Cycloaddition reactions of the manganese vinylidene $Cp'(CO)_2Mn=C=C(H)R$, carbyne $[Cp'(CO)_2Mn\equiv CCH_2R]^+$, and anionic carbene $[Cp'(CO)_2Mn=C(OEt)CHR]^-$ (R = H, Me) complexes with 1,4-diphenyl-1-azabutadiene

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Abstract

The reactivity of vinylidene $Cp'(CO)_2Mn=C=CH(R)$ (3a–b), cationic carbyne $[Cp'(CO)_2Mn\equiv CCH_2R]^+$ ($[2a-b]^+$), and anionic carbene $[Cp'(CO)_2Mn=C(OEt)CHR]^-$ ($[1a-b]^-$) complexes towards 1,4-diphenyl-1-azabutadiene (4) was examined. Complexes 3a–b react with 4 to give selectively the 2-azetidinylidene complexes $Cp'(CO)_2Mn=\overline{CN(Ph))CH(CH=CH(Ph))CH}(R)$ (5a–b) through net [2 + 2] cycloaddition reactions. The same complexes 5a–b were obtained upon treatment of $[2a-b]^+$ first with 4 followed by addition of triethylamine. By contrast, complexes $[1a-b]^-$ react with 4 to afford primarily the 2-tetrahydropyridinylidene complexes $Cp'(CO)_2Mn=\overline{CN(Ph)C(H)=C(H)CH(Ph)CH}(R)$ (8a–b), and the 2-dihydropyridinylidene complex $Cp'(CO)_2Mn=\overline{CN(Ph)-C(H)=C(H)C(Ph)=CH}$ (9a), resulting from net [2 + 4] cycloaddition reactions. The solid state structure of 9a was determined by X-ray crystallography.

Keywords: Manganese; Azabutadienes; Cycloadditions; X-ray structure; Carbene; Carbyne

1. Introduction

Some of us recently reported that both the neutral vinylidene complexes $Cp'(CO)_2Mn=C=CHR$ (Cp' = $\eta^5 - MeC_5H_4$, R = H, Me), or the cationic carbyne complexes $[Cp'(CO)_2Mn\equiv CCH_2R]^+$ can undergo a wide variety of addition and cycloaddition reactions with unsaturated nitrogen-containing substrates. Particularly, these complexes were found to react with N-benzylideneaniline to give the [2 + 2] cycloadducts $Cp'(CO)_2Mn=\overline{CN(Ph)CH(Ph)CH}(R)$ as final products [1]. With these results in mind, we thought about extending the scope of such reactions to α, β unsaturated imines for which the possibility of formation of [2 + 4] cycloadducts could also be considered [2]. We then envisioned that reaction of anionic carbene complexes $[Cp'(CO)_2Mn=C(OEt)CHR]^-$ with these α, β unsaturated substrates could also lead to cycloaddition prod-

ucts. Indeed, anionic carbene complexes resulting from deprotonation of alkylalkoxycarbene complexes possess in some aspect a chemistry similar to that of ester enolates [3], and this chemistry includes cycloaddition reactions with α, β unsaturated imines [4]. In this paper, we report our results concerning the comparative reactivity of cationic carbyne $[Cp'(CO)_2Mn\equiv CCH_2R]^+$ (R = H, Me), neutral vinylidene $Cp'(CO)_2Mn=C=CHR$, and anionic carbene $[Cp'(CO)_2Mn=C(OEt)CHR]^-$ complexes towards, 1,4-diphenyl-1-azabutadiene.

2. Results and discussion

The vinylidene complexes $Cp'(CO)_2Mn=C=CHR$ (3a–b; 3a: R = H, 3b: R = Me), generated in situ by reaction of $[Cp'(CO)_2Mn\equiv CCH_2R]^+$ ($[2a-b]^+$) with triethylamine at -78 °C in CH_2Cl_2 [1], react with 1,4-diphenyl-1-azabutadiene (4) to afford selectively the 2-azetidinylidene complexes $Cp'(CO)_2Mn=\overline{CN(Ph)}$-

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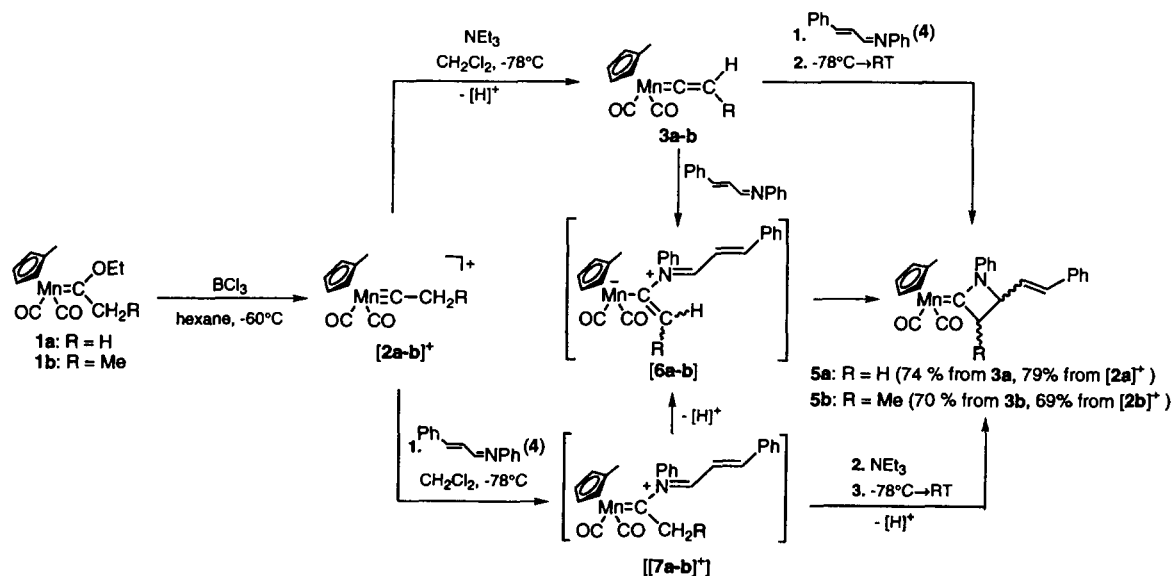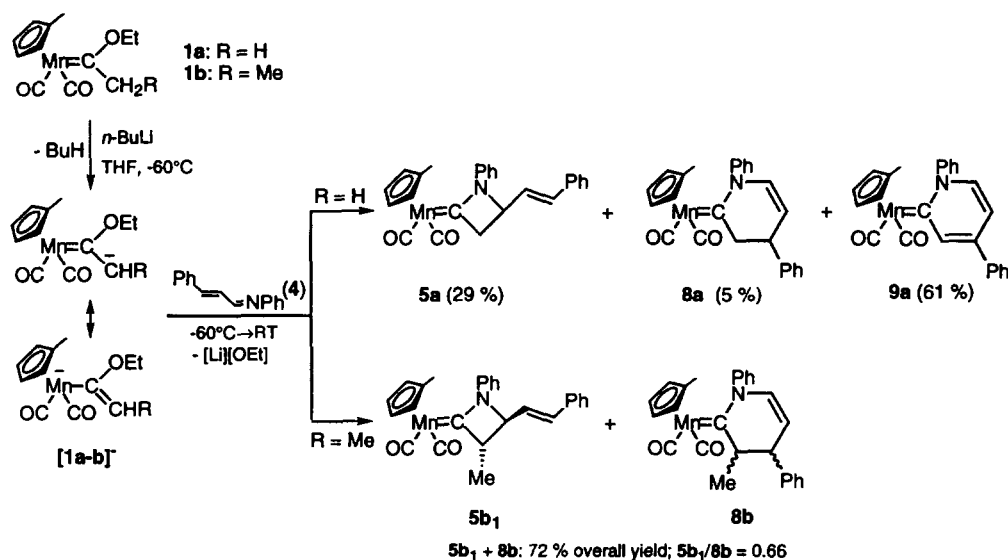
Scheme 1.

CH(CH=CH(Ph))CH(R) (5a-b) (Scheme 1). Alternatively, the treatment of the cationic carbyne complexes [Cp'(CO)$_2$Mn≡CCH$_2$R]$^+$ ([2a-b]$^+$) by first the azabutadiene 4 at −78 °C, followed by addition of triethylamine affords the same azetidinylidene complexes 5a-b. With the vinylidene complexes as starting material, complexes 5a-b were isolated in 74% and 70% yields respectively; whilst using the carbyne complexes as precursors, they were isolated in 79% and 69% yields respectively.

The structures of complexes 5a-b were determined by the usual spectroscopic techniques. For 5b, which possesses two chiral atoms, NMR analysis shows the compound to form in each instance as a mixture of diastereoisomers, 5b$_1$ and 5b$_2$. No significant differ-

ence in the diastereoselectivity of the reaction was observed starting from either 3b (5b$_1$/5b$_2$ = 1.9) or [2b]$^+$ (5b$_1$/5b$_2$ = 1.6). Examination of the coupling constants between the two protons within the four-membered ring (5b$_1$: $^3J_{HH}$ = 1.8 Hz, 5b$_2$: $^3J_{HH}$ = 4.8 Hz) suggests the major diastereoisomer is the one in which these protons are trans to each other, i.e. the RR(SS) diastereoisomer. In the low field region, the ^{1}H NMR spectra of 5a-b clearly show AB(X) patterns characteristic of the exocyclic vinyl fragments, and the values of the $^3J_{HH}$ coupling constants within these signals indicate a trans arrangement of the protons (5a: $^3J_{HH}$ = 15.8 Hz; 5b$_1$: $^3J_{HH}$ = 15.7 Hz; 5b$_2$: $^3J_{HH}$ = 15.7 Hz).

As for the reaction of 4a-b with N-benzylideneaniline [1] and other vinylidene complexes with imines [5],

Scheme 2.

the formation of complexes **5a–b** would proceed via nucleophilic attack of the nitrogen atom of the azabutadiene onto the electrophilic α-carbon atom of the vinylidene complexes to give adducts such as [**6a–b**], which upon ring closure would afford the final azetidinylidene complexes. Complexes **5a–b** can be seen as the net [2 + 2] cycloaddition products between the $C_\alpha = C_\beta$ bond of the vinylidene complexes **3a–b** and the imine function of the 1,4-diphenyl-1-azabutadiene. Noticeably, no [2 + 4] cycloadduct that could also form from [**6a–b**] was observed in this reaction (vide infra). Using the [**2a–b**]$^+$ as precursors, the first step is thought to be a nucleophilic attack of the azabutadiene onto the α-carbon atom of the carbyne complexes to give the adducts [**7a–b**]$^+$. Then, addition of triethylamine would deprotonate the CH_2R group to give [**6a–b**].

The anionic carbene complex [($Cp'(CO)_2Mn=$ C(OEt)CH_2]$^-$ ([**1a**]$^-$), generated in situ by reaction of **1a** with ^nBuLi in THF at -60 °C [6], reacts with **4** upon stirring at room temperature to afford **5a**, the 2-tetrahydropyridinylidene complex $Cp'(CO)_2Mn=CN-$ (Ph)C(H)=C(H)CH(Ph)CH_2 (**8a**), and the 2-dihydropyridinylidene complex $Cp'(CO)_2Mn=CN(Ph)-C(H)=$ C(H)C(Ph)=CH (**9a**) (Scheme 2); these complexes were separated by extensive column chromatography and isolated in 29%, 5%, and 61% yields respectively. In similar reaction conditions, the carbene anion [$Cp'(CO)_2Mn=C(OEt)CHMe$]$^-$ ([**1b**]$^-$) leads to a mixture of **5b** and $Cp'(CO)_2Mn=CN(Ph)C-$ (H)=C(H)CH(Ph)CH(Me) (**8b**), isolated in a 72% overall yield. Attempts to separate these complexes by column chromatography were unsuccessful, and the ratio **5b/8b** was estimated to be 0.66 by ^1H NMR. Noticeably, only the RR(SS) diastereoisomer **5b₁** could be observed in the reaction mixture. The structure of the new complexes **8a–b** was determined by the usual spectroscopic techniques. Endocyclic vinyl functionalities are evidenced in the ^1H NMR spectra by signals at 5.94 and 5.20 ppm for **8a**, and 5.85 and 5.05 ppm for **8b**, with $^3J_{HH}$ coupling constants of 7.4 Hz between the vinylic protons for the two complexes. As for **5b**, complex **8b** also forms in a diastereoselective manner. Its configuration could not, however, be unambigously determined based on the NMR data only. No evidence of the formation of the other possible diastereoisomer was obtained, even in the crude reaction mixture.

Complexes **5a–b** and **8a–b** can respectively be seen as the net [2 + 2] and [2 + 4] cycloaddition products between the anionic carbenes [**1a–b**]$^-$ and the azabutadiene **4**. They could form via initial nucleophilic attack of the α-carbon atom of the anionic carbenes on, respectively, the 2 and the 4 position of the azabutadiene, followed by an intramolecular nucleophilic substitution of the ethoxy group by the amide group that would be produced in the first step. Attempts to trap 1,2 or 1,4 addition products, similar to those isolated from reac-
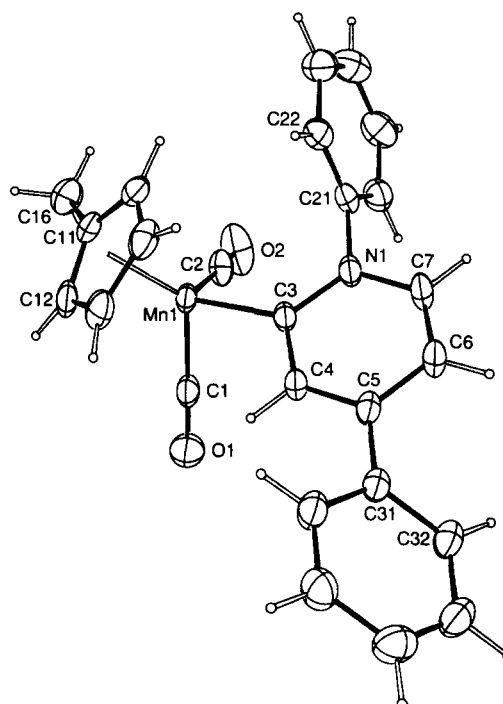

Fig. 1. Perspective view of complex **9a**.

tions between anionic carbene complexes and ketones or vinylketones [3e,7], by acidic hydrolysis during the course of the reaction were unsuccessful. It is therefore likely that the cyclizations proceed in a concerted way, rather than in a stepwise manner.

In the reaction between [**1a**]$^-$ and **4**, complex **8a** forms in trace amounts only. The main product of the reaction is complex **9a**, whose solid-state structure was established by X-ray crystallography.

As shown in Fig. 1, the structure of complex **9a** consists of a $Cp'(CO)_2Mn$ unit bonded to an N-phenyl-4-phenyl-2-dihydropyridin-2-ylidene fragment. The molecule displays a slightly distorted pseudo octahedral geometry about manganese, as reflected in the values of the bond angles between the carbonyls and the carbene ligand (C(2)–Mn(1)–C(1), 90.2(2)°; C(2)–Mn(1)–C(3), 98.2(2)°; C(1)–Mn(1)–C(3), 90.5(2)°). The manganese atom, the atoms of the six-membered ring, and the phenyl ipso carbon atoms of the exocylic NPh and CPh groups are essentially coplanar (average deviation from the mean plane of 0.0553 Å with a maximum deviation of 0.147 Å associated with C(21)). Noticeably, the Mn–C(3) bond length of 1.994(4) Å is significantly longer than in other manganese aminocarbene complexes (e.g. for $Cp(CO)_2Mn=CN(Ph)CH(Ph)CH_2$, $Mn=C = 1.889(4)$ Å [1]), and lies between the value of 1.87 Å expected for a Mn=C double bond [8] and the value of 2.07 Å found for Mn–C(aryl) single bonds [9]. The C(3)–C(4) (1.412(6) Å), and N(1)–C(5) (1.410(6) Å) bond lengths are significantly shorter than the corresponding C–C (1.540 Å) and N–C (1.473 Å) bond
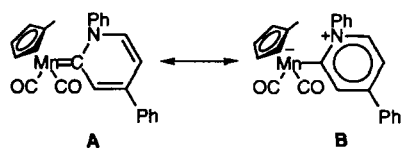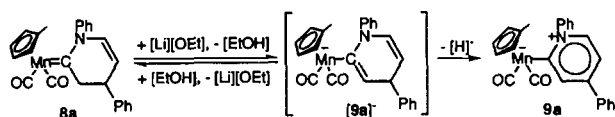
Scheme 3.

values found in manganese azetidinylidene complexes [1]. In addition, the C(5)–C(6) (1.410(6) Å) bond length is shorter than a typical $C=C-C=C$ bond (1.460 Å) [10], and is close to carbon–carbon bond values in aromatic systems (1.395 Å) [10]. Taken altogether, these structural features indicate a substantial electronic delocalization within the dihydropyridinylidene ring, due to the contribution of the resonance form **B** to the structure of **9a** (Scheme 3). The contribution of resonance form **B** may also be detected in solution. Indeed, the $\nu_{C=O}$ stretches for compound **9a** are significantly displaced towards the low wavenumbers compared, for instance, with **8a** (**9a**: $\nu_{C=O} = 1910, 1845$ cm^{-1} vs. **8a**: $\nu_{C=O} = 1942, 1880$ cm^{-1}).

It is likely that the formation of complex **9a** could result from dehydrogenation of **8a** under the reaction conditions. Indeed, the lithium ethoxide, which must be released during the formation of **8a** (and **5a**) (Scheme 2), could be basic enough to deprotonated **8a** and generate an anionic carbene such as **[9a]⁻** (Scheme 4). The stabilizing effect of the pseudo aromaticity within the dihydropyridinylidene ring evidenced in the X-ray structure of **9a** would then account for its formation upon hydride lost from **[9a]⁻**.

Support for this possible mechanism is the observation that treatment of **8a** by a slight excess of [Na][OMe] in THF at room temperature did lead to the formation of **9a**. It is worth noting that no complex similar to **9a** has ever been observed from the reaction of **[1b]⁻** and **3**. This could be because the α-carbon atom in **8b** is a tertiary carbon atom and it then cannot be deprotonated by lithium ethoxide under the reaction conditions. Attempts to deprotonate **8b** by a stronger base (lithium bis(trimethylsilyl)amide), in the presence of **5b** because these two complexes could not be separated, led to intractable mixtures of compounds from which no evidence of a complex similar to **9a** was obtained.

In conclusion, the neutral vinylidene $Cp'(CO)_2Mn=C=CHR$, or the cationic carbyne $[Cp'(CO)_2Mn\equiv CCH_2R]^+$, and the anionic carbene $[Cp'(CO)_2Mn=C(OEt)CHR]^-$ complexes, all deriving from the carbene com-

plexes $[Cp'(CO)_2Mn=C(OEt)CH_2R]$ (R = H, Me), react with 1,4-diphenyl-1-azabutadiene with significant differences. From the vinylidene complexes, net [2 + 2] cycloadducts of the type $Cp'(CO)_2Mn=CN(Ph)CH-(CH=CH(Ph))CH(R)$ are obtained as final products in a selective manner, but with little diastereoselectivity (for R = Me). The same cycloadducts are obtained upon treatment of the carbyne complexes first with the azabutadiene followed by addition of triethylamine. From the anionic carbenes, the main products are net [2 + 4] cycloadducts of the type $Cp'(CO)_2Mn=CN(Ph)C(H)=C(H)CH(Ph)CH(R)$, and $Cp'(CO)_2Mn=CN(Ph)-C(H)=C(H)C(Ph)=CH$ (for R = H). The latter reaction, although highly diastereoselective (R = Me), is not, however, totally regioselective, since the complexes $Cp'(CO)_2Mn=CN(Ph)CH(CH=CH(Ph))CH(R)$, which can be seen as the net [2 + 2] cycloadducts, also form. Noticeably, in our hands, the chromium analogues $[(CO)_5Cr=C(OMe)CH_2]^-$, well known to react with a wide variety of electrophilic substrates [3a–d,7], failed to react with 1,4-diphenyl-1-azabutadiene in the same reaction conditions. This observation would suggest that manganese carbene anions are better nucleophiles than their chromium (or tungsten) analogues. Since the $Cp'(CO)_2Mn$ fragment presents a poorer acceptor ability than the $(CO)_5M$ (M = Cr, W) fragment [11], it can indeed be expected that hydrogen atoms α to the carbene carbon in complexes of the type $(\eta^5-RC_5H_4)(CO)_2Mn=(OR)CH_2R$ are less acidic than their $(CO)_5M=(OR)CH_2R$ analogues; as a consequence, their conjugate base is more reactive towards electrophiles. Extensions of this type of cycloaddition reaction to other α,β unsaturated substrates, including vinyl ketones, in the direction of the synthesis of cyclohexenones are underway and will be reported in due course.

3. Experimental

3.1. General

The compounds $Cp'(CO)_2Mn=C(OEt)CH_3$ (**1a**) [12], $Cp'(CO)_2Mn=C(OEt)CH_2CH_3$ (**1b**) [6], $Cp'(CO)_2-Mn=C=CHR$ (R = H, Me) [1], $[Cp'(CO)_2Mn\equiv CCH_2R][BF_4]$ (R = H, Me) [1,13], and 1,4-diphenyl-1-azabutadiene [14] were prepared by published procedures. Tetrahydrofuran (THF) used for the syntheses was distilled under nitrogen from sodium benzophenone ketyl just before use. Other solvents were purified following standard procedures, and stored under nitrogen. The reagent grade chemicals BCl_3 (1.0 M solution in hexanes) and ^nBuLi (1.6 M solution in hexane) were obtained from Aldrich. All synthetic manipulations were carried out using standard Schlenk techniques under an

Scheme 4.

atmosphere of dry nitrogen. A liquid-N_2–isopropanol slush bath was used to maintain samples at the desired low temperature. Chromatographic separation of the complexes was performed on alumina (neutral, activity III (Aldrich)). Solution IR spectra were recorded on a Perkin–Elmer 225 spectrophotometer with 0.1 mm cells equipped with CaF_2 windows. ^1H and ^{13}C spectra were obtained on Brucker WH90, AC200, or WM250 spectrometers in C_6D_6 and were referenced to the residual signals of the solvent. In order to fully assign all the NMR signals, $^{13}C\{^1H\}$–$^1H\{^1H\}$ 2D HSC NMR experiments were performed on each complex (except for **8a**), on the Bruker AC200 instrument. Mass spectra were recorded on a Nermag R10-10 mass spectrometer (EI). Microanalysis of C, H, and N elements were performed on a Perkin–Elmer 2400 CHN analyzer.

3.2. Reaction of $Cp'(CO)_2Mn=C=CH_2$ (3a) with 1,4-diphenyl-1-azabutadiene to afford 5a

The carbene complex $Cp'(CO)_2Mn=C(OEt)Me$ (0.58 g, 2.2 mmol) was dissolved in 15 ml of hexane, the solution was cooled to $-78°C$, and BCl_3 (4.9 ml of 1 M solution in hexane) was added dropwise via syringe; this caused formation of a light-yellow precipitate of the carbyne $[Cp'(CO)_2Mn\equiv CCH_3][BF_4]$. The supernatant was removed by means of a cannula tipped with filter paper. The solid residue was washed with 1 : 1 hexane–Et_2O (2 × 20ml) at $-78°C$. The carbyne complex was suspended in CH_2Cl_2 (10 ml) at $-78°C$, and NEt_3 (0.335 ml, 2.4 mmol) was added to generate the vinylidene complex $Cp'(CO)_2Mn=C=CH_2$. After stirring for 5 min, 1,4-diphenyl-1-azabutadiene (0.52 g, 2.5 mmol) was added. The cooling bath was removed, and stirring was continued while the reaction mixture was warmed to room temperature. The resulting brown solution was then concentrated under vacuum and chromatographed on alumina. Elution with pure pentane gave a yellow band containing mainly $Cp'(CO)_3Mn$ which was discarded. Elution with 9 : 1 pentane–diethyl ether gave an orange band. Removal of the solvents from this band gave the complex $Cp'(CO)_2Mn=CN(Ph)CH(CH=CH(Ph))CH(Ph)CH_2$ (**5a**, 0.69 g, 74% yield) as an oil.

5a. Anal. Found: C, 71.21; H, 5.45; N, 3.33. $C_{25}H_{22}MnNO_2$. Calc.: C, 70.92; H, 5.24; N, 3.31%. IR (THF): $\nu_{C=O} = 1930, 1870$; $\nu_{C=C} = 1692(m)$ cm^{-1}. ^1H NMR (C_6D_6): δ 7.7–6.9 (m, 10H, C_6H_5), 6.06 (AB(X) pattern, 2H, $J_{HH} = 15.8, 0.0, 8.3$ Hz, $C(H)=C(H)Ph$), 4.89 (ddd, 1H, $J_{HH} = 8.3, 4.8, 2.2$ Hz, CH), 4.5–4.3 (m, MeC_5H_4), 2.70 (AB(X) pattern, 2H, $J_{HH} = 15.6, 2.2, 4.8$ Hz, CH_2), 1.85 (s, 3H, MeC_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 291.8 (Mn=C), 235.8, 235.1 (Mn–CO), 134.0, 127.6 (C(H)=C(H)Ph), 122–130 (C_6H_5), 102.6, 86.2, 86.0, 84.8, 84.7 (MeC_5H_4), 71.7 (CH), 52.1 (CH$_2$), 14.5 (MeC$_5$H$_4$). MS (EI): m/z 423 (M$^+$).

3.3. Reaction of $[Cp'(CO)_2Mn\equiv CCH_3]^+$ ([2a]$^+$) with 1,4-diphenyl-1-azabutadiene to afford 5a

The carbyne complex $[Cp'(CO)_2Mn\equiv CCH_3][BF_4]$, generated as above from $Cp'(CO)_2Mn=C(OEt)CH_3$ (0.51 g, 1.9 mmol) and BCl_3 (4.3 ml of 1 M solution in hexane), was suspended in CH_2Cl_2 (10 ml) at $-78°C$. To this was added 1,4-diphenyl-1-azabutadiene (0.44 g, 2.1 mmol), which caused the solid to dissolve and gave an orange solution. The reaction mixture was stirred for 10 min, and NEt_3 (0.300 ml, 2.2 mmol) was added. The cooling bath was then removed, and stirring was continued while the reaction mixture was warmed to room temperature. The mixture was then treated as above to give complex **5a** (0.65 g, 79% yield).

3.4. Reaction of $Cp'(CO)_2Mn=C=C(H)Me$ (3b) with 1,4-diphenyl-1-azabutadiene to afford 5b

The vinylidene complex $Cp'(CO)_2Mn=C=C(H)Me$ was generated by addition of NEt_3 (0.320 ml, 2.3 mmol) to a suspension of $[Cp'(CO)_2Mn\equiv CCH_2Me][BF_4]$ (from $Cp'(CO)_2Mn=C(OEt)CH_2Me$ (0.58 g, 2.1 mmol) and BCl_3 (4.6 ml of a 1.0 M solution in hexanes)) in CH_2Cl_2 (10 ml) at $-78°C$. To this was added 1,4-diphenyl-1-azabutadiene (0.48 g, 2.3 mmol). The cooling bath was then removed and stirring was continued while the reaction mixture was warmed to room temperature. The mixture was then concentrated under vacuum and chromatographed on alumina. Elution with pure pentane gave a yellow band containing mainly $Cp'(CO)_3Mn$ which was discarded. Elution with 95 : 5 pentane–diethyl ether gave two orange bands. Removal of the solvent from each band afforded complexes $Cp'(CO)_2Mn=CN(Ph)CH(CH=CH(Ph))CH(Ph)CH(Me)$ (**5b$_2$**, 0.22 g, 24% yield) and $Cp'(CO)_2Mn=CN(Ph)CH(CH=CH(Ph))CH(Ph)CH(Me)$ (**5b$_1$**, 0.42 g, 46% yield) as golden-yellow and orange solids respectively.

5b$_1$. Anal. Found: C, 71.95; H, 5.75; N, 3.14. $C_{26}H_{24}MnNO_2$. Calc.: C, 71.39; H, 5.53; N, 3.20. IR (THF): $\nu_{C=O} = 1930, 1870$ cm^{-1}. ^1H NMR (C_6D_6): δ 7.6–6.8 (m, 10H, C_6H_5), 6.10 (AB(X) pattern, 2H, $J_{HH} = 15.7, 0.0, 7.9$ Hz, $C(H)=C(H)Ph$), 4.46 (dd, 1H, $J_{HH} = 7.9, 1.8$ Hz, CH), 4.2–4.4 (m, MeC_5H_4), 2.64 (dq, 1H,H$_1$,$J_{HH} = 7.8, 1.8$ Hz, $C(H)Me$), 1.81 (s, 3H, MeC_5H_4), 1.31 (d, 3H, $J_{HH} = 7.8$ Hz, $C(H)Me$). $^{13}C\{^1H\}$ NMR (C_6D_6, 63 MHz): δ 299.7 (Mn=C), 234.3, 233.9 (Mn–CO), 134.1, 127.2 (C(H)=C(H)Ph), 122–130 (C_6H_5), 101.3, 84.8, 84.1, 83.7, 83.2 (MeC_5H_4), 80.1 (CH), 57.8 (C(H)Me), 16.7 (C(H)Me), 14.4 (MeC$_5$H$_4$). MS (EI): m/z 437 (M$^+$).

5b$_2$. Anal. Found: C, 71.00; H, 5.73; N, 3.00. $C_{26}H_{24}MnNO_2$. Calc.: C, 71.39; H, 5.53; N, 3.20%. IR (THF): $\nu_{C=O} = 1930, 1870$ cm^{-1}. ^1H NMR (C_6D_6): δ 7.6–6.8 (m, 10H, C_6H_5), 6.05 (AB(X) pattern, 2H,

J_{HH} = 15.7, 0.0, 7.9 Hz, C(H)=C(H)Ph), 5.08 (dd, 1H, J_{HH} = 8.8, 4.8 Hz, CH)), 4.2–4.4 (m, MeC$_5$$H_4$), 3.00 (dq, 1H, J_{HH} = 7.7, 4.8 Hz, CH(Me)), 1.25 (s, 3H, MeC$_5$H$_4$), 1.21 (d, 3H, J_{HH} = 7.7 Hz, CH(Me)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 299.8 (Mn=C), 234.6, 234.3 (Mn–CO), 135.6, 124.5 (C(H)=C(H)Ph), 122–130 (C_6H$_5$), 101.2, 84.6, 84.4, 84.2, 83.5 (MeC_5H$_4$), 74.5 (CH), 55.4 (C(H)Me), 14.4 (C(H)Me), 14.4 (MeC$_5$H$_4$). MS (EI): m/z 437 (M$^+$).

3.5. Reaction of [Cp'(CO)$_2$Mn≡CCH$_2$Me]$^+$ ([2b]$^+$) with 1,4-diphenyl-1-azabutadiene to afford 5b

The carbyne complex [Cp'(CO)$_2$Mn≡CCH$_2$Me] [BF$_4$], generated from Cp'(CO)$_2$Mn=C(OEt)CH$_2$Me (0.61 g, 2.2 mmol) and BCl$_3$ (4.9 ml of 1 M solution in hexane), was suspended in CH$_2$Cl$_2$ (10 ml) at −78°C. To this was added 1,4-diphenyl-1-azabutadiene (0.50 g, 2.4 mmol) which caused the solid to dissolve and gave an orange solution. The reaction mixture was stirred for 10 min, and NEt$_3$ (0.340 ml, 2.4 mmol) was added. The cooling bath was then removed and stirring was continued while the reaction mixture was warmed to room temperature. The resulting solution was treated as above to give 5b$_2$ (0.26 g, 26% yield) and 5b$_1$ (0.42 g, 43% yield).

3.6. Reaction of [Cp'(CO)$_2$Mn=C(OEt)CH$_2$]$^-$ ([1a]$^-$) with 1,4-diphenyl-1-azabutadiene to afford 5a, 8a, and 9a

The carbene complex Cp'(CO)$_2$Mn=C(OEt)CH$_3$ (1a) (1 g, 3.8 mmol) was dissolved in 30 ml of THF, the solution was cooled at −60°C, and ^{n}BuLi (2.6 ml of a 1.6 M solution in hexanes, 4.2 mmol) was added dropwise via syringe. After stirring for 30 min, the solution was cooled to −78°C, and 1,4-diphenyl-1-azabutadiene (0.870 g, 4.2 mmol) was added. The cooling bath was removed and the reaction mixture was stirred overnight at room temperature. THF was removed under vacuum, the residue was dissolved in diethyl ether, and the solution was filtered on a short column of alumina. The mixture was then chromatographed on alumina. Elution with pure pentane gave a yellow band containing the starting material which was discarded. Elution with 9:1 pentane–diethyl ether gave three bands, red, yellow, then purple, which contained the new complexes 5a, 8a and 9a respectively. Cp'(CO)$_2$Mn=CN(Ph)CH=CH-CH(Ph)CH$_2$ (8a, 0.09 g, 5% yield) and Cp'(CO)$_2$Mn=CN(Ph)CH(CH=CHPh)CH(Ph)CH$_2$ (5a, 0.46 g, 29% yield) were obtained as oils, whereas Cp'(CO)$_2$Mn=CN(Ph)CH=CHC(Ph)=CH (9a, 0.98 g, 61% yield) was isolated as a black crystalline material.

8a. IR (THF): $\nu_{C=O}$ = 1880, 1942 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.4–6.9 (m, 10H, C$_6$$H_5$), 5.94 (dd, 1H,

J_{HH} = 7.4, 1.6 Hz, C(H)=), 5.20 (dd, 1H, J_{HH} = 7.4, 4.2 Hz, C(H)=), 4.1–3.9 (m, MeC$_5$$H_4$), 3.53 (AB(X) pattern, 2H, J_{HH} = 16.1, 8.8, 6.7 Hz, CH_2), 3.20 (m, 1H, CH(Ph), 1.69 (s, 3H, MeC$_5$H$_4$). MS (EI): m/z 423 (M$^+$).

9a: Anal. Found: C, 71.13; H, 4.88; N, 3.22. C$_{25}$H$_{20}$MnNO$_2$% Calc.: C, 71.26; H, 4.78; N, 3.32%. IR (THF): $\nu_{C=O}$ = 1910, 1845 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.76 (d, 1H, J_{HH} = 2.3 Hz, C(H)=), 7.97 (d, 1H, J_{HH} = 6.8 Hz, C(H)=), 7.8–7.4 (m, 10H, C$_6$$H_5$), 7.06 (dd, 1H, J_{HH} = 2.3, 6.8 Hz, C(H)=), 4.10 (m, 4H, MeC$_5$$H_4$), 1.79 (s, 3H, MeC$_5H_4$). ^{13}C{^{1}H} NMR (CD$_2Cl_2$): δ 241.4 (Mn=C), 235.1 (Mn–CO), 150.8 (C(Ph), 144.6 (CH), 144.6 (CH), 122–130 (C_6H$_5$), 114.9 (CH), 99.6, 84.2, 82.9 (C_5H$_4$CH$_3$), 13.9 (MeC$_5$H$_4$). MS (EI): m/z 421 (M$^+$). Incidentally, C$_2$ and C$_5$ carbon atoms in complex 9a present the exact same chemical shift in the ^{13}C NMR spectra; this was confirmed by ^{13}C{^{1}H}–^{1}H{^{1}H} 2D HSC NMR experiments.

3.7. Reaction of [Cp'(CO)$_2$Mn=C(OEt)CHMe]$^-$ ([1b]$^-$) with 1,4-diphenyl-1-azabutadiene to afford 5b, and 8b

The carbene complex Cp'(CO)$_2$Mn=C(OEt)CH$_2$Me (1b) (0.62 g, 2.2 mmol) was dissolved in 30 ml of THF, the solution was cooled at −60°C, and ^{n}BuLi(1.5 ml of a 1.6 M solution in hexanes, 2.5 mmol) was added dropwise via syringe. After stirring for 30 min, the solution was cooled to −78°C, and 1,4-diphenyl-1-azabutadiene (0.52 g, 2.5 mmol) was added. The cooling bath was removed and the reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, the residue was dissolved in diethyl ether, and the solution was filtered on a short column of alumina. The mixture was then chromatographed on alumina. Elution with pure pentane gave a yellow band containing traces of the starting material which was discarded. Elution with 9:1 pentane–diethyl ether gave a red band which contained a mixture of the complexes Cp'(CO)$_2$Mn=CN(Ph)CH(CH=CH(Ph))CH(Ph)CH(Me) (5b$_1$) and Cp'(CO)$_2$Mn=CN(Ph)CH=CHCH(Ph)CH(Me) (8b) (0.71 g, 72% overall yield). NMR analysis of the mixture showed compounds 5b$_1$ and 8b to be present in a 2:3 ratio.

8b. ^{1}H NMR (C$_6$D$_6$, from a mixture of 5b$_1$ and 8b): δ 7.6–6.8 (m, 10H, C$_6$$H_5$), 5.85 (d, 1H, J_{HH} = 7.4 Hz, C(H)=), 5.05 (ddd, 1H, J_{HH} = 7.4, 6.5, 1.6 Hz, C(H)=), 4.23 (m, 1H, C(H)Me), 3.9–3.6 (m, MeC$_5$$H_4$), 2.78 (d, 1H, J_{HH} = 6.5 Hz, C(H)Ph), 1.57 (s, 3H, MeC$_5$H$_4$), 1.35 (d, 3H, J_{HH} = 7.3 Hz, C(H)Me). ^{13}C{^{1}H} NMR (C$_6$D$_6$, from a mixture of 5b$_1$ and 8b): δ 297.3 (Mn=C), 233.8, 233.3 (Mn–CO), 130.8, 111.3 (C(H)=C(H)), 122–130 (C_6H$_5$), 99.9, 85.7, 85.4, 80.0

Table 1
Experimental data for X-ray study of compound **9a**

Formula	$C_{25}H_{20}MnNO_2$
F_w (amu)	421.38
a (Å)	7.892(1)
b (Å)	9.576(3)
c (Å)	27.306(3)
β (deg)	97.41(2)
V (Å^3)	2046(1)
Z	4
D(calcd) (g cm^{-3})	1.368
Space group	$P2_1/c$
t (°C)	22
Radiation	Mo K α
	($\lambda = 0.71073$ Å)
Linear absorption coefficient (cm^{-1})	6.381
Transmission factors [a]	0.999–0.973
Receiving aperture (mm^2)	4.0×4.0
Scan speed (deg min^{-1})	variable, 2–8
Scan mode	$\omega-2\theta$
Scan range (deg)	0.8 below K α_1 to
	0.8 above K α_2
2θ limit (deg)	2–48
Unique data used in final refinement, $F_0^2 > 3\sigma(F_0^2)$	2315
Final no. of variables	262
R (on F_0, $F_0^2 > 3\sigma(F_0^2)$) [b]	0.041
Rw (on F_0, $F_0^2 > 3\sigma(F_0^2)$) [c]	0.045
Error in observations of unit weight	1.328

[a] Ψ-scan method; [b] $R = \Sigma \|F_0| - |F_c\| / \Sigma |F_0|$; [c] $R_w = [\Sigma w(|F_0| - |F_c|)^2 / (\Sigma w |F_0|^2)]^{1/2}$, unit weights.

Table 2
Bond distances (Å) and bond angles (deg) of interest for compound **9a**

Bond distances	
Mn(1)–C(2)	1.743(5)
Mn(1)–C(1)	1.745(5)
Mn(1)–C(3)	1.994(4)
N(1)–C(7)	1.376(5)
N(1)–C(3)	1.388(5)
N(1)–C(21)	1.454(6)
C(1)–O(1)	1.173(6)
C(2)–O(2)	1.170(7)
C(3)–C(4)	1.412(6)
C(4)–C(5)	1.383(6)
C(5)–C(6)	1.410(6)
C(5)–C(31)	1.472(6)
C(6)–C(7)	1.336(7)
Bond angles	
C(2)–Mn(1)–C(1)	90.2(2)
C(2)–Mn(1)–C(3)	98.2(2)
C(1)–Mn(1)–C(3)	90.5(2)
C(7)–N(1)–C(3)	122.8(4)
O(1)–C(1)–Mn(1)	178.2(4)
O(2)–C(2)–Mn(1)	174.1(4)
N(1)–C(3)–C(4)	113.2(3)
N(1)–C(3)–Mn(1)	126.9(3)
C(4)–C(3)–Mn(1)	119.9(3)
C(5)–C(4)–C(3)	125.2(4)
C(4)–C(5)–C(6)	117.2(4)
C(7)–C(6)–C(5)	119.1(4)
C(6)–C(7)–N(1)	122.3(4)

Table 3
Fractional atomic coordinates and isotropic or equivalent temperature factors (Å^2 × 100) with e.s.d.s in parentheses for compound **9a** ($U_{eq} = 1/3$ trace U)

Atom	x	y	z	U_{eq} / U_{iso}
Mn(1)	0.15702(8)	0.45554(6)	0.39298(3)	3.91(3)
O(1)	−0.1760(5)	0.4300(4)	0.4278(2)	8.5(3)
O(2)	0.0020(6)	0.3754(4)	0.2945(2)	9.4(3)
N(1)	0.2938(4)	0.1586(3)	0.3963(1)	4.2(2)
C(1)	−0.0411(6)	0.4385(4)	0.4143(2)	5.0(3)
C(2)	0.0675(6)	0.4006(5)	0.3345(2)	5.5(3)
C(3)	0.2284(5)	0.2691(4)	0.4210(2)	3.9(2)
C(4)	0.2128(5)	0.2385(4)	0.4708(2)	4.2(3)
C(5)	0.2502(5)	0.1112(4)	0.4936(2)	4.2(2)
C(6)	0.3059(6)	0.0030(4)	0.4644(2)	5.0(3)
C(7)	0.3269(6)	0.0295(4)	0.4175(2)	5.2(3)
C(11)	0.2345(6)	0.6515(4)	0.3638(2)	5.7(3)
C(12)	0.1707(7)	0.6742(4)	0.4093(2)	5.8(3)
C(13)	0.2766(7)	0.5999(5)	0.4472(2)	6.0(3)
C(14)	0.4043(6)	0.5314(5)	0.4246(2)	6.1(3)
C(15)	0.3805(6)	0.5631(5)	0.3745(2)	6.3(3)
C(16)	0.1677(8)	0.7146(6)	0.3150(2)	8.6(4)
C(21)	0.3415(6)	0.1749(4)	0.3469(2)	4.5(3)
C(22)	0.4902(6)	0.2426(5)	0.3417(2)	5.4(3)
C(23)	0.5429(7)	0.2506(6)	0.2958(2)	6.7(4)
C(24)	0.4479(7)	0.1897(7)	0.2560(2)	7.8(4)
C(25)	0.3003(7)	0.1206(6)	0.2614(2)	7.3(4)
C(26)	0.2453(6)	0.1117(5)	0.3076(2)	5.9(3)
C(31)	0.2345(5)	0.0902(4)	0.5462(2)	4.2(2)
C(32)	0.1751(6)	−0.0376(5)	0.5631(2)	5.3(3)
C(33)	0.1596(6)	−0.0550(6)	0.6125(2)	6.6(3)
C(34)	0.2055(7)	0.0489(7)	0.6462(2)	7.2(4)
C(35)	0.2656(7)	0.1757(5)	0.6298(2)	6.5(3)
C(36)	0.2783(6)	0.1957(5)	0.5806(2)	5.5(3)

(MeC_5H$_4$), 60.5 (C(H)Me), 42.2 (C(H)Ph), 18.5 (C(H)*Me*), 13.9 (*Me*C$_5$H$_4$).

3.8. X-ray diffraction studies

Crystals of **9a** suitable for X-ray diffraction were obtained through recrystallization from hexane–dichloromethane solution at room temperature. Data were collected on an Enraf–Nonius CAD4 diffractometer at 22°C. Cell constants were obtained by the least squares refinement of the setting angles of 25 reflections in the range $20 < 2\theta$(Mo Kα_1) $< 24°$. The space group was determined by careful examination of systematic extinctions in the listing of the measured reflections.

All calculations were performed on a Micro Vax 3400. Data reductions were carried out using the SDP crystallographic computing package [15]. The intensities were corrected for absorption by using the empirical Ψ-scan method [16]. Full crystallographic data are given in Table 1. The structure was solved by using SHELXS-86 program [17], which revealed the position of the Mn atom. All remaining non-hydrogen atoms were located by the usual combination of full matrix least squares refinement and difference electron density syntheses by using the SHELX-76 program [18]. Atomic scattering

factors were taken from the usual tabulations [19]. Anomalous dispersion terms for Mn, and P atoms were included in F_c [20]. All non-hydrogen atoms were allowed to vibrate anisotropically. The hydrogen atoms were set in idealized position (C–H = 0.97 Å). Scattering factors for the hydrogen atoms were taken from Stewart et al. [21]. Selected distances and angles are given in Table 2. Final atomic coordinates for non-hydrogen atoms are given in Table 3.

4. Supplementary material

Tables S4 and S5, giving anisotropic temperature factors and atomic coordinates for hydrogen atoms respectively, are available from the authors upon request.

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