Reaction of (η^5-Pentadienyl)tricarbonylmanganese with Secondary Amines. Synthesis and Characterization of (1-Amino-η^3-pentenyl)tricarbonylmanganese Complexes and Their Phosphine or Tetracarbonyl Derivatives[†]

N. Zúñiga Villarreal,[‡] M. A. Paz-Sandoval,*[,‡] P. Joseph-Nathan,[‡] and R. O. Esquivel[§]

Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, Apartado Postal 14-740, México, DF, 07000 México, and Departamento de Química, Universidad Autónoma Metropolitana, Apartado Postal 55-534, México, DF, 09340 México

Received December 3, 1990

Secondary amines react with (η^5-pentadienyl)tricarbonylmanganese to give complexes $Mn{\leftarrow}N(R_2)(\eta^3\text{-}CH{\cdots}CH{\cdots}CHCH_2CH_3)(CO)_3$ [$R_2 = (CH_2)_4$ (**5**), $(CH_2)_5$ (**6**), $O(CH_2)_4$ (**7**), $HN(CH_2)_4$ (**8**); $R = C_2H_5$ (**9**); $R = CH_3$, $R = C_6H_{11}$ (**10**)] in which the nitrogen is added stereospecifically to the terminal carbon atom. The regioisomers $Mn{\leftarrow}N(R_2)(\eta^3\text{-}C(CH_3){\cdots}CH{\cdots}CHCH_2CH_3)(CO)_3$ [$R_2 = (CH_2)_4$ (**13**), $(CH_2)_5$ (**15**)] and $Mn{\leftarrow}N(R_2)(\eta^3\text{-}CH{\cdots}CH{\cdots}CHCH_2CH_2CH_3)(CO)_3$ [$R_2 = (CH_2)_4$ (**14**), $(CH_2)_5$ (**16**)] are obtained from the reaction of (η^5-methylpentadienyl)tricarbonylmanganese and pyrrolidine or piperidine. The interconversion between **15** and **16** suggests that **15** is the kinetic and **16** the thermodynamic product in these reactions. Single-crystal X-ray diffraction studies of $Mn{\leftarrow}N(R_2)(\eta^3\text{-}CH{\cdots}CH{\cdots}CHCH_2\text{-}CH_3)(CO)_3$ (**5**, **6**) have been undertaken to confirm the unprecedented formation of the novel (1-amino-η^3-pentenyl)tricarbonylmanganese complexes in which the aminopentenyl ligand is bonded to a manganese center through an η^3-fashion and also by the nitrogen coordination in anti conformation. Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.025$ (3) Å, $b = 9.205$ (4) Å, $c = 9.374$ (4) Å, $\alpha = 90.32$ (4)°, $\beta = 91.41$ (3)°, $\gamma = 104.33$ (3)°, $Z = 2$, and $D_{calcd} = 1.37$ g cm^{-3}, and for **6** the space group is $P2_1/c$ with $a = 7.531$ (3) Å, $b = 14.455$ (4) Å, $c = 13.318$ (4) Å, $\beta = 101.7$ (3)°, $Z = 4$, and $D_{calcd} = 1.36$ g cm^{-3}. The final R factors were 7.9 and 6.8% for 1338 and 1305 independent reflections, respectively. The stereochemistry of **6** in solution was completely established by ^1H and ^{13}C NMR spectroscopy. Displacement of the coordinated nitrogen by CO or PMe_2Ph occurs easily to give compounds $Mn(\eta^3\text{-}CH(NR_2){\cdots}CH{\cdots}CHCH_2CH_3)(CO)_3L$ [$R_2 = (CH_2)_4$, $L = PMe_2Ph$ (**5a**); $R_2 = (CH_2)_5$, $L = PMe_2Ph$ (**6a**); $R_2 = (CH_2)_5$, $L = CO$ (**6b**); $R = C_2H_5$, $L = PMe_2Ph$ (**9a**); $R = CH_3$, $L = CO$ (**11b**)]. The tetracarbonyl species **6b** exhibits a reversible reaction with the tricarbonyl complex **6**. The addition of the amines directly to the pentadienyl ligand, with no evidence for preliminary interaction at either the manganese center or the CO carbon atom, is also discussed. Evidence favoring a 1,5-addition for the formation of these compounds was gained by following the reaction of **2** with C_4H_8ND.

Introduction

The reaction of nucleophiles with transition-metal organometallic complexes can be divided into two general categories, those that involve nucleophilic attack at the metal center itself and those that involve nucleophilic attack at a metal-coordinated organic ligand.[1]

In the first studies of the reactivity of the pentadienyl complex $\eta^5\text{-}C_5H_7Mn(CO)_3$ (**2**), we observed the former process when addition of tertiary phosphines, phosphites, and arsines afforded the complexes $Mn(\eta^5\text{-}C_5H_7)(CO)_2L$ (such as **4**) via an associative ligand substitution involving η^5 to η^3 interconversion, as demonstrated by the isolation of $Mn(\eta^3\text{-}C_5H_7)(CO)_3L$ intermediates[2] (such as **3**) (Scheme I). The earliest known cyclopentadienyl $Mn(\eta^5\text{-}C_5H_5)(CO)_2L$ analogues of **4** also involved nucleophilic attack at the metal center.[3] However, it is well-known that substitution of carbon monoxide in $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ takes place via a dissociative mechanism, through the 16-electron fragment $Mn(\eta^5\text{-}C_5H_5)(CO)_2$[3] and this reactive fragment has affinity for a wide variety of two-electron ligands, including amines,[4] such as trimethylamine, dimethylamine, piperidine, pyrrolidine, and piperazine and also less basic aromatic amines such as aniline[4c] and pyridine.[5] Nevertheless, exclusive metal attack in these compounds is in contrast with the reactivity of the open-chain pentadienyl complex **2** and $Mn(\eta^5\text{-}C_5H_6CH_3)(CO)_3$ (**12**) toward amines, which has been shown to involve nucleophilic attack at the metal-coordinated organic ligand. From a reactivity point of view, one might expect the open pentadienyl ligand to undergo nucleophilic attack more easily than the cyclopentadienyl unit, as is the case.[6]

Since limited studies of nucleophilic addition reactions for neutral pentadienyl compounds have been described,[6,7] it is interesting to compare them with the ample precedent for cationic pentadienyl and cyclohexadienyl species and, to less extent, to arene isoelectronic species.[8-16] As far as

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[†] This paper is dedicated to Dr. Paul Powell in gratitude for his enthusiasm and encouragement.

[‡] Centro de Investigación y de Estudios Avanzados del IPN.

[§] Universidad Autónoma Metropolitana.

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0276-7333/91/2310-2616$02.50/0

isoelectronic $Fe(CO)_3$ species are concerned, dienyl cations react readily with a variety of nucleophiles, thus generating compounds that contain either the stable butadienetricarbonyliron fragment when the nucleophilic reaction takes place at a terminal carbon or the σ,η^3-iron complexes if the attack occurs at the C2 position.[6,13,17,18]

Theoretical attempts to analyze the factors controlling the nucleophilic additions have been published elsewhere.[6,7b,19] Recently, (η^5-1-azapentadienyl)tricarbonylmanganese complexes have been prepared by treatment of the 1-oxopentadienyl complex with the corresponding isopropyl or *tert*-butyl primary amine[20] in the presence of $F_3B{\cdot}OEt_2$.

Only few reports of organometallic complexes in which a nitrogen ligand is attached to the organic acyclic ligand as well as to the metal center are known. Some compounds of this class have been obtained as unexpected products from various chemical reactions. An interesting example in this respect is the pentadienyl–acetonitrile coupling, which afforded a dimeric product $[Ti(\eta^5\text{-}C_5H_5)\text{-}(CH_3)_3C_6H_5N]_2$ and which also permitted us to establish the greater chemical reactivity of the more strongly bound pentadienyl ligand as compared to cyclopentadienyl.[21] Other reported examples are the niobium complex $(\eta^5\text{-}C_5H_5)Nb{\leftarrow}NH[\eta^6\text{-}C(CH_3)\{C(C_6H_5)\}_3CH(C_6H_5)]$[22] obtained from the condensation of diphenylacetylene and acetonitrile and the aziridinylmethyltetracarbonylmanganese complex $Mn(CH_2NCH_2CH_2)(CO)_4$[23] as well as the two 2-azabutadiene complexes $Mn(C(CH_3)_2CHNC_5H_9)(CO)_3$ and $Mn(C(CH_3)_2CHN(CH_3)CH_2)(CO)_3$.[24] The alkylation, reduction, and ring opening of diphenylcyclopropenethione, on treatment with $Mn(CO)_5^-$ and methyl iodide in aqueous methanol, affords the η^3-allyl–sulfur donor complex $Mn{\leftarrow}SH[\eta^3\text{-}CH\overline{\cdot\cdot}C(C_6H_5)\overline{\cdot\cdot}C(CH_3)(C_6H_5)](CO)_3$.[25]

Thus, in order to expand our knowledge concerning the behavior of **2**, we decided to perform a thorough investigation of the chemical properties of this complex in the presence of secondary amines. This allowed us to find a general route for the synthesis of nitrogen donor ligand (η^3-pentenyl)manganese complexes, which, to our knowledge, have not been previously reported.

Table I. Reaction Conditions and Yields for the Preparation of Complexes 5–10

compd	molar ratio 2:amine	reflux time, h	yield, %
5	1:14	7	32.7
	1:20	7	53.5
6	1:6	7	43.1
7	1:6	7	43.5
8	1:6	23	28.2
9	1:25	68	14.8
10	1:6	39	19.4

Experimental Section

All manipulations were performed under inert atmosphere or vacuum by using Schlenk techniques. Solvents were purified by distillation from appropriate drying/deoxygenating agents prior to use.[26] The following starting materials were purchased: Florisil (60–100 mesh) and amines (Aldrich), morpholine (Eastman), and PMe_2Ph (Strem). Infrared spectra were recorded on a Nicolet MX-1-FT spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300GS spectrometer, and chemical shifts are reported relative to internal Me_4Si. In general, ^1H connectivities were determined from ^1H–^1H shift-correlated (COSY) 2D spectra; ^1H and ^{13}C peak assignment were made by using ^{13}C gated-decoupled spectra and ^{13}C–^1H shift-correlated (HETCOR) 2D spectra. ^{31}P NMR spectra were recorded on a Jeol FX90Q spectrometer using H_3PO_4 (85%) as the external reference. Analyses were performed by Oneida Research Services, Inc., Whitesboro, NY, and mass spectra were obtained by using a Hewlett-Packard 5985-A instrument operated at 70 eV.

General Method for the Preparation of the Complexes $Mn{\leftarrow}N(R_2)(\eta^3\text{-}CH\overline{\cdot\cdot}CH\overline{\cdot\cdot}CHCH_2CH_3)(CO)_3$. A mixture of **2** (500 mg, 2.43 mmol) and an excess of the amine (Table I) was heated in refluxing cyclohexane (40 cm^3) until infrared monitoring of the reaction mixture showed complete consumption of the starting material and no further change in the spectrum was observed. The reaction times (h) were as described in Table I. The solvent was evaporated under reduced pressure to yield either a yellow solid or an oil. Further purification was carried out by using chromatography on Florisil and different eluent mixtures as described below. In every case the first collected band corresponds to **2** and the second band to the new species.

NR_2 = Pyrrolidine (5). The crystalline yellow residue was dissolved in the minimum volume of hexane and chromatographed by using petroleum ether. Removal of solvents gave pale yellow crystals, mp 50–51 °C. Anal. Calcd for $MnC_{12}H_{16}O_3N$: C, 51.98; H, 5.78; N, 5.05. Found: C, 51.55; H, 5.71; N, 4.71. Mass spectrum [*m*/*e* (relative intensity)]: 55 (9), 138 (100), 193 (5), 221 (4), 249 (4), 277 (5).

NR_2 = Piperidine (6). The yellow crystalline compound was isolated in an analogous manner as described for **5**, mp 64–66 °C. Anal. Calcd for $C_{13}H_{18}O_3NMn$: C, 53.43; H, 6.51; N, 4.80. Found: C, 53.21; H, 6.14; N, 4.66. Mass spectrum [*m*/*e* (relative intensity)]: 55 (27), 152 (100), 207 (4), 235 (3), 263 (4), 291 (4).

NR_2 = Morpholine (7). The yellow oil was dissolved in the minimum volume of dichloromethane and chromatographed by using a mixture of hexane–dichloromethane (1:1). Removal of the solvents gave a light yellow oil. Mass spectrum [*m*/*e* (relative intensity)]: 55 (34), 154 (100), 209 (5), 237 (4), 265 (4), 293 (4).

NR_2 = Piperazine (8). A similar procedure to that given above for **5** gave a yellow oil. Mass spectrum [*m*/*e* (relative intensity)]: 55 (28), 153 (100), 208 (29), 236 (4), 264 (3), 292 (5).

NR_2 = Diethylamine (9). The red brown oil was chromatographed by using petroleum ether–diethyl ether (1:1). Removal of the solvent afford a lemon yellow oil. Mass spectrum [*m*/*e* (relative intensity)]: 55 (17), 140 (100), 195 (7), 223 (4), 251 (6), 279 (5).

NR_2 = Methylcyclohexylamine (10). The golden yellow oil was dissolved in the minimum volume of diethyl ether and chromatographed by using a mixture of petroleum ether–diethyl ether (12:1). Removal of the solvents gave yellow crystals, mp 58 °C. Mass spectrum [*m*/*e* (relative intensity)]: 55 (30), 180 (100), 235 (8), 263 (3), 291 (3), 319 (4).

General Method for the Preparation of the Complexes $Mn{\leftarrow}N(R_2)(\eta^3\text{-}C(CH_3)\overline{\cdot\cdot}CH\overline{\cdot\cdot}CHCH_2CH_3)(CO)_3$ (13, 15) and $Mn{\leftarrow}N(R_2)(\eta^3\text{-}CH\overline{\cdot\cdot}CH\overline{\cdot\cdot}CHCH_2CH_2CH_3)(CO)_3$ (14, 16). A mixture of **12** (500 mg, 2.27 mmol) and pyrrolidine or piperidine in a complex:amine ratio of 1:8 was heated in refluxing cyclohexane

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(60 cm^3) until infrared monitoring of the reaction mixture showed complete consumption of the starting material. The reaction times were 3 h for pyrrolidine and 8 h for piperidine. The solvent was removed under reduced pressure and the residue chromatographed on Florisil by using petroleum ether to afford in each case a golden yellow oil, which proved to be a mixture of isomers **13** and **14** (40:60) and **15** and **16** (50:50), respectively, in 31.3 and 60% yield, respectively. Mass spectrum of **13**, **14** [*m/e* (relative intensity)]: 55 (20), 152 (100), 207 (5), 235 (3), 263 (4), 291 (3).

General Method for the Preparation of the Complexes $Mn(\eta^3\text{-}CH(NR_2)\cdots CH\cdots CHCH_2CH_3)(CO)_3PMe_2Ph$ (5a, 6a, 9a). A mixture of **5** (618 mg, 2.23 mmol) and PMe_2Ph (308 mg, 2.23 mmol) was stirred 22 h in cyclohexane (50 cm^3) at room temperature until the infrared spectrum remained unchanged. Similarly for **6** and **9** the reflux times were 4 and 2 h, respectively. Removal of the solvent under reduced pressure left in each case a golden yellow oil, which was purified by chromatography on Florisil by using a mixture of hexane–diethyl ether (1:12). The isolated lemon yellow oils yielded **5a** (18.1%), **6a** (54.1%), and **9a** (72.0%). Mass spectrum [*m/e* (relative intensity)]: **5a**, 55 (40), 121 (99), 123 (98), 138 (100), 139 (24), 193 (12.5), 331 (4); **6a**, 55 (43), 121 (38), 123 (33), 138 (41), 139 (40), 152 (100), 193 (3), 207 (15), 235 (5), 263 (4), 277 (4), 291 (3), 345 (5), 429 (3); **9a**, 55 (43), 121 (41), 123 (33), 138 (58), 139 (31), 140 (100), 193 (5), 195 (26), 223 (5), 251 (3), 265 (5), 279 (3), 333 (7), 417 (6).

Method for the Preparation of the Complexes $Mn(\eta^3\text{-}CH(NR_2)\cdots CH\cdots CHCH_2CH_3)(CO)_4$ (6b, 11b). NR_2 = Piperidine (6b). A 60-cm^3 cyclohexane solution of **2** (500 mg, 2.43 mmol) with piperidine (1.02 g, 12 mmol) in a vacuum-sealed ampule was heated, inside a stainless steel container, in an oil bath at 90 °C for 7 h. After removal of the solvent in vacuo, the residue was chromatographed on Florisil with hexane as the eluting solvent. A yellow band eluting first from the column was identified as unreacted **6**. A second yellow band was collected and the solvent evaporated to dryness to give a golden yellow oil (300 mg, 0.94 mmol) in 38.7% yield. Mass spectrum [*m/e* (relative intensity)]: 55 (38), 152 (100), 207 (5), 235 (19), 263 (3), 291 (18), 319 (4).

NR_2 = Dimethylamine (11b). This complex was prepared as above, but dimethyl amine was bubbled into the solvent until 3.3 g (72.9 mmol) was present. Then 0.5 g (2.43 mmol) of the complex **2** was added and the mixture was heated for 10 h. Workup as above afforded the complex (30 mg, 0.12 mmol) as a golden yellow oil. Mass spectrum [*m/e* (relative intensity)]: 55 (23), 112 (100), 167 (8), 195 (3), 223 (8), 251 (4), 279 (8).

Single-Crystal X-ray Diffraction Studies. Suitable crystals of **5** and **6** were mounted in glass capillaries under inert atmosphere. The X-ray data collections, structures resolution, and refinements were done on a Nicolet R3m four-circle automatic diffractometer at room temperature using Cu Kα graphite-monochromated radiation (λ = 1.54178 Å), which was operated in the $\theta/2\theta$ scanning mode. The cell parameters were established by least-squares adjustment of the setting angles of 25 machine-centered strong reflections. The crystal data and the details of the data collections and structure analyses are summarized in Table II. During the data collections two standard reflections were measured after measurement of 46 reflections as check reflections to monitor crystal deterioration and/or misalignment. The measured data were corrected for background, Lorentz, and polarization effects as well as for absorption, for which the crystal was considered to have a pseudoellipsoid shape. The coordinates of the manganese atoms were determined from Patterson syntheses and checked by use of the direct methods package included in the software provided by the diffractometer manufacturer. All remaining non-hydrogen atoms were found after successive full-matrix least-squares refinements and difference Fourier map calculations. After anisotropic refinement of the non-hydrogen atoms all hydrogen atoms were located in difference Fourier maps. Excepting the three hydrogen atoms at the η^3 portion of the molecules, the hydrogen atoms were placed at idealized positions (C–H = 1.09 Å) and included in the structure factor calculation with fixed isotropic thermal parameters (U_{iso} = 0.08 Å^2). After several full-matrix least-squares cycles of refinement the three remaining hydrogen atoms were also included in the calculation by using the coordinates provided by difference Fourier maps, and their most probable position as completely free hydrogen atoms were further refined. The least-squares weighting scheme used is $w = 1/[\sigma^2(F_o) + G(F_o)^2]$, where σ is the standard deviation of observed amplitudes based on counting statistics and G is a variable adjusted after each cycle to minimize the function $\sum w(\Delta F)^2$. Some reflections were discarded to improve the final refinements. The final G value and other relevant refinement values are summarized in Table II. The fractional atomic coordinates for all non-hydrogen atoms in **5** and in **6** are given in Tables III and IV, respectively, while the relevant bond distances and bond angles for **5** and **6** are given in Tables V and VI, respectively.

Table II. Crystallographic Data Summary

	compd	
	6	**5**
	(1) Crystal Data	
cryst size, mm	0.40 × 0.40 × 0.32	0.24 × 0.12 × 0.10
stoichiometry	$C_{13}H_{18}MnNO_3$	$C_{12}H_{16}MnNO_3$
mol wt	291.23	277.20
cryst system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	7.531 (3)	8.025 (3)
b, Å	14.455 (4)	9.205 (4)
c, Å	13.318 (4)	9.374 (4)
α, deg	90.0	90.32 (4)
β, deg	101.7 (3)	91.41 (3)
γ, deg	90.0	104.33 (3)
V, Å^3	1420.0 (8)	670.7 (3)
cryst color	yellow	yellow
Z	4	2
T, K	298	298
D_{exptl}, g cm^{-3}	1.36	1.37
F_{000}	608	288
μ(Cu Kα, 1.54178 Å), cm^{-1}	79.7	80.1
	(2) Data Collection	
mode	$\theta/2\theta$	$\theta/2\theta$
2θ limits, deg	3–110	3–110
scan width, below Kα1, deg	1.0	1.0
scan width, above Kα2, deg	1.1	1.2
scan speed (variable), deg min^{-1}	4.0–29.3	4.0–29.3
exposure time, h	31.05	41.42
stability cor range on I	1.000–1.000	1.000–1.000
min range in *hkl*	0,0,–15	0,–10,–10
max range in *hkl*	9,16,15	9,10,10
min, max calcd transm factors, %	50.32, 99.85	60.44, 99.90
no. of tot. reflcns collcd	2054	1832
no. of unique reflcns [$I \geq 3\sigma(I)^2$]	1305	1338
	(3) Structure Refinement	
no. of reflcns for final refinement	1298	1322
no. of params refined	184	175
$R(F)$, %	6.8	7.9
R_w, %	7.4	8.0
goodness of fit for last cycle	1.07	1.08
final G	0.00396	0.00385
resid electron dens, e/Å^3	0.63	0.52

The systematic absences for **6** were consistent with $P2_1/c$, in agreement with the successful structure refinement, while for **5** the systematic absences were consistent with either $P1$ or $P\bar{1}$. A structure solution for the heavy atoms in $P1$ with two molecules in the asymmetric unit showed that $x,y,z = \bar{x},\bar{y},\bar{z}$, meaning the correct space group is actually $P\bar{1}$ with one molecule in the asymmetric unit. This is further in agreement with the successful structure refinement in $P\bar{1}$.

Synthetic and Spectroscopic Results

Reactivity of $Mn(\eta^5\text{-}C_5H_6R)(CO)_3$. The reaction of $Mn(\eta^5\text{-}C_5H_7)(CO)_3$ (**2**) with secondary amines in refluxing cyclohexane leads to the formation of the appropriate $Mn\leftarrow N(R_2)(\eta^3\text{-}CH\cdots CH\cdots CHCH_2CH_3)(CO)_3$ complexes

Table III. Positional Parameters ($\times10^4$) with Their Estimated Standard Deviations and Temperature Factors (Å^2 × 10^3) for (1-Pyrrolidyl-η^3-pentenyl)tricarbonylmanganese (5)

atom	*x*	*y*	*z*	*U*
Mn	1827 (2)	1329 (2)	2331 (1)	46 (1)
N	2087 (8)	−859 (8)	2680 (7)	50 (3)
C1	2018 (12)	−514 (11)	1197 (10)	54 (4)
C2	3229 (11)	641 (10)	688 (8)	54 (3)
C3	4468 (11)	1626 (10)	1588 (10)	53 (3)
C4	5590 (13)	3064 (12)	1035 (11)	74 (4)
C5	6303 (14)	4236 (12)	2166 (12)	89 (5)
C6	3623 (12)	−1412 (11)	3215 (11)	69 (4)
C7	567 (12)	−1974 (10)	3210 (11)	68 (4)
C8	3023 (15)	−3087 (12)	3361 (15)	96 (5)
C9	1098 (16)	−3398 (14)	3515 (18)	126 (7)
C10	−430 (11)	861 (10)	2674 (9)	56 (4)
O10	−1869 (9)	671 (9)	2931 (8)	90 (3)
C11	1472 (12)	2901 (10)	1389 (10)	62 (4)
O11	1204 (11)	3897 (8)	743 (9)	101 (4)
C12	2592 (11)	2400 (11)	3941 (11)	61 (4)
O12	3097 (9)	3075 (10)	4978 (8)	101 (4)

Table IV. Positional Parameters ($\times10^4$) with Their Estimated Standard Deviations and Temperature Factors (Å^2 × 10^3) for (1-Piperidyl-η^3-pentenyl)tricarbonylmanganese (6)

atom	*x*	*y*	*z*	*U*
Mn	172 (2)	7209 (1)	8669 (1)	41 (1)
N	−525 (9)	6481 (4)	7241 (4)	41 (2)
C1	831 (11)	7152 (6)	7231 (6)	44 (3)
C2	2447 (12)	7066 (6)	7979 (7)	42 (3)
C3	2679 (11)	6441 (7)	8792 (7)	44 (3)
C4	4355 (11)	6576 (7)	9655 (7)	58 (4)
C5	4138 (14)	6166 (8)	10668 (7)	73 (4)
C6	−120 (12)	5483 (5)	7053 (6)	47 (3)
C7	−2310 (11)	6714 (6)	6567 (6)	49 (3)
C8	−1549 (13)	4883 (6)	7392 (7)	61 (4)
C9	−3793 (13)	6139 (7)	6870 (7)	66 (4)
C10	−3428 (14)	5104 (7)	6797 (8)	75 (4)
C11	−1790 (12)	7961 (6)	8430 (7)	51 (3)
O11	−2981 (11)	8464 (6)	8371 (6)	98 (4)
C12	1211 (12)	8076 (6)	9536 (6)	49 (3)
O12	1796 (10)	8666 (4)	10092 (4)	76 (3)
C13	−524 (11)	6492 (6)	9647 (7)	45 (3)
O13	−934 (9)	6037 (5)	10268 (4)	67 (3)

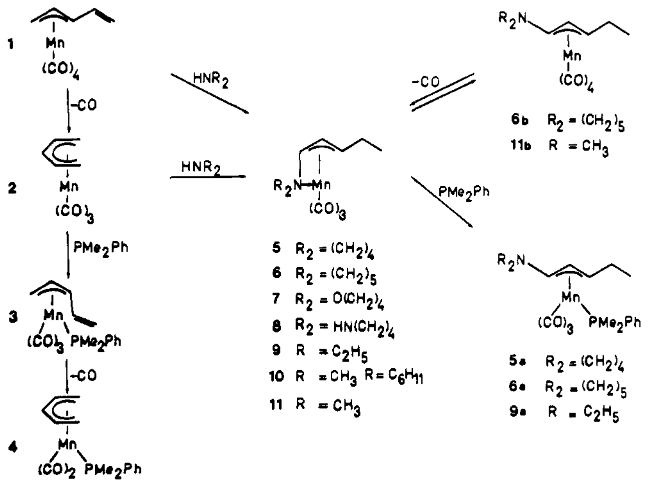
Table V. Selected Bond Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviations for (1-Pyrrolidyl-η^3-pentenyl)tricarbonylmanganese (5)

Bond Distances			
Mn–N	2.102 (7)	Mn–Cl	2.037 (10)
Mn–C2	2.113 (9)	Mn–C3	2.200 (9)
Mn–C10	1.793 (8)	Mn–C11	1.777 (10)
Mn–C12	1.807 (10)	N–Cl	1.430 (11)
N–C6	1.520 (13)	N–C7	1.485 (11)
C1–C2	1.349 (12)	C2–C3	1.424 (11)
C3–C4	1.507 (13)	C4–C5	1.506 (14)
C10–O10	1.156 (11)	C11–O11	1.163 (13)
C12–O12	1.159 (12)		
Bond Angles			
N–Mn–Cl	40.4 (3)	N–Mn–C2	69.1 (3)
C1–Mn–C2	37.9 (3)	N–Mn–C3	81.5 (3)
C1–Mn–C3	70.0 (4)	C2–Mn–C3	38.5 (3)
N–Mn–C10	94.1 (4)	C1–Mn–C10	100.7 (4)
C2–Mn–C10	131.4 (4)	C3–Mn–C10	169.8 (4)
N–Mn–C11	158.8 (3)	C1–Mn–C11	118.7 (4)
C2–Mn–C11	94.6 (4)	C3–Mn–C11	94.2 (4)
C10–Mn–C11	86.7 (4)	N–Mn–C12	106.9 (4)
C1–Mn–C12	142.8 (4)	C2–Mn–C12	129.7 (4)
C3–Mn–C12	91.5 (4)	C10–Mn–C12	98.5 (4)
C11–Mn–C12	93.9 (4)	Mn–N–Cl	67.3 (5)
Mn–N–C6	130.6 (5)	C1–N–C6	117.2 (7)
Mn–N–C7	117.4 (6)	C1–N–C7	115.6 (7)
Mn–C1–C2	74.1 (6)	Mn–C1–N	72.3 (5)
Mn–C2–C1	68.0 (6)	N–C1–C2	118.7 (7)
C1–C2–C3	122.7 (8)	Mn–C2–C3	74.1 (5)
Mn–C3–C4	125.4 (7)	Mn–C3–C2	67.5 (5)
C3–C4–C5	114.6 (8)	C2–C3–C4	121.5 (8)
Mn–C11–O11	177.8 (7)	Mn–C10–O10	174.8 (9)
Mn–C12–O12	179.1 (9)		

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviations for (1-Piperidyl-η^3-pentenyl)tricarbonylmanganese (6)

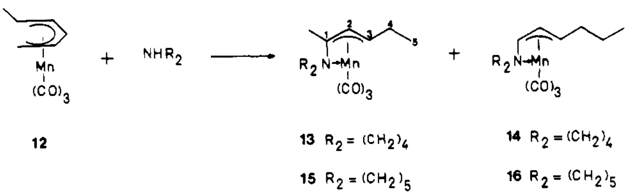
Bond Distances			
Mn–N	2.144 (6)	Mn–C1	2.074 (9)
Mn–C2	2.111 (10)	Mn–C3	2.167 (9)
Mn–C11	1.810 (9)	Mn–C12	1.775 (8)
Mn–C13	1.822 (9)	N–Cl	1.410 (11)
N–C6	1.505 (10)	N–C7	1.496 (10)
C1–C2	1.414 (11)	C2–C3	1.394 (13)
C3–C4	1.538 (11)	C4–C5	1.513 (14)
C11–O11	1.145 (12)	C12–O12	1.156 (10)
C13–O13	1.147 (11)		
Bond Angles			
N–Mn–C1	39.0 (3)	N–Mn–C2	68.9 (3)
C1–Mn–C2	39.5 (3)	N–Mn–C3	82.5 (3)
C1–Mn–C3	71.5 (3)	C2–Mn–C3	38.0 (3)
N–Mn–C11	95.4 (3)	C1–Mn–C11	101.5 (4)
C2–Mn–C11	133.4 (4)	C3–Mn–C11	171.3 (4)
N–Mn–C12	157.0 (3)	C1–Mn–C12	118.2 (4)
C2–Mn–C12	93.6 (4)	C3–Mn–C12	92.8 (4)
C11–Mn–C12	85.8 (4)	N–Mn–C13	107.5 (3)
C1–Mn–C13	142.6 (4)	C2–Mn–C13	129.2 (4)
C3–Mn–C13	91.5 (4)	C11–Mn–C13	97.2 (4)
C12–Mn–C13	95.1 (4)	Mn–N–C1	67.8 (4)
Mn–N–C6	126.6 (4)	C1–N–C6	119.1 (7)
Mn–N–C7	116.8 (5)	C1–N–C7	113.8 (6)
Mn–C1–C2	71.7 (5)	Mn–Cl–N	73.2 (5)
Mn–C2–C1	68.9 (5)	N–Cl–C2	117.0 (7)
C1–C2–C3	124.0 (8)	Mn–C2–C3	73.2 (6)
Mn–C3–C4	124.3 (6)	Mn–C3–C2	68.8 (5)
C3–C4–C5	113.3 (8)	C2–C3–C4	116.9 (8)
Mn–C11–O11	173.6 (8)	Mn–C12–O12	176.2 (8)
Mn–C13–O13	178.9 (7)		

Scheme I



(**5–10**) (Scheme I), which were isolated in fair yields as yellow crystalline solids or yellow liquids. The complexes **5–10**, which closely resemble one to another, are slightly air sensitive and readily soluble in organic solvents. Spectroscopic characterization proved that the nitrogen has been added stereospecifically to the terminal carbon atom on the pentadienyl ligand and also coordinates to the manganese atom. The proton abstraction from the NH group occurs with formation of the neutral substituted aminopentenyl derivatives in which the nitrogen atom acts as a σ-donor ligand in order to achieve stable 18-electron species.

When a stoichiometric ratio of reactants was used, the reaction, monitored qualitatively by infrared spectroscopy, Scheme II



showed that no considerable conversion to products took place, from where it is clear that an excess of ligand is always necessary. The reaction rate was also shown to depend on the concentration of the ligand (see compound **5**, Table I). However, the role of the basicity of the amine is not clear because piperidine and morpholine afford quite similar results (Table I). Reactions between **2** and an excess of aniline (1:20) or benzylamine (1:40) did not afford the corresponding aminopentenyl species, even after refluxing in cyclohexane during 15 and 20 h, respectively. These facts contrast with the reaction products obtained from benzylamine and the isoelectronic pentadienyltricarbonyliron cation, which affords the corresponding (dienylamine)iron tricarbonyl complex.[27]

Apparently, steric reasons prevent addition reactions of methyl-substituted piperidines ($C2(CH_3)$ and $C2,C6(CH_3)_2$) to **2** even after 7 h under reflux, while trimethylamine did not undergo an addition reaction, since **2** is recovered after 3 h of heating in a vacuum-sealed ampule.

Treatment of *syn*-(1-methylpentadienyl)tricarbonylmanganese (**12**) with pyrrolidine or piperidine in stoichiometric ratios 1:8 lead to two different regioisomers **13**, **14** and **15**, **16**, respectively (Scheme II).

The attack of the nucleophile for the unsymmetrically substituted pentadienyl **12** is not preferential at the least hindered carbon, as observed for **13** and **15**. The regioisomers are in equilibrium, and the isomer ratios found were 60:40 for **13**, **14** and 50:50 for **15**, **16**. ^1H NMR spectroscopy showed that an interconversion takes place when **15** and **16** are heated in refluxing cyclohexane for 32 h, giving an isomer ratio 25:75, thus suggesting that **13** and **15** are the kinetic products while **14** and **16** are the thermodynamic products.

The nonregioselective attack at C1 and C5 may be rationalized on the basis of weak steric effects and predominant charge control effects on C1 by the methyl substituent. Similar reactivity patterns with carbon nucleophiles[18] or hydrides[17] and η^5-1-substituted pentadienyltricarbonyliron cations have been reported.

In all aminopentenyl derivatives **5**–**10** and **13**–**16** the nitrogen is in the anti conformation, a fact caused by the stereochemical requirement that the pentenyl ligand is forced to adopt in order to bond satisfactorily to the manganese atom.

Infrared and Mass Spectra. The metal carbonyl fragments in complexes **5**–**10** and **15**, **16** produce three strong ν(CO) absorption bands in the infrared region (Table VII). The observed intensity pattern is consistent with the *fac* arrangement for the three carbonyl groups in a pseudooctahedral complex.[28] The ν(CO) pattern is very similar to that observed for unsymmetrical tricarbonyl complexes $Mn(\eta^3\text{-}C_5H_7)(CO)_3L^2$ and $Mn(\eta^3\text{-}C_3H_5)(CO)_3L$,[28,29] although smaller frequencies are found that reflect the reduced π-back-bonding capability of the nitrogen atom and the negative charge enhancement on the manganese atom (Table VII), and thus, from the IR data it becomes clear that aminopentenyl ligands act as good electron donors.

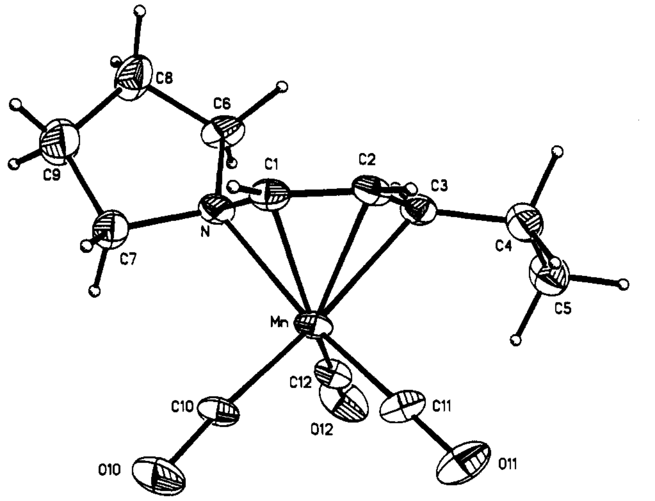


Figure 1. Perspective molecular view of (1-pyrrolidyl-η^3-pentenyl)tricarbonylmanganese (**5**).

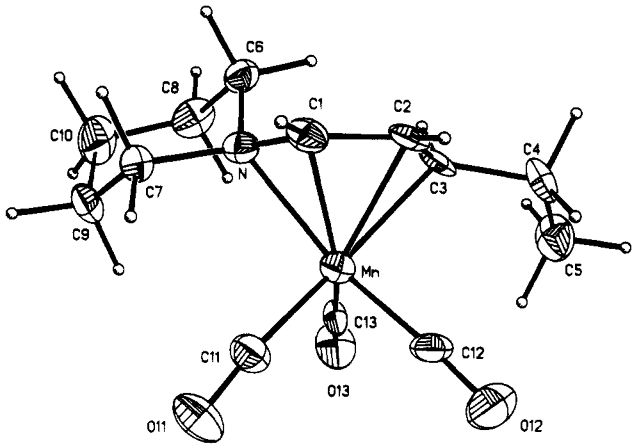


Figure 2. Perspective molecular view of (1-piperidyl-η^3-pentenyl)tricarbonylmanganese (**6**).

Further evidence that the amine has been added to the pentadienyl ligand comes from the mass spectra of **5**–**10**, since in all cases the molecular ion is observed and the base peak corresponds to the fragment [amine–pentenyl]$^+$. There is no indication of a [Mn–amine]$^+$ fragment, and this pattern differs from that found in the mass spectrum of **3**, in which [Mn–phosphine]$^+$ is present but a [pentadienyl–phosphine]$^+$ ion is absent.[30] The mass spectra also confirm that all complexes contain three carbonyl groups.

Crystallographic Studies for (1-Pyrrolidyl-η^3-pentenyl)tricarbonylmanganese (5) and (1-Piperidyl-η^3-pentenyl)tricarbonylmanganese (6). The molecular structures of **5** and **6** are shown in Figures 1 and 2. Pertinent positional, bonding, and thermal parameters may be found in Tables III–VI, while least-squares plane information and structure factor tables are available as supplementary material. The single-crystal X-ray structural analyses of **5** and **6** confirm the unprecedented formation of novel (1-amino-η^3-pentenyl)tricarbonylmanganese complexes, in which the aminopentenyl ligand is bonded to a manganese center through an η^3-fashion and

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Table VII. Frequencies of CO Stretching Modes (cm^{-1}) for the Aminopentenyl Tricarbonyl and Tetracarbonyl Complexes[a]

complex	ν(CO)					
	hexane			chloroform		
5	2000	1920	1900	1990	1900	1870
6	2000	1920	1900	1990	1910	1882
7	2005	1922	1905	2000	1914	1898
8	2003	1918	1902	1998	1911	1889
9	2003	1919	1902	1990	1905	1875
10[b]	2003	1918	1899			
15, 16[b]	2001	1918	1902			
5a	1976	1899	1880	1969	1890	1871
6a	1977	1901	1881	1972	1888	1875
9a[b]	1975	1896	1880	1963	1880	1859
6b	2004	1989 (w)	1920, 1905			
11b	2045	1985 (m)	1960, 1920 (m)	2040	1945 (vs, br)	1920 (sh)

[a] All bands have strong intensity. [b] In cyclohexane.

Table VIII. ^1H NMR Data (δ) for the Aminopentenyl Complexes[a]

complex	H1	H2	H3	H4	H5	R₂									
						H6		H7		H8		H9		H10	
						H_{eq}	H_{ax}	H_{eq}	H_{ax}	H_{eq}	H_{ax}	H_{eq}	H_{ax}	H_{eq}	H_{ax}
5	5.55 (d, 3.0)	4.60 (dd, 9.1)	2.05–2.30 (m)	1.77, 1.93 (m, 6.1)	1.2 (t, 7.3)	2.2 (m)		2.87 (m)		1.64 (br)		1.64 (br)			
5[b]	4.65 (d, 3.0)	4.0 (dd, 9.1)	1.65–1.8 (m)	1.55, 1.68 (m, 6.1)	1.0 (t, 7.3)	1.7 (m)		2.05 (m)		0.7 (br)		0.7 (br)			
6	5.45 (d, 5.0)	4.55 (dd, 10)	1.2–2.1 (m)	1.2–2.1 (m)	1.2 (t, 7.5)	1.1–2.1 (m)		2.85 (dd, 7.7)		1.1–2.1 (m)		1.1–2.1 (m)		1.1–2.1 (m)	
6[b]	4.83 (d, 5.1)	4.22 (dd, 9.6)	1.86–2.04 (m)	1.86–2.04 (m)	1.31 (t, 7.7)	1.5 (m)	1.0 (m)	2.52 (dd, br)	2.12 (dt, 2.6, 11.8)	1.1–1.2 (m)	0.96 (m)	1.1–1.2 (m)	1.23–1.39 (m)	0.78 (m)	0.63 (m)
7	4.39 (d, 3.9)	3.80 (dd, 11.5)	1.50 (m)	1.50 (m)	0.90 (t, 7.7)	0.90 (m)		1.95 (m)		2.55 (m)		2.89 (m)			
8	5.40	4.45	1.5–2.1 (m)	1.5–2.1 (m)	0.8–1.2 (t)	2.2–3.0 (m)		2.2–3.0 (m)		1.5–2.1 (m)		1.5–2.1 (m)			
9	5.65 (d, 4.5)	4.65 (dd, 10.5)	1.6–2.2 (m)	1.6–2.2 (m)	0.84 (t)	2.65 (m)		2.98 (m)		1.15 (t)		1.30 (t)			
10	5.55 (d)	4.5	0.5–2.0 (m)	0.5–2.0 (m)	1.1 (t)	0.5–2.0 (m)		2.42 (s)		0.5–2.0 (m)		0.5–2.0 (m)		0.5–2.0 (m)	
13[b,c]		4.10 (d, 8.3)	1.7–2.0 (m)	1.7–2.0 (m)	1.27 (t, 7)	1.37 (m)		2.7 (d)	2.2 (m)	0.77 (m)		0.77 (m)			
14[b,d]	4.76 (d, 2.8)	4.19 (dd, 9.4)	1.7–2.0 (m)	1.7–2.0 (m)	1.5–1.7 (m, 7)	1.2–1.4 (m)		2.2 (m)		0.77 (m)		0.77 (m)			
15[c]		4.35 (d, 11.3)	1.4–2.0 (m)	1.4–2.0 (m)	1.15 (t, 7)	1.2–2.0 (m)		2.99 (dd, br)	2.7 (t, br)	1.2–2.0 (m)		1.2–2.0 (m)		1.2–2.0 (m)	
16[d]	5.40 (d, 3.8)	4.50 (dd, 11.3)	1.4–2.0 (m)	1.4–2.0 (m)	1.4–2.0 (m)	1.2–2.0 (m)		2.8 (dd, br)	1.2–2.0 (m)	1.2–2.0 (m)		1.2–2.0 (m)		1.2–2.0 (m)	
6b[b]	4.40 (d, 12.5)	3.50 (t, 10)	1.6–1.85 (m)	1.6–1.85 (m)	1.16 (t, 7.5)	2.32 (m)		2.32 (m)		1.16–1.4 (m)		1.16–1.4 (m)		1.16–1.4 (m)	
11[b]	4.93 (d, 11.3)	3.52 (t, 10.8)	1.8–2.02 (m)	1.8–2.02 (m)	1.10 (t, 6.8)	2.50 (s)		2.50 (s)							

[a] For numbering, see Figure 2. In $CDCl_3$ relative to Me_4Si (δ = 0), 300 MHz, *J* value (Hz) in parentheses. [b] In C_6D_6. [c] For numbering, see Scheme II. CH_3(C1), δ = 1.87 (s) (**13**), 2.38 (s) (**15**). [d] CH_3(C5), δ = 0.99 (t, 7.2) (**14**), 0.92 (t, 7.5) (**16**).

also by the nitrogen coordination. The nitrogen atom is bonded in an anti fashion in the allyl fragment in order to achieve an 18-electron complex, and both compounds adopt an approximately octahedral coordination geometry around the manganese atom.

The average manganese carbonyl distances, excluding the CO groups opposite to nitrogen, are 1.80 and 1.81 Å for **5** and **6**, respectively. Some shortening of the manganese–carbonyl distance in the remaining CO group would be expected due to the trans effect of the amine group, and indeed an average of 1.78 Å was found; although the differences are not quite large, they are in reasonable good agreement with those found in similar manganese–carbonyl complexes.[2,20,23]

The bond distances C1–N [1.430 (11) for **5** and 1.411 (11) Å for **6**] reflect that some charge delocalization is present in both species, since a C–N bond length for sp^3-N and sp^2-N accounts for 1.47 and 1.36 Å, respectively.[31] The coordinated nitrogen–manganese bond is slightly shorter in **5** as compared to that in **6** as a result of the different Mn–N–C7 bond angles 130.6 (5) and 116.8 (5)°, respectively, derived from the corresponding conformation of the amine. The η^3-pentenyl fragment bonded to the metal is not symmetrical, since the manganese–carbon distances are different with Mn–C1 = 2.037 (9) and 2.074 (9) Å, Mn–C2 = 2.113 (10) and 2.111 (10) Å, and Mn–C3 = 2.200 (9) and 2.167 (9) Å for complexes **5** and **6**, respectively. The central carbon–metal bonds are quite similar to distances found in pentadienyl and symmetric allyl systems, such as $Mn(\eta^3\text{-}C_5H_7)(CO)_3PMe_3$ (2.116 (10) Å),[2] $Mn(\eta^3\text{-}C_5H_7)(dmpe)_2$ (2.10 (2) Å),[32] or $Mn(\eta^3\text{-}C_3H_5)(CO)_2[P(OMe)_3]_2$ (2.114 (15) Å).[28] Meanwhile, the substituted allyl carbon atoms C3 show shorter distances to the metal atoms than in pentadienyl complexes.[2,32]

The C1–C2 bond in **5** appears to be anomalously short in comparison to **6**, 1.349 (12) Å, and although one could attribute this to an artifact of the data set, a similar short bond has been reported for CH_2–CH (1.349 (5) Å), in the oxopentadienyl complex $Mn(\eta^5\text{-}CH_2CHCHCOCH_3)(CO)_3$.[20] No such difference is observed for C3–C4, but the larger standard deviations make a significant comparison impossible. Probably, the high observed standard deviations observed are associated with the Cu radiation source used, since a similar situation is described for $Mn(\eta^5\text{-}CH_2CHCHCOCH_3)(CO)_2PPh_3$ where Cu Kα radiation was also used.[20]

The piperidine derivative **6** shows a chair conformation both in solution and in the solid state, as established by ^1H NMR spectroscopy and crystallographic studies.

Torsion angles [C6–N–C1–C2 = −65.5 (1.1)° for **5** and −62.2 (1.0)° for **6** and C7–N–C1–C2 = 170.5 (0.9)° for **5** and 169.0 (0.8)° for **6**] reflect the different character of C6 and C7 in both species. While C7 atoms are nearly on the plane of the delocalized system, C6 atoms are out of the plane. This feature is clearly distinguished by ^{13}C NMR spectroscopy and also supported by theoretical studies (vide infra).

Charge Distribution Study. A theoretical analyses by the relativistic ITEREX-85[33a] and nonrelativistic ICON8[33b] extended Hückel programs afforded basically the same information about overlap between orbitals. For net charges we used the charge-iterative calculations within the ITEREX-85 procedure. Geometrical parameters from X-ray data have been used for both programs.

An exploration of the charge distribution of complexes **5** and **6** gave results that are in good agreement with the crystal structure of both compounds, since excellent fits were obtained.

The diastereotopic pair C6 and C7 in complexes **5–10** and **13–16** motivated us to investigate charge distributions in the title (aminopentenyl)manganese complexes.

For compounds **5** and **6** there is no interaction between Mn 3d orbitals and the 2p orbitals from C6 and C7. However, these last orbitals do have an interaction with the 2s and 2p orbitals from the nitrogen atom. Nevertheless, this interaction is very weak, being 1.77% higher for C7 as compared to C6. Contrastingly, the mixing between p orbitals from C6 or C7 and C1 allows a stronger interaction between C7 and C1 than between C6 and C1, even when bond distances are 2.44 and 2.51 Å, respectively. The atomic charges show positive interactions between the delocalized fragments N–C1–C2–C3 in both complexes, the highest observed interactions being for Mn←N and Mn–C2.

The most interesting feature of the net charge analyses is that the (aminopentenyl)manganese fragment is very similar in **5** and **6**, while the cyclic $N(R_2)$, $R_2 = (CH_2)_n$ (n = 4, 5), fragments show an appreciable difference (17%). The balance of the charge in each compound reflects the highest electronegativity of piperidine as compared to pyrrolidine. Also of relevance is the localization of charge observed for C1 and C2 in **5**.

Finally, there is evidence for hydrogen–hydrogen interactions between H1, the two hydrogens at C6, and those of C7 in **6**. The strongest interaction is that between H1 and the equatorial H7 atom, which is 12 times higher than that between H1 and the equatorial H6 atom.

NMR Spectroscopy. ^1H and ^{13}C NMR data for aminopentenyl complexes are listed in Tables VIII and IX, respectively. The similarity of the NMR spectra of **7–10** to those of **5** and **6** led us to believe that all these complexes have the same pentenyl ligand conformation. The most characteristic feature in the ^1H NMR spectra of complexes **5–10** is a downfield doublet signal ($\delta \sim 5.4$) for H1 and a double of doublets for H2 ($\delta \sim 4.5$). The coupling constants $J_{1,2} \cong 4$ Hz and $J_{2,3} \cong 10.3$ Hz indicate that H1 and H2 are syn, whereas H2 and H3 are anti. In addition H2 appears always at lower fields than H3, a situation that suggests, as in previously related complexes,[2] that there is an anti conformation in the pentenyl ligand. The signals due to H3 and to the diastereotopic methylene hydrogens H4 were overlapped except for complexes **5** and **9** (Table VIII). However, the assignments can be made by the combined use of ^1H–^1H and ^1H–^{13}C shift-correlated 2D spectra. The methyl group is clearly observed as a triplet at high field in each case. The $^{13}C\{^1H\}$ NMR spectra were assigned unambiguously and show that all the carbon atoms of the new complexes are nonequivalent, suggesting restricted rotation around the C–N bond due to the nitrogen coordination to manganese. Perhaps, the most characteristic spectral feature of compounds **5–10** is the wide $\Delta\delta$ found for α-carbons C6 and C7 on the amine residue. The high chemical shift of C1 ($\delta \sim 85$) reflects the addition of nitrogen to this atom, since a common "allyl" system, such as $Mn(\eta^3\text{-}CH_2CHCHCH_2CH_3)(CO)_4$ shows signals at δ = 37.0, 92.7, 71.0, 28.7, and 17.2 ppm, respectively.[34]

By use of double-resonance techniques and due to the different abundances, the assignment of the individual

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Table IX. ^{13}C NMR Data (δ) for the Aminopentenyl Complexes[a]

						R$_2$				
complex	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
5	87.4	92.1	64.0	28.0	17.4	51.8	64.0	24.1	24.6	
	(d, 189)	(d, 156)	(d, 156)	(t, 117)	(q, 130)	(t, 143)	(t, 143)	(t, 130)	(t, 130)	
5[b]	86.4	90.8	62.4	27.1	16.3	50.2	62.6	22.5	23.1	
6	85.7	92.5	64.5	28.4	17.4	46.3	64.4	23.7	26.6	23.4
	(d, 189)	(d, 152)	(d, 168)	(t, 137)	(q, 122)	(t, 137)	(t, 137)	(t, 137)	(t, 137)	(t, 137)
6[b]	85.7	92.4	64.1	28.7	17.6	45.9	64.1	23.5	26.5	23.3
7	82.7	91.3	63.2	27.3	16.2	44.4	61.6	62.9	65.3	
8	84.7	92.5	64.5	28.2	17.2	46.3	64.4	43.5	43.6	
9	86.4	91.3	63.5	26.9	16.0	39.6	57.5	11.5	12.6	
13[b,c]	97.3	92.8	61.8	28.5	17.8	50.0	57.9	22.7	23.5	
14[b,d]	87.4	92.4	61.1	37.4	26.6	51.3	63.7	23.7	24.3	
15[c]	*e*	91.2	61.5	25.9	16.5	43.5	60.1	22.7	25.5	22.3
16[d]	84.6	91.9	60.9	36.4	27.2	45.3	63.5	22.7	25.1	22.4
5a[f]	103.3	72.9	54.7	29.4	17.8	50.6	50.6	24.2	24.2	
6a[f]	101.0	73.1	55.5	29.1	17.6	51.7	51.7	24.7	24.7	23.9
6b	113.0	65.5	51.6	30.8	18.7	51.7	51.7	25.1	25.1	24.2
11b	115.4	65.2	50.9	30.1	18.0	42.1	42.1			
	(d, 172)	(d, 153)	(d, 153)	(t, 126)	(q, 134)	(q, 134)	(q, 134)			

[a] For numbering, see Figure 2. In $CDCl_3$ relative to Me_4Si ($\delta = 0$), 75.43 MHz. [b] In C_6D_6. [c] For numbering, see Scheme II. CH_3(C1), δ = 16.9 (**13**), 15.5 (**15**). [d] CH_3(C5), δ = 14.1 (**14**), 12.9 (**16**). [e] Not observed. [f] PMe_2Ph, **5a**, δ = 15.9, 128.3–129.2. ^{31}P NMR (36.23 MHz, $CDCl_3$), δ = 27.7 (**6a**), 16.2, 128.7–129.5. ^{31}P δ = 26.9.

resonances of **13** and **14** are straightforward and can further be extrapolated to **15** and **16**, the pertinent results being given in Tables VIII and IX. The quaternary carbon signal for C1 in **13** provides evidence for the nitrogen addition to the more substituted carbon, and the regioisomers **14** and **16** can easily be compared to **5** and **6**.

Reactivity of $\mathbf{Mn{\leftarrow}N(R_2)(\eta^3\text{-}CH{\cdots}CH{\cdots}CHCH_2CH_3)(CO)_3}$. In an attempt to confirm the presence of a labile coordinate bond Mn←N in compounds **5**–**10**, the complexes **5a**, **6a**, **9a**, **6b**, and **11b** were prepared and isolated as oily products (Scheme I). The complexes **5**, **6**, and **9** were treated with 1 equiv of PMe_2Ph in cyclohexane, thus affording the lemon yellow complexes $Mn(\eta^3\text{-}CH(NR_2){\cdots}CH{\cdots}CHCH_2CH_3)(CO)_3PMe_2Ph$ ($R_2 = (CH_2)_4$ (**5a**) $R_2 = (CH_2)_5$ (**6a**), and R = Et (**9a**), respectively). When **2** reacts with an excess of piperidine (1:6) or dimethylamine (1:30) in cyclohexane in a vacuum-sealed ampule, without the addition of carbon monoxide, the golden yellow complexes $Mn(\eta^3\text{-}CH(NR_2){\cdots}CH{\cdots}CHCH_2CH_3)(CO)_4$ ($R^2 = (CH_2)_5$ (**6b**), R = Me (**11b**)) are formed, respectively.

A remarkable aspect of the last reaction is that it is reversible (Scheme I), since **6b** in refluxing cyclohexane under a nitrogen stream during 10 h leads to a color change from golden yellow to pale yellow and the loss of CO is evidenced by a tricarbonyl pattern in the CO stretching region of the IR spectrum (Table VII). Also, consistent with the formation of **6** (92.5% yield) are the NMR (Tables VIII and IX) and mass spectral data.

The reaction of **2** with dimethylamine in deuterated benzene was followed by ^{1}H NMR spectroscopy, thus showing the initial formation of the complex $Mn{\leftarrow}NMe_2(\eta^3\text{-}CH{\cdots}CH{\cdots}CHCH_2CH_3)(CO)_3$ (**11**) as an intermediate, which later affords the isolated complex **11b**.

Infrared and Mass Spectra. The tetracarbonylmanganese complexes **6b** and **11b** exhibit a typical pattern for octahedral *cis*-$M(CO)_4L_2$ species,[35] the ν(CO) bands appearing at smaller wavenumbers than those of similar tetracarbonyl species.[36] This reflects the influence of the nitrogen ligand bonded to the allyl fragment, which prevents, even uncoordinated from the metal, effective π back-bonding through the π-allyl–manganese system, increasing this effect on the CO groups.

In the infrared spectra of **5a**, **6a**, and **9a** the three ν(CO) bands appear at lower frequency than those for **5**, **6**, and **9** (Table VII), suggesting that in these systems the phosphine is acting as a stronger electron donor to the metal than the amine. Comparison between analogue phosphine derivatives of oxodienyl or pentadienyl[37] complexes and **5a**, **6a**, and **9a** clearly shows that π back-bonding increases substantially at CO groups in the amino derivatives. These data confirm the σ-donor ability of the nitrogen ligand already described for the nitrogen-coordinated species **5**–**10** and also the low contribution for π back-bonding through the allyl–nitrogen fragment. It can be generalized that the electron density on the manganese increases, according to the atom substituted in the dienyl or enyl fragment, in the following order: N > C > O. The same trend has been observed for η^5-aza- and η^5-oxopentadienyl species and η^5-pentadienyl itself.[20]

Addition of PEt_3 to **5** results in IR band positions at ν(CO) 1974, 1886, and 1877 cm^{-1} (cyclohexane) almost identical with those observed for isolated species (Table VII), although we were unable to isolate the pure compound. No reaction between **5** and an excess of PPh_3 took place after 5 h in refluxing cyclohexane.

In contrast to our results, it has been recently reported that the azapentadienyl complexes $Mn(\eta^5\text{-}CH_2CHCHC(CH_3)NR(CO)_3$ [R = $CH(CH_3)_2$, $C(CH_3)_3$] do not react with tertiary phosphines.[20]

The mass spectra of the tetracarbonyl complexes **6b** and **11b** and of the tricarbonyl complexes with PMe_2Ph (**5a**, **6a**, **9a**) show the familiar stepwise loss of carbonyl groups. The molecular ions are observed for **6a**, **6b**, **9a**, and **11b**, and the $[C_5H_8NR_2]^+$ fragment has the highest intensity for compounds **5**–**10** (vide supra). In the case of **5a** the base peak could correspond either to $[C_5H_8NR_2]^+$ or to $[PMe_2Ph]^+$, but according to the intensity ratio of this fragment in **6a** and **9a** and the similar pattern observed in all spectra, we propose that the $[C_5H_8NR_2]^+$ fragment is more probable.

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(36) IR spectral data (ν(CO), cm^{-1}) are as follows: $Mn(\eta^3\text{-}CH_2CHCHCOOCH_3)(CO)_4$, 2082, 2065, 1992, 1965 (CH_2Cl_2);[20] $Mn(\eta^3\text{-}C_5H_7)(CO)_4$, 2062, 1995, 1976, 1966 (hexane);[35] $Mn(\eta^3\text{-}C_6H_9)(CO)_4$, 2055, 1987, 1970, 1959 (CH_2Cl_2);[16] $Mn(\eta^3\text{-}C_3H_5)(CO)_4$, 2072 (m), 1995 (m), 1978 (s), 1963 (s) (cyclohexane).[29]

(37) IR spectral data (ν(CO), cm^{-1}) are as follows: $Mn(\eta^3\text{-}CH_2CHCHCOOCH_3)(CO)_3PMe_3$, 2014, 1933, 1914 ($CH_2Cl_2$);[20] $Mn(\eta^3\text{-}CH_2CHCHCHCH_2)(CO)_3PR_3$, R = Me, 2000, 1973, 1905; $R_3 = Me_2Ph$, 2000, 1935, 1903 (Nujol).[2]

NMR Studies. The ^{1}H NMR spectra of **6b** and **11b** are consistent with a syn configuration for the amino-η^3-pentenyl ligand, as indicated by the coupling constants $J_{12} \cong 12$ Hz and $J_{23} \cong 10.5$ Hz (Table VIII), and provide evidence for the absence of nitrogen coordination to manganese. Unfortunately, useful NMR data for phosphine complexes were difficult to attain due to an important signal broadening that causes a loss of resolution of the obtained spectra, thus precluding any interpretation. However, good ^{13}C NMR spectra of tetra- and tricarbonyl complexes **5a**, **6a**, **6b**, and **11b** (Table IX) confirm conclusions based on the ^{1}H NMR data of **6b** and **11b** and also show strong evidence for the absence of Mn←N coordination, thus demonstrating the weakness of this bond, which is evidenced by the magnetic equivalence of the α,α'-carbons (C6, C7) and the β,β'-carbons (C8, C9).

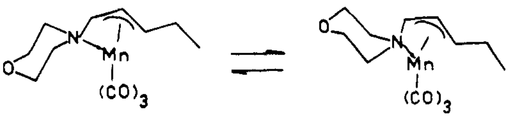
Also, the resonance of C1, which appears at $\delta \cong 114$ ppm, clearly indicates the enamine character of this carbon atom as compared to C1 in **5**–**10**, in which a degree of delocalization is reflected from the $\delta \simeq 85$ ppm values (Table IX). Finally, there is a strong high-field shift for the signals due to C2 and, to a lesser extent, for those of C3, a situation that is unusual for allyl systems. This would require a definitive X-ray test, but unfortunately compounds **5a**, **6a**, **6b**, **9a**, and **11b** failed to crystallize in our hands.

Discussion

It has been possible to prepare a variety of aminopentenyl complexes by a regioselective reaction. A key to the isolation of such complexes seems to be the utilization of strong basic amines. The stereochemistry of the addition of amines to isoelectronic species, such as $[Fe(\eta^5\text{-}C_5H_7)(CO)_3]^+$ [27] and [Fe(*syn*,*syn*-1,5-dimethylpentadienyl)$(CO)_3]^+$,[38] has been shown to depend on the basicity of the amine. Hence, the addition of the amine, as for manganese neutral complexes, is always at the terminal carbon atom, being isolated from strongly basic amines, such as for Fe(*syn*,*anti*-dienylamine)$(CO)_3$ complexes.[27]

A detailed NMR study of complex **6** in deuterated benzene shows that coordination of nitrogen to manganese fixes the configuration at the quaternized atom, with the consequent formation of a diastereotopic center, which is reflected by the total asymmetry of the molecule. A chair conformation of the piperidine ring with the metal atom in an axial position is established from the ^{1}H NMR spectrum at room temperature. The absence of a symmetry plane perpendicular to the heterocycle plane permits one to observe the 10 protons from the piperidine ring. Equatorial and axial hydrogen atoms appear as separate signals for the piperidine ring, the equatorial atoms being more shifted to low field than the corresponding axial protons, with the exception of H9. The former appear as broad signals due to complex coupling patterns, whereas axial hydrogen atoms are comparatively sharp signals. All hydrogens are assigned on the bases of ^{1}H–^{1}H and ^{1}H–^{13}C correlation spectra as well as a ^{1}H-gated-decoupled ^{13}C NMR spectrum. The stereochemistry of **6** was also established with a NOE experiment. The signal at $\delta = 2.85$ assigned to hydrogen atoms from the α-carbon C7 ($\delta = 64$) was irradiated, producing an increase (~15%) in the intensity of the signal at δ 5.45. Thus, in **6** the equatorial hydrogen atom at C7 has a spatial interaction with the corresponding hydrogen at C1. This is precisely what is reflected by the theoretical analysis.

Scheme III



As already mentioned, both in solution and in the solid state **6** adopts the same conformation (Figure 2), in contrast to the behavior of **7** in which a dynamic process is detected at room temperature by ^{1}H NMR measurements. Since there may be two reasons accounting for such a dynamic process, which are the weaker Mn←N bond and the presence of the ring oxygen atom that is not contributing to the 1,3-diaxial interaction in the morpholine complex **7**, we obtained evidence for a conformational equilibrium between the two chair conformers (Scheme III) as deduced from four broad multiplet signals arising from an average between the equatorial and axial hydrogen atoms. This is supported by a ^{1}H–^{1}H COSY spectrum, which shows exclusive correlation between signals at δ 2.89 and 1.95 ppm and δ 2.55 and 0.90 ppm (Table VIII). The ^{1}H–^{13}C HETCOR contour plot confirms conclusions based on the ^{1}H NMR studies, since the four broad 1 H multiplets corresponds to four different carbon signals. Therefore it seems that the conformational mobility of the six-membered ring is mainly due to the absence of 1,3-diaxial interactions, since otherwise for instance the equatorial hydrogen α to the nitrogen atom would be averaged.

An attempt to perform addition of pyrrolidine to **3**[2] [^{31}P NMR (36.23 MHz, $CDCl_3$, δ 38.0)] after 9 h in refluxing cyclohexane was unsuccessful, since it afforded the CO-substitution compound $Mn(\eta^5\text{-}C_5H_7)(CO)_2PMe_2Ph$ (**4**)[2] [^{31}P NMR (36.23 MHz, $CDCl_3$, δ 49.8)] in 72% yield. The complex **4** was also unreactive toward an excess of pyrrolidine. The presence of the better donor PMe_2Ph coordinated to the manganese atom prevents the amine from attacking the pentadienyl ligand. This enhancement of charge on the manganese atom has also been reflected on the oxopentadienyl complex $Mn(\eta^5\text{-}CH_2CHCHCOR)(CO)_2PPh_3$, R = CH_3, OCH_3, in which PPh_3 deactivates the ketonic carbon toward an amine attack.[20]

Complex **2** has been shown to react with tertiary phosphines by an associative process involing an η^3-pentadienyl intermediate, such as **3**. There is also evidence that pentadienyl–transition-metal complexes present an enhanced reactivity as compared to their cyclopentadienyl analogues due to η^5–η^3 conversion in reactions with nucleophiles.[1,6] We therefore sought to obtain evidence for the intermediate species in the formation of the aminopentenyl complexes.

The reaction mechanisms between **2** and piperidine or dimethylamine were studied by ^{1}H NMR and IR methodology, whereby both failed to evidence the formation of a vinylic fragment, characteristic of an η^3-pentadienyl intermediate,[2,6] thus suggesting that an anti-Markownikoff addition is not involved. The lack of evidence for an associative mechanism in the acyclic pentadienyl ligand along with the proposed associative mechanism for the pyrrolyl compound $Mn(\eta^5\text{-}C_4H_4N)(CO)_3$[39] and their 3,4- and 2,5-dimethylpyrrolyl derivatives,[40] in which an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ ring slippage is involved, are in striking contrast. A similar interconversion feature has also been observed for pentadienyl- and cyclopentadienylvanadium carbonyl com-

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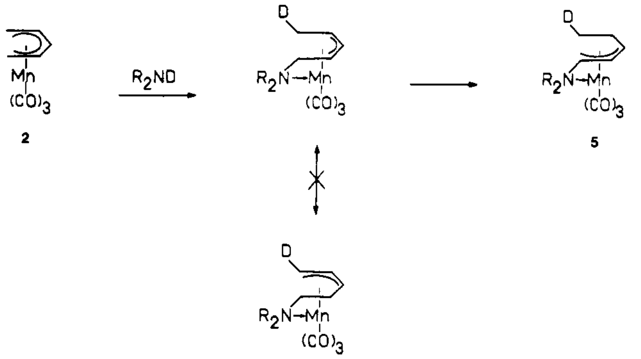
Scheme IV



plexes.[41] Therefore, in order to verify the role of η^3-intermediate 1 in the reaction, we performed the reaction between 1[42] and piperidine or diethylamine to produce compounds **6** and **9**, respectively. However, infrared monitoring of the reaction mixture for diethylamine showed first the formation of complex **2** and subsequently the formation of **9**. According to these and previously discussed results, along with the lack of evidence for metal hydride intermediates or nucleophilic attack on carbonyl groups, it might be possible to propose that the attack of the amine group occurs directly on the pentadienyl ligand through a 1,5-addition process. Furthermore, the reaction between the neutral complex **2** and the secondary amines, without involving nucleophilic attack at the metal atom, is in agreement with the absence of (dienylamine)-hydridemanganese tricarbonyl complexes, thus contrasting with the chemistry of cationic isoelectronic species,[27] which affords the stable butadienetricarbonyliron moiety. In order to gain further evidence for the reaction mechanism of **2** with secondary amines, an experiment using *N*-deuteriopyrrolidine was performed, from where the isotopically labeled species **5** with an approximate 50% of deuterium was isolated. Cogent structural evidence is provided by the proton-decoupled ^{13}C NMR spectrum, which shows the methyl signal of the undeuterated species at 16.34 ppm and the deuterated species as a triplet $^1J_{CD}$ = 19.6 Hz with a $^1\Delta$ DHIECS[43] of +0.3 ppm, as well as two signals for the methylene group at 27.11 and 27.02 ppm, thus reflecting a $^2\Delta$ DHIECS of 0.1 ppm. It is further relevant to mention that no deuterium incorporation was detected at C1, thus precluding a reversible isomerization process of the intermediate species involved on going from **2** to **5** (see Scheme IV). Therefore, it seems clear that an 1,5-addition mechanism is operating for the syntheses of these compounds.

Acknowledgment. We are indebted to CONACYT (México) and to Proyectos Estratégicos-SEP (México) for partial financial support. N.Z.V. thanks CONACYT for a research studentship. We also thank Dr. M. J. Rosales-Hoz for helpful discussions and Q. L. Velasco (Instituto de Quimica-UNAM) for the mass spectra.

Supplementary Material Available: Tables of atom coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates and temperature factors, torsion angles, and charge distributions (17 pages); tables of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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