spectrum (KBr pellets): $\nu(\text{C}\equiv\text{O})$ 1980, 1926; $\nu(\text{C}=\text{O})$ 1652; $\delta(\text{NH})$ 1590; $\nu(\text{C}=\text{C})$ 1440 cm^{-1} . ^1H NMR spectrum ($\text{THF}-d_8$, δ , ppm): 3.12 (d, 1 H, $=\text{CHC}(\text{O})$, $^3J(\text{H},\text{H}) = 10.3$ Hz), 4.15 (d, 1 H, $=\text{CHPh}$), 4.42 (d, 2 H, CH_2 , $^3J(\text{H},\text{N}) = 5.9$ Hz), 3.29 (s, br., 1 H, NH), 6.95–7.85 (m, 10 H, 2 Ph).

Reaction of III with Et_2NH

To a solution of III (1 mmol) in 30 ml of absolute ether, prepared as above, was added Et_2NH (0.073 g, 1 mmol). The mixture was stirred for 30 min at 20 °C until appearance of yellow product, $\text{Cp}(\text{OC})_2\text{Mn}(\pi\text{-Ph}(\text{H})\text{C}=\text{C}=\text{C}(\text{NEt}_2)\text{NHC}_6\text{H}_{11})$ (by TLC). To the solution was added 0.02 ml (1 mmol) H_2O and the mixture was stirred for 4 h. The solvent was removed in vacuo, and the residue was chromatographed on SiO_2 . A yellow band (VI) was eluted with ether/ CH_2Cl_2 (2/1). The residue was

recrystallized from hexane/ CH_2Cl_2 (1/1) to give VI (0.26 g, 64%), as identified from its IR, mass and ^1H NMR spectra.

Reaction of V with *n*-donors

(a) To a solution of V (0.379 g, 1 mmol) in 50 ml THF was added Py (0.16 g, 2 mmol). The mixture was refluxed at 65°C for 4 h (until disappearance of starting complex, monitored by TLC). The solvent was removed in vacuo, and the residue was chromatographed on SiO_2 . An orange band ($\text{Cp}(\text{OC})_2\text{MnPy}$) was eluted with hexane, and a colourless band (organic ligand) was eluted with hexane/ether (1/2). The organic ligand was chromatographed on Silufol (eluent: hexane/ether (1/2)) to give 0.1 g (49%) of *cis*- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NH-t-Bu}$ as colourless crystals, m.p. $52\text{--}53^\circ\text{C}$. Found: C, 76.95; H, 8.26; N, 6.63. $\text{C}_{13}\text{H}_{17}\text{NO}$ calc.: C, 76.85; H, 8.37; N, 6.85%. Mass spectrum (m/z): 203 (M^+), 188 ($M^+ - \text{NH}$), 160 ($M^+ - \text{C}(\text{O})\text{NH}$), 146 ($M^+ - \text{t-Bu}$), 131 ($M^+ - \text{NH-t-Bu}$), 103 ($M^+ - \text{C}(\text{O})\text{NH-t-Bu}$), 77 (Ph^+), 57 (t-Bu^+). IR spectrum (KBr pellets): $\nu(\text{C}=\text{O})$ 1650; $\delta(\text{NH})$ 1550 cm^{-1} . ^1H NMR spectrum (THF- d_8 , δ , ppm): 1.42 (s, 9 H, t-Bu), 6.00 (d, 1 H, $=\text{CHC}(\text{O})$, $^3J(\text{H,H}) = 12.5\text{ Hz}$), 6.62 (d, 1 H, $=\text{CHPh}$), 6.88 (s, br., 1 H, NH), 7.3–7.7 (m, 5 H, Ph); and 0.07 g (35%) *trans*- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NH-t-Bu}$ as colourless crystals, m.p. $56\text{--}57^\circ\text{C}$. Found: C, 76.92; H, 8.22; N, 6.90. $\text{C}_{13}\text{H}_{17}\text{NO}$ calc.: C, 76.85; H, 8.37; N, 6.85%. Mass spectrum (m/z): 203 [M^+], 188 [$M^+ - \text{NH}$], 160 [$M^+ - \text{NH, CO}$], 146 [$M^+ - \text{t-Bu}$], 131 [$M^+ - \text{NH-t-Bu}$], 103 [$M^+ - \text{C}(\text{O})\text{NH-t-Bu}$], 77 [Ph^+], 57 [t-Bu^+]. IR spectrum (KBr pellets): $\nu(\text{C}=\text{O})$ 1652; $\delta(\text{NH})$ 1550 cm^{-1} . ^1H NMR spectrum (THF- d_8 , δ , ppm): 1.48 (s, 9 H, t-Bu), 6.60 (d, 1 H, $=\text{CHC}(\text{O})$, $^3J(\text{H,H}) = 15.7\text{ Hz}$), 7.59 (d, 1 H, $=\text{CHPh}$), 6.99 (s, br., 1 H, NH), 7.4–7.8 (m, 5 H, Ph).

(b) The reaction of V (0.379 g, 1 mmol) and PPh_3 (0.52 g, 2 mmol) required the same procedure as in a. The solvent was removed in vacuo, and the residue was chromatographed on SiO_2 . A yellow band ($\text{Cp}(\text{OC})_2\text{MnPPh}_3$) was eluted with hexane/ether (4/1). A colourless zone (of the organic ligand) was eluted with hexane/ CH_2Cl_2 (1/1) to give 0.15 g (74%) of a mixture of *cis*- and *trans*- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NH-t-Bu}$.

Reaction of VII with *n*-donors

(a) The reaction of VII (0.413 g, 1 mmol) with Py (0.16 g, 2 mmol) was carried out as described above. The organic ligand was isolated as described above to give 0.18 g (76%) colourless crystals of *cis*- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NHCH}_2\text{Ph}$, m.p. $38\text{--}39^\circ\text{C}$. Mass spectrum (m/z): 237 [M^+], 160 [$M^+ - \text{Ph}$], 146 [$M^+ - \text{CH}_2\text{Ph}$], 131 [$M^+ - \text{NHCH}_2\text{Ph}$], 106 [PhCH_2NH^+], 103 [$M^+ - \text{C}(\text{O})\text{NHCH}_2\text{Ph}$], 91 [CH_2Ph^+], 77 [Ph^+]. IR spectrum (KBr pellets): $\nu(\text{C}=\text{O})$ 1650; $\delta(\text{NH})$ 1550 cm^{-1} . ^1H NMR spectrum (THF- d_8 , δ , ppm): 4.49 (d, 2 H, CH_2 , $^2J(\text{H,N}) = 5.9\text{ Hz}$), 6.08 (d, 1 H, $=\text{CHC}(\text{O})$, $^3J(\text{H,H}) = 12.8\text{ Hz}$), 6.72 (d, 1 H, $=\text{CHPh}$), 5.27 (s, br., 1 H, NH), 7.35–7.8 (m, 10 H, 2 Ph).

(b) Reaction of VII (0.413 g, 1 mmol) and PPh_3 (0.52 g, 2 mmol) was carried out as described above. The organic ligand was isolated as above to give 0.16 g (67%) of the colourless crystals of *cis*- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{NHCH}_2\text{Ph}$.

Preparation of IX

t-BuNC (0.166 g, 2.00 mmol) was added to a solution of VIII (0.366 g, 1 mmol) in 50 ml of absolute ether. The mixture was stirred for 16 h at 20°C (until

disappearance of starting complex, monitored by TLC). To the solution was added 0.02 ml (1 mmol) H_2O and the mixture was stirred for 8 h. The solvent was removed in vacuo and residue was chromatographed on Al_2O_3 . Yellow band (IX) was eluted with ether. The solvent was removed in vacuo and the residue was recrystallized from hexane/ CH_2Cl_2 (3/1) to give 0.16 g (34%) of the yellow crystals of IX, m.p. 151–152°C. Found: C, 69.50; H, 5.46; N, 3.52; Mn, 11.81. $\text{C}_{27}\text{H}_{26}\text{NO}_3\text{Mn}$ calc.: C, 69.38; H, 5.56; N, 3.00; Mn, 11.77%. Mass spectrum (m/z): 395 [$M^+ - \text{NH-t-Bu}$], 339 [$M^+ - 2 \text{ CO}, \text{NH-t-Bu}$], 219 [$\text{Ph}_2\text{C}_3\text{HC(O)}^+$], 204 [CpMn(CO)_3^+], 191 [$\text{Ph}_2\text{C}_3\text{H}^+$], 176 [CpMn(CO)_2^+], 148 [CpMn(CO)^+], 120 [CpMn^+], 65 [Cp^+], 55 [Mn^+]. IR spectrum (CH_2Cl_2): $\nu(\text{C}\equiv\text{O})$ 2000, 1940; $\nu(\text{C}=\text{O})$ 1675; $\delta(\text{NH})$ 1600 cm^{-1} . ^1H NMR spectrum (CDCl_3 , δ , ppm): 0.83 (s, 9 H, t-Bu), 4.24 (s, 5 H, Cp), 4.51 (s, 1 H, NH), 6.89 (s, 1 H, $\text{C}=\text{C}=\text{CH}$), 6.99–7.20 (m, 10 H, 2 Ph).

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