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## Reactions of ( $\eta$ -methylcyclopentadienyl)manganese tricarbonyl with primary amines

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### Abstract

( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>3</sub> reacts with RNH<sub>2</sub> (R = n-C<sub>4</sub>H<sub>9</sub>, sec-C<sub>4</sub>H<sub>9</sub>, n-C<sub>5</sub>H<sub>11</sub>, n-C<sub>6</sub>H<sub>13</sub>, cyclo-C<sub>6</sub>H<sub>11</sub>, n-C<sub>7</sub>H<sub>15</sub>, n-C<sub>8</sub>H<sub>17</sub>, n-C<sub>9</sub>H<sub>19</sub> or C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) to give corresponding *sym*-dialkylureas when a 1:2 molar mixture of the two reactants is irradiated with UV light for 100–250 h. The complexes ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>(CONHR)(H) were isolated for R = n-C<sub>4</sub>H<sub>9</sub>, n-C<sub>6</sub>H<sub>13</sub> and cyclo-C<sub>6</sub>H<sub>11</sub>.

### Introduction

Although there has been much study of the behaviour of the ligands mono- and di-*t*-phosphines [1–5], mono- and di-*t*-arsines [1,4] and 1,1'-bis(diphenylphosphino)-ferrocene [6] in displacement of CO from ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>3</sub>, relatively little attention has been paid to the behaviour of nitrogen donor ligands in such processes. Previously, only pyridine [7], 4-cyano-pyridine [8], 4-vinylpyridine [9], piperidine [10,11], adenine [12] and adenosine [12] have been used, and found to yield simple monosubstitution or ligand-bridged complexes. We describe here the reactions of ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>3</sub> with nine primary amines, RNH<sub>2</sub> (R = n-C<sub>4</sub>H<sub>9</sub>, sec-C<sub>4</sub>H<sub>9</sub>, n-C<sub>5</sub>H<sub>11</sub>, n-C<sub>6</sub>H<sub>13</sub>, cyclo-C<sub>6</sub>H<sub>11</sub>, n-C<sub>7</sub>H<sub>15</sub>, n-C<sub>8</sub>H<sub>17</sub>, n-C<sub>9</sub>H<sub>19</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) in which the metal carbonyl acts only as a carbonylating agent and does not yield simple substitution products.

### Results and discussion

Although the reactions of a number of aliphatic, alicyclic and heterocyclic amines with various metal carbonyls, e.g., M(CO)<sub>6</sub> [13–16], (*o*-phen or 2,2'-bipy)M(CO)<sub>4</sub> [17] (M = Cr, Mo, W), [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)W(CO)<sub>3</sub>]<sub>2</sub> [18] and [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> [19] are known, there are no reports of cases in which amines are carbonylated. In all cases amine molecules displace CO from metal carbonyls to give substitution products, but in the present work they were found to behave differently.

*n*-Butyl-, *n*-hexyl- and cyclohexylamine yielded two products—the corresponding dialkylureas and the very unstable carboxamido derivatives ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>-

(CONHR)(H) (R = n-C<sub>4</sub>H<sub>9</sub>, n-C<sub>6</sub>H<sub>13</sub>, cyclo-C<sub>6</sub>H<sub>11</sub>), but sec-butyl-, n-pentyl-, n-heptyl-, n-octyl-, n-nonyl- and benzylamine gave only dialkylureas when 1 : 2 molar mixtures of ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>3</sub> and neat amines were irradiated with UV light for 100–250 h at ambient temperature under argon. In all cases in which carbox-amido derivatives could not be isolated brown, CO- and amine-free products were obtained; the latter were insoluble in organic solvents and were not identified. The complexes ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>(CONHR)(H) were found to decompose slowly when kept as solids for a few hours, but to decompose rapidly when dissolved in organic solvents; immediate precipitation of identical CO- and amine-free brown products took place in all cases. This made it difficult to establish unequivocally the presence of Mn–H bonds by NMR spectroscopy; however the appearance of a new band at  $\sim 1820\text{ cm}^{-1}$  in the IR spectrum and the diamagnetic character may be attributed to the presence of an Mn–H bond.

The IR spectra of ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>(CONHR)(H) (R = n-C<sub>4</sub>H<sub>9</sub>, n-C<sub>6</sub>H<sub>13</sub> and cyclo-C<sub>6</sub>H<sub>11</sub>) show two terminal  $\nu(\text{C}\equiv\text{O})$  bands at  $\sim 1895$  and  $\sim 1805\text{ cm}^{-1}$  along with one intense  $\nu(\text{C}=\text{O})$  band at  $\sim 1625\text{ cm}^{-1}$ . (The spectra of these substances are similar to those of carboxamido derivatives of ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>3</sub> prepared previously by the reaction of primary amines with [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>-NO]<sup>+</sup> [20].) The yields of the ureas are better when the amines have longer aliphatic chains.

The *sym*-dialkylureas were identified from their microanalyses, and IR and mass spectral data. Their IR spectra exhibited a strong  $\nu(\text{C}=\text{O})$  band at  $\sim 1630\text{ cm}^{-1}$  and N–H stretch and N–H deformation modes at  $\sim 3310$  and  $\sim 1575\text{ cm}^{-1}$ , respectively, in each case. In the mass spectra the molecular ion was also the parent ion (Table 1). The fragmentation patterns (to be published elsewhere) are in excellent agreement with those expected for *sym*-dialkylureas.

Although the detailed mechanism of formation of the ureas cannot be defined it seems likely that the carboxamido hydride derivatives decompose under the conditions used to give RNCO and a transient species ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>2</sub>H<sub>2</sub>, analogous to ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>2</sub>H<sub>2</sub> complexes obtained by another route [21]. The RNCO so formed gives *sym*-RNHCONHR by reaction with RNH<sub>2</sub>.

The outcome contrasts with the formation of substituted ureas and formamides in the few reported reactions of amines with CO at high temperatures and pressures in the presence of some metal carbonyls, such as Mn<sub>2</sub>(CO)<sub>10</sub> [22], CH<sub>3</sub>Mn(CO)<sub>5</sub> [22], Fe(CO)<sub>5</sub> [23], Co<sub>2</sub>(CO)<sub>8</sub> [24], Ni(CO)<sub>4</sub> [25] and K[Ru(EDTA-H)CO] [26,27], as catalysts. In our reactions the ( $\eta$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)Mn(CO)<sub>3</sub> does not act as a catalyst but as a source of CO under irradiation with UV light, with carbonylation of the amines at room temperature to yield the corresponding *sym*-dialkylureas.

## Experimental

All reactions and isolation procedures were carried out under dry argon or *in vacuo*. The amines were distilled before use. UV irradiation was carried out in a quartz vessel in which an inert atmosphere could be maintained. The UV light source (30 W) was made by Philips Co., Holland. The IR spectra were recorded on a Perkin Elmer model 577 in KBr discs, and mass spectra were obtained with a Jeol JMS-D300 mass spectrometer.

Table 1  
Preparative details and analyses and physical data of carbamido derivatives and *sym*-dialkylureas

Amine	Reaction time (h)	Products	Yield (%)	M.p. (°C) lit.	Analysis (Found (calc.)) (%)			$m/e$	$\nu(\text{C=O})$ ( $\text{cm}^{-1}$ )	$\nu(\text{C=O})$ ( $\text{cm}^{-1}$ )
					C	H	N			
<i>n</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	160	( $\eta$ -CH <sub>3</sub> C <sub>3</sub> H <sub>4</sub> )Mn(CO) <sub>2</sub> (CONHC <sub>4</sub> H <sub>9</sub> )(H)	28.2	97-98d	53.4 (53.6)	6.0 (6.1)	4.7 (4.8)		1895vs 1805vs	1628s
		C <sub>4</sub> H <sub>9</sub> NHCONHC <sub>4</sub> H <sub>9</sub>	9.6	71 (71)[29]	62.7 (62.7)	11.7 (11.6)	16.1 (16.2)	172		1628s
<i>n</i> -C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>	140	( $\eta$ -CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )Mn(CO) <sub>2</sub> (CONHC <sub>6</sub> H <sub>13</sub> )(H)	31.7	120-22d	56.1 (56.4)	7.0 (6.8)	4.2 (4.3)		1895vs 1805vs	1630s
		C <sub>6</sub> H <sub>13</sub> NHCONHC <sub>6</sub> H <sub>13</sub>	18.9	78	68.6 (68.4)	12.2 (12.2)	12.1 (12.2)	228		1620s
<i>sec</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	250	C <sub>4</sub> H <sub>9</sub> NHCONHC <sub>4</sub> H <sub>9</sub>	9.2	135 (135)[30]	62.6 (62.7)	11.8 (11.6)	16.2 (16.2)	172		1628s
<i>n</i> -C <sub>5</sub> H <sub>11</sub> NH <sub>2</sub>	150	C <sub>5</sub> H <sub>11</sub> NHCONHC <sub>5</sub> H <sub>11</sub>	18.2	84 (84)[31]	65.8 (66.0)	12.1 (12.0)	13.8 (14.0)	200		1625s
<i>n</i> -C <sub>7</sub> H <sub>15</sub> NH <sub>2</sub>	190	C <sub>7</sub> H <sub>15</sub> NHCONHC <sub>7</sub> H <sub>15</sub>	30.7	92 (91)[31]	70.3 (70.3)	12.4 (12.5)	10.8 (10.9)	256		1625s
<i>n</i> -C <sub>8</sub> H <sub>17</sub> NH <sub>2</sub>	100	C <sub>8</sub> H <sub>17</sub> NHCONHC <sub>8</sub> H <sub>17</sub>	32.8	90 (89-90)[30]	71.8 (71.8)	12.8 (12.6)	9.8 (9.8)	284		1620s
<i>n</i> -C <sub>9</sub> H <sub>19</sub> NH <sub>2</sub>	140	C <sub>9</sub> H <sub>19</sub> NHCONHC <sub>9</sub> H <sub>19</sub>	48.6	101	72.8 (73.0)	12.6 (12.8)	8.9 (8.9)	312		1625s
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub>	160	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NHCONHC <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	15.5	168 (168)[29]	74.9 (75.0)	6.6 (6.6)	11.5 (11.6)	240		1630s

*Reaction of ( $\eta$ -methylcyclopentadienyl)manganese tricarbonyl with cyclohexylamine*

A mixture of ( $\eta$ -methylcyclopentadienyl)manganese tricarbonyl (2.0 ml) and cyclohexylamine (3.0 ml) was irradiated with UV light in a quartz vessel under argon for 140 h. The mixture became deep yellow during ca 25 h and dirty white needle-shaped crystals began to sublime onto the upper portion of the reaction vessel after ca 90 h. Some crystals were also present at the bottom of the reaction vessel; when the reactions was complete the crystals were filtered off and mixed with the sublimed crystals. The crystals were refluxed in the ethanol (30 ml), and the brown material which remained undissolved was removed by filtration. Evaporation of the filtrate gave brilliant white needle-shaped crystals. The product was identified as *sym*-dicyclohexylurea (1.14 g, 40.2%), m.p. 233°C (lit. [28] 233°C) (Anal. Found: C, 69.5; H, 10.6; N, 12.5. C<sub>13</sub>H<sub>24</sub>N<sub>2</sub>O calc.: C, 69.6, H, 10.7, N, 12.5%); *m/e*: found 224, calc. 224).  $\nu(\text{C=O})$ : 1630 cm<sup>-1</sup>.

The mother liquor after filtering off of the *sym*-dicyclohexylurea was concentrated *in vacuo* to give a viscous residue, which after washing with light petroleum (40–60°C) yielded a yellow powder. Since it tended to decompose in solution it was not recrystallised. It was judged to be cyclohexamidodicarbonyl( $\eta$ -methylcyclopentadienyl)manganese hydride (0.81 g, 39.9%) m.p. 112–115°C, d. (Anal. Found: C, 56.4; H, 6.6; N, 4.5. C<sub>15</sub>H<sub>20</sub>NMnO<sub>3</sub> calc.: C, 56.7; H, 6.3; N, 4.4%);  $\nu(\text{C}\equiv\text{O})$ : 1891 vs and 1803 vs cm<sup>-1</sup>;  $\nu(\text{C=O})$ : 1623 s cm<sup>-1</sup>. It was almost insoluble in light petroleum but dissolved in all other common organic solvents.

*Reactions with other amines*

*n*-Butyl- and *n*-hexyl-amines reacted similar with ( $\eta$ -methyl-cyclopentadienyl)manganese tricarbonyl to give ureas and carboxamido hydride derivatives. Other amines yielded only *sym*-dialkylureas, which were purified by chromatography on silica gel with diethyl ether as eluant. Reaction conditions and characterization data are given in Table 1.

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