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Cycloaddition of Transition-Metal–η^1-Dienyl Complexes with Dienophiles: [4 + 2] versus [3 + 2] Reaction Pathways

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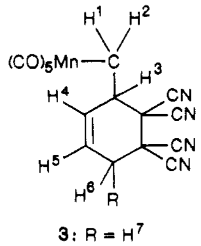
Mn(CO)$_5$(η^1-pentadienyl) (1) and the corresponding η^1-2,4-hexadien-1-yl complex (2) undergo [4 + 2] cycloaddition with tetracyanoethylene and maleic anhydride to produce the adducts (CO)$_5$MnCH$_2$CHC(CN)$_2$C(CN)$_2$CH(R)CH=CH$_2$ (R = H (3), CH$_3$ (4)) and (CO)$_5$MnCH$_2$CHCHCOOCOCHCHRCH=CH (R = H (5), CH$_3$ (6)). The anhydride adducts 5 and 6 undergo further intramolecular carbonylation to give the acyl complexes (CO)$_4$MnCOCH$_2$CHCHCOOCOCHCHRCH=CH (R = H (7), CH$_3$ (8)). For the η^1-5-methyl-2,4-hexadien-1-yl complexes M(η^1-CH$_2$CH=CHCH=C(Me)$_2$) (M = Mn(CO)$_5$ (9), CpFe(CO)$_2$ (10), CpMo(CO)$_3$ (11)), cycloaddition of each complex with tetracyanoethylene gives the [3 + 2] cycloadduct M(CHCH(CH=CMe$_2$)C(CN)$_2$C(CN)$_2$CH$_2$) (M = Mn (CO)$_5$ (12), CpFe(CO)$_2$ (13), CpMo(CO)$_3$ (14)) in moderate yields. X-ray diffraction studies of 4 and 14 were undertaken. Crystallographic data for 4: space group *Pbca*; a = 13.353 (3) Å, b = 19.010 (4) Å, c = 14.437 (3) Å; V = 3664.6 Å^3; Z = 8; R_F = 3.7, R_w = 2.4. For 14: space group $P2_1/n$; a = 10.760 (8) Å, b = 15.898 (6) Å, c = 12.57 (4) Å, β = 96.97 (14) Å; V = 2134.54 Å^3; Z = 4; R_F = 3.9, R_w = 4.3.

Introduction

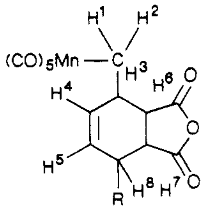
In recent years, there has been a growing interest in the chemistry of acyclic transition-metal–pentadienyl complexes. The structural chemistry of these complexes is particularly interesting because various geometries are possible for the metal–ligand bonding such as η^1, syn-η^3, anti-η^3, and η^5 forms.[1] We are particularly interested in the chemistry of η^1-pentadienyl[2] compounds because the related compound Me$_3$M(η^1-pentadienyl) (M = Si, Sn)[2b–d] has shown versatile reactivity in organic reactions. The latter compound has been shown to undergo [4 + 2] cycloaddition and electrophilic addition with various electrophiles. Nevertheless, if the η^1-pentadienyl complexes are considered to be a higher homologue of transition-metal–allyl complexes,[3] they should undergo [3 + 2] cycloaddition with dienophiles. In our preceding papers,[4,5] we have reported the cycloaddition reaction of the compounds having η^1-pentadienyl or η^1-2,4-hexadien-1-yl as a ligand of iron or molybdenum with alkenes such as tetracyanoethylene and maleic anhydride. Although only [4 + 2] cycloadducts were obtained, we believed that a [3 + 2] cycloaddition pathway was still possible. We speculated that, if the ϵ-carbon of the dienyl ligand were disubstituted, the [3 + 2] cycloaddition would likely occur. In this paper we report a controllable [3 + 2] and the [4 + 2] cycloaddition of manganese–η^1-dienyl compounds. Crystal structures of [4 + 2] and [3 + 2] cycloadducts are presented. The aim of this paper is to verify our previous speculation.

Results and Discussion

[4 + 2] Cycloaddition. Stirring of Mn(CO)$_5$(η^1-2,4-pentadienyl) (1)[4b] and its derivative Mn(CO)$_5$(η^1-2,4-hexadien-1-yl) (2) with an equimolar amount of TCNE at 0 °C for 2 h gave a greenish solution. After evaporation of the solvent to dryness, the residues were extracted with chloroform, followed by recrystallization from CHCl$_3$/hexane, yielding yellow blocklike crystals of Mn(CO)$_5$(CH$_2$CHC(CN)$_2$C(CN)$_2$CH(R)CH=CH$_2$) (R = H (3), CH$_3$ (4)). The IR and ^{1}H and ^{13}C NMR spectra of 3 and 4 have established the [4 + 2] structures as depicted below.



3: R = H^7
4: R = CH$_3$



5: R = H^9
6: R = CH$_3$

The ^{1}H NMR spectrum shows the resonance of H^1 and H^2 as an AB quartet at δ 1.00–1.50 ppm further split by H^3 and the resonances of the two olefinic protons H^4 and H^5 at δ 5.70–5.90 ppm. The IR spectra show the ν(CN) bands at 2230 (s) and 2204 (s) cm^{-1} and a weak ν(C=C) band at 1648 (s) cm^{-1} in addition to five ν(CO) bands in the 2120–1960 cm^{-1} regions. The molecular structure of 4 was

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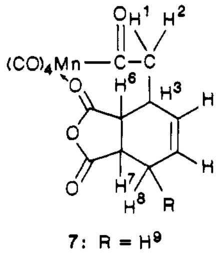
further characterized by an X-ray diffraction study (vide post).

Compounds 1 and 2 each readily form a 1:1 adduct with maleic anhydride to give $(CO)_5MnCH_2CHCHCOOCOCHCHRCH{=}CH$ (R = H (5), CH_3 (6)). The reaction conditions, however, require a low temperature (0–5 °C) as the adducts readily undergo subsequent intramolecular carbonylation at room temperature over a prolonged period. Purification of 5 and 6 was achieved by repeated precipitation from a $CHCl_3$/ether mixed solvent at 0 °C, yielding an analytically pure yellow crystalline solid as shown by the elemental analysis. According to the spectroscopic data, only one isomer was detected for 5 and 6. The ^1H and ^{13}C spectra are compatible with the proposed structure. The proton resonances of H^1 and H^2 show the expected AB pattern at δ 1.20–1.45 ppm and further split by H^3, and the ^{13}C NMR shows resonances at δ 4.4 or 7.3 ppm, assigned to the CH^1H^2 carbon of 5 or 6, respectively.

Compounds 5 and 6 undergo an intramolecular carbonylation reaction to give the acyl compounds $(CO)_4MnCOCH_2CHCHCOOCOCHCHRCH{=}CH$ (R = H (7), CH_3 (8)). When a chloroform solution of 5 and 6 was placed under argon at 23 °C for 36 h, platelike colorless crystals of 7 and 8 slowly deposited in good yields (75–90%). Elemental analyses were consistent with the given formulae. Although X-ray diffraction studies of 7 and 8 were hampered by the poor crystallinity, the proposed structures are supported by the solution IR and ^1H and ^{13}C NMR spectra. A solution IR spectrum in the 1900–2150 cm^{-1} region of 7 and 8 in THF shows four strong carbonyl bands (3A′ + A″). The ν(CO) bands of the anhydride moiety are shifted from ~1780 (s) cm^{-1} of 5 and 6 to ~1775 (s) and ~1720 (s) cm^{-1} of 7 and 8. The band at ~1720 (s) cm^{-1} suggests that one anhydride carbonyl group is coordinated to the manganese atom. The proton resonances of the ABX pattern of the H^1 and H^2 hydrogens are shifted downfield to δ 3.20–3.80 ppm, and the ^{13}C NMR resonances of the CH^1H^2 carbon are shifted downfield to δ 66 ppm. This information suggests that CO has inserted into the σ Fe–CH^1H^2 bond.[5] The presence of an acyl group is further indicated by an IR absorption band at 1640–1630 (s) cm^{-1} and the ^{13}C NMR resonance of a singlet at δ 258 ppm.[7] On the basis of these data, we propose that the product is an acyl complex with the carbonyl group of the anhydride moiety bound to the manganese atom. Such a structure is not unique in the literature. Several manganese compounds,[6,8,9] analogous to 7 and 8 having the organic carbonyl-coordinated cyclic structure, have been well-characterized. Interestingly, this class of chelate compounds commonly resulted from the insertion reaction as we observed in our studies.



7: R = H^9
8: R = CH_3

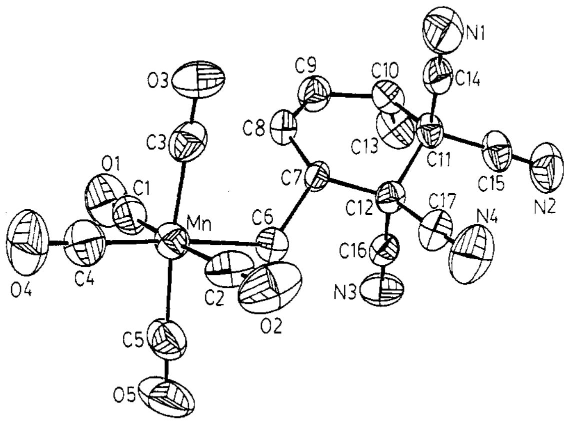


Figure 1. ORTEP drawing of the molecule 4.

Table I. Atomic Parameters *x*, *y*, and *z* and B_{eq} (Å²) for Compound 4[a,b]

	x	*y*	*z*	B_{eq}
Mn	0.01204 (4)	0.21071 (3)	0.13073 (4)	3.39 (3)
C(1)	0.0612 (3)	0.24203 (22)	0.0188 (3)	4.06 (22)
C(2)	−0.0408 (3)	0.19240 (23)	0.2462 (3)	4.49 (22)
C(3)	−0.1138 (3)	0.20065 (22)	0.0792 (3)	4.01 (21)
C(4)	0.0439 (3)	0.12030 (22)	0.1067 (3)	4.90 (25)
C(5)	0.1353 (3)	0.23108 (23)	0.1863 (3)	4.78 (25)
C(6)	−0.0190 (3)	0.32002 (21)	0.1643 (3)	3.18 (20)
C(7)	−0.1179 (3)	0.35436 (19)	0.1344 (3)	2.71 (18)
C(8)	−0.1261 (3)	0.36753 (22)	0.0329 (3)	3.21 (19)
C(9)	−0.1622 (3)	0.4241 (3)	−0.0068 (3)	3.61 (23)
C(10)	−0.2051 (3)	0.48675 (21)	0.0411 (3)	3.44 (20)
C(11)	−0.2257 (3)	0.46790 (19)	0.1445 (3)	2.97 (19)
C(12)	−0.1360 (3)	0.42440 (19)	0.18839 (24)	2.74 (17)
C(13)	−0.1430 (4)	0.5525 (3)	0.0239 (4)	4.7 (3)
C(14)	−0.3163 (3)	0.42221 (22)	0.1478 (3)	3.59 (20)
C(15)	−0.2431 (3)	0.53159 (21)	0.1998 (3)	3.75 (22)
C(16)	−0.0441 (3)	0.46874 (20)	0.1893 (3)	3.09 (20)
C(17)	−0.1604 (3)	0.40827 (22)	0.2867 (3)	3.84 (21)
N(1)	−0.38511 (25)	0.38733 (19)	0.1469 (3)	5.59 (21)
N(2)	−0.2527 (3)	0.58130 (18)	0.2408 (3)	6.01 (22)
N(3)	0.0243 (3)	0.50261 (18)	0.19392 (24)	4.71 (19)
N(4)	−0.1816 (3)	0.39587 (22)	0.3603 (3)	6.8 (3)
O(1)	0.09118 (24)	0.26297 (17)	−0.04941 (22)	6.34 (19)
O(2)	−0.0729 (3)	0.18484 (19)	0.31759 (20)	7.26 (20)
O(3)	−0.19095 (22)	0.19525 (18)	0.04849 (23)	6.44 (18)
O(4)	0.0621 (3)	0.06161 (16)	0.09126 (24)	7.68 (22)
O(5)	0.020688 (21)	0.24575 (18)	0.2214 (3)	7.63 (22)
H(6A)	0.0279 (24)	0.3420 (17)	0.1326 (24)	4.2 (11)
H(6B)	−0.012 (3)	0.3242 (16)	0.2284 (22)	3.8 (9)
H(7)	−0.1706 (19)	0.3245 (14)	0.1494 (19)	1.5 (7)
H(8)	−0.1034 (22)	0.3306 (15)	−0.0067 (21)	2.7 (8)
H(9)	−0.1593 (25)	0.4278 (19)	−0.0663 (21)	3.5 (10)
H(10)	−0.2672 (23)	0.5014 (18)	0.0111 (22)	3.4 (9)
H(13A)	−0.140 (3)	0.5639 (25)	−0.043 (3)	8.9 (17)
H(13)	−0.068 (3)	0.5461 (22)	0.050 (3)	8.4 (14)
H(13C)	−0.167 (3)	0.5957 (21)	0.050 (3)	7.6 (15)

[a] Esds refer to the last digit printed. [b] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Molecular Structure of the [4 + 2] Cycloadduct 4. An X-ray diffraction study of the TCNE adduct 4 was performed. The ORTEP drawing is shown in Figure 1, and the atomic coordinates and bond distances and angles are given in Tables I and II, respectively. The molecular structure confirms that the 2,4-hexadien-1-yl ligand undergoes [4 + 2] cycloaddition with TCNE. The coordination geometry around the molybdenum atom is approximately an octahedron with the five carbonyls and C(6) atom occupying the six coordination sites. The C(6)–(7) bond is parallel to the Mo–C(3) bond with a di-

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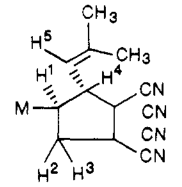
Table II. Bond Distances (Å) and Angles (deg) for Compound 4

Mn–C (1)	1.843 (5)	C(8)–H(8)	0.96 (3)
Mn–C(2)	1.844 (5)	C(9)–C(10)	1.492 (6)
Mn–C(3)	1.848 (4)	C(9)–H(9)	0.86 (3)
Mn–C(4)	1.804 (4)	C(10)–C(11)	1.560 (6)
Mn–C(5)	1.871 (4)	C(10)–C(13)	1.521 (7)
Mn–C(6)	2.174 (4)	C(10)–H(10)	0.98 (3)
C(1)–O(1)	1.135 (6)	C(11)–C(12)	1.588 (5)
C(2)–O(2)	1.125 (6)	C(11)–C(14)	1.489 (5)
C(3)–O(3)	1.126 (5)	C(11)–C(15)	1.468 (5)
C(4)–O(4)	1.163 (5)	C(12)–C(16)	1.488 (5)
C(5)–O(5)	1.118 (5)	C(12)–C(17)	1.488 (5)
C(6)–C(7)	1.535 (6)	C(13)–H(13A)	0.99 (4)
C(6)–H(6A)	0.88 (3)	C(13)–H(13B)	1.08 (4)
C(6)–H(6B)	0.93 (3)	C(13)–H(13C)	0.96 (4)
C(7)–C(8)	1.490 (6)	C(14)–N(1)	1.133 (5)
C(7)–C(12)	1.562 (5)	C(15)–N(2)	1.123 (5)
C(7)–H(7)	0.93 (3)	C(16)–N(3)	1.120 (5)
C(8)–C(9)	1.310 (6)	C(17)–N(4)	1.125 (6)
C(1)–Mn–C(2)	172.00 (19)	C(7)–C(8)–H(8)	116.2 (18)
C(1)–Mn–C(3)	90.23 (18)	C(9)–C(8)–H(8)	117.3 (18)
C(1)–Mn–C(4)	93.17 (19)	C(8)–C(9)–C(10)	126.4 (4)
C(1)–Mn–C(5)	89.76 (19)	C(8)–C(19)–H(9)	119.0 (24)
C(1)–Mn–C(6)	87.41 (18)	C(10–C(9)–H(9)	114.5 (25)
C(2)–Mn–C(3)	89.81 (18)	C(9)–C(10)–C(11)	109.2 (3)
C(2)–Mn–C(4)	94.83 (20)	C(9)–C(10)–C(13)	111.8 (4)
C(2)–Mn–C(5)	89.32 (19)	C(9)–C(10)–H(10)	110.4 (20)
C(2)–Mn–C(6)	84.59 (18)	C(11)–C(10)–C(13)	116.2 (4)
C(3)–Mn–C(4)	92.22 (19)	C(11)–C(10)–H(10)	110.0 (19)
C(3)–Mn–C(5)	173.65 (19)	C(13)–C(10)–H(10)	98.9 (20)
C(3)–Mn–C(6)	90.87 (17)	C(10)–C(11)–C(12)	111.6 (3)
C(4)–Mn–C(5)	94.12 (19)	C(10)–C(11)–C(14)	107.9 (3)
C(4)–Mn–C(6)	176.85 (18)	C(10)–C(11)–C(15)	111.0 (3)
C(5)–Mn–C(6)	82.79 (17)	C(12)–C(11)–C(14)	107.2 (3)
Mn–C(1)–O(1)	178.3 (4)	C(12)–C(11)–C(15)	109.4 (3)
Mn–C(2)–O(2)	176.4 (4)	C(14)–C(11)–C(15)	109.6 (3)
Mn–C(3)–O(3)	179.1 (4)	C(7)–C(12)–C(11)	111.2 (3)
Mn–C(4)–O(4)	178.4 (4)	C(7)–C(12)–C(16)	111.1 (3)
Mn–C(5)–O(5)	176.8 (4)	C(7)–C(12)–C(17)	109.5 (3)
Mn–C(6)–C(7)	120.5 (3)	C(11)–C(12)–C(16)	109.3 (3)
Mn–C(6)–H(6A)	101.6 (22)	C(11)–C(12)–C(17)	108.8 (3)
Mn–C(6)–H(6B)	106.4 (19)	C(16)–C(12)–C(17)	106.8 (3)
C(7)–C(6)–H(6A)	105.3 (22)	C(10)–C(13)–H(13A)	111 (3)
C(7)–C(6)–H(6B)	109.6 (22)	C(10)–C(13)–H(13B)	110.9 (23)
H(6A)–C(6)–H(6B)	113 (3)	C(10)–C(13)–H(13C)	117.3 (25)
C(6)–C(7)–C(8)	114.3 (3)	H(13A)–C(13)–H(13B)	109 (3)
C(6)–C(7)–C(12)	110.8 (3)	H(13A)–C(13)–H(13C)	102 (4)
C(6)–C(7)–H(7)	109.0 (16)	H(13B)–C(13)–H(13C)	105 (3)
C(8)–C(7)–C(12)	109.7 (3)	C(11)–C(14)–N(1)	177.6 (4)
C(8)–C(7)–H(7)	106.1 (17)	C(11)–C(15)–N(2)	177.1 (4)
C(12)–C(7)–H(7)	106.7 (16)	C(12)–C(16)–N(3)	177.0 (4)
C(7)–C(8)–C(9)	126.5 (4)	C(12)–C(17)–N(4)	178.0 (5)

hedral angle 3.9 (2)°. The C(5)–Mn bond tilts toward the Mn-C(6) bond with the bond angles C(6)–Mn–C(5) (82.79 (17)°) and C(4)–Mn–C(5) (94.12 (19)°), which show distortion from an ideal octahedron. The Mn–C(6) bond distance of 2.174(4)Å is comparable to that of the σ Mn–C bond (2.180 Å) of the complex $(C_9H_7N_2)Mn(CO)_5$.[10] In the cyclohexene moiety, the bond distances of the C(8)–C(9) (1.310 (6) Å) and four cyano groups (1.120 (5)–1.133 (5) Å) represent double and triple bonds. The C(13) and C(6) carbons respectively occupy the two equatorial positions of the six-membered ring. Such a stereochemistry implies that the cycloaddition proceeds by a concerted mechanism.[11]

[3 + 2] Cycloaddition. Treatment of $Mn(CO)_5(\eta^1$-5-methyl-2,4-hexadien-1-yl) (**9**) with an equimolar amount of tetracyanoethylene in THF at 0 °C gave 1:1 adducts in moderate yields (41%). Greenish yellow crystals, very sensitive to air, were obtained after recrystallization from a saturated chloroform solution at −20 °C. According to the spectroscopic data, only one stereoisomer is detected. The NMR data are not compatible with those expected for the [4 + 2] structure; in contrast, a [3 + 2] cycloaddition structure is fully compatible. The key ^1H NMR feature is that only one olefinic proton is observed at δ 5.09 ppm as a doublet, assignable to the resonance of H^3. The ^{13}C NMR resonances of the carbons CH^5 and $C(CH_3)_2$ are characteristic of unbound double bonds (118.6 and 146.1 ppm, respectively). The remaining NMR resonances are in conformity with the proposed structure. Attempts to perform an X-ray diffraction study were hampered by the sensitivity of the crystals to air. In order to characterize further the molecular structure of this class of compounds, we have prepared the iron and molybdenum analogues (**13**) and (**14**) from the η^1-dienyl compounds $M(\eta^1$-5-methyl-2,4-hexadien-1-yl) (M = $CpFe(CO)_2$ (**10**), $CpMo(CO)_3$ (**11**)). Compounds **10** and **11** were obtained in moderate yields from the reaction between 1-halo-5-methyl-2,4-hexadiene and $CpFe(CO)_2Na$ ($CpMo(CO)_3Na$). In our previous papers[4a,5] we have shown that cycloaddition of $M(\eta^1$-2,4-pentadienyl) and $M(\eta^1$-2,4-hexadien-1-yl) (M = $CpMo(CO)_3$, $CpFe(CO)_2$) with reactive alkenes led only to the [4 + 2] cycloadducts. The reaction of **10** and **11** with an equimolar amount of tetracyanoethylene proceeded smoothly at ambient temperatures. Yellow crystals, fairly stable to air, of 1:1 adducts **13** and **14** were obtained in reasonable yields (40–45%) after workup. Elemental analyses were satisfactory for the given formulae. The ^1H and ^{13}C NMR spectra of these two compounds show a pattern resembling those of **12**; hence a [3 + 2] cycloaddition structure is assignable.



12: M = $Mn(CO)_5$
13: M = $CpFe(CO)_2$
14: M = $CpMo(CO)_3$

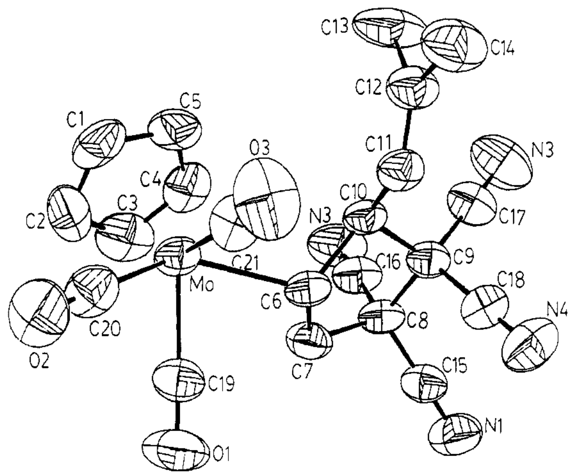


Figure 2. ORTEP drawing of the molecule 14.

X-ray Structure Analysis of the [3 + 2] Cycloadduct 14. An X-ray diffraction study of the molybdenum adduct **14** was undertaken. The ORTEP drawing shown in Figure 2 confirms that the 5-methyl-2,4-hexadien-1-yl ligand undergoes 1,3 [3 + 2] cycloaddition with tetra-

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[10] $C_9H_7N_2$ = 5*H*-dipyrroloimidazol-5-yl: Burser, U.; Perret, C.; Pernardinelli, G.; Kundis, E. P. *Helv. Chim. Acta* **1984**, *67*, 2063.

[11] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; 2nd ed. Plenum Press: New York, 1977; Part B.

Table III. Atomic Parameters x, y, and z and B_{iso} (Å^2) for Compound 14[a,b]

	x	y	z	B_{iso}
M0	0.17125 (4)	0.155018 (24)	0.21790 (3)	3.952 (18)
C1	0.0919 (6)	0.2018 (4)	0.0497 (4)	6.3 (3)
C2	0.0296 (5)	0.1260 (5)	0.0703 (4)	6.9 (3)
C3	0.1175 (7)	0.0609 (4)	0.0750 (4)	6.6 (3)
C4	0.2306 (5)	0.0953 (4)	0.0578 (3)	5.34 (25)
C5	0.2174 (5)	0.1818 (4)	0.0428 (3)	5.7 (3)
C6	0.3685 (4)	0.1051 (3)	0.2876 (3)	3.82 (19)
C7	0.3755 (4)	0.0095 (3)	0.2898 (4)	4.69 (20)
C8	0.5132 (4)	−0.0163 (3)	0.2706 (3)	4.19 (20)
C9	0.5856 (4)	0.0699 (3)	0.2758 (3)	4.08 (20)
C10	0.4816 (4)	0.13533 (24)	0.2334 (3)	3.80 (18)
C11	0.5223 (4)	0.2236 (3)	0.2587 (3)	4.25 (20)
C12	0.5597 (5)	0.2811 (3)	0.1947 (4)	5.21 (23)
C13	0.5696 (7)	0.2699 (4)	0.0766 (4)	8.5 (4)
C14	0.5977 (6)	0.3672 (3)	0.2379 (5)	7.1 (3)
C15	0.5694 (4)	−0.0778 (3)	0.3513 (4)	4.85 (22)
C16	0.5121 (5)	−0.0528 (3)	0.1616 (4)	5.09 (24)
Cu7	0.6919 (5)	0.0690 (3)	0.2108 (4)	5.38 (24)
C18	0.6361 (4)	0.0882 (3)	0.3892 (4)	4.91 (22)
C19	0.1366 (4)	0.0791 (3)	0.3376 (4)	5.00 (23)
C20	0.0244 (5)	0.2077 (3)	0.2765 (4)	5.46 (24)
C21	0.2447 (5)	0.2584 (3)	0.2897 (4)	5.46 (24)
O1	0.1120 (4)	0.0357 (3)	0.4039 (3)	7.81 (21)
O2	−0.0608 (4)	0.2363 (3)	0.3085 (3)	7.48 (21)
O3	0.2794 (4)	0.32065 (25)	0.3277 (4)	8.43 (25)
N1	0.6102 (4)	−0.1237 (3)	0.4148 (4)	6.61 (23)
N2	0.5069 (5)	−0.0793 (3)	0.0783 (4)	7.2 (3)
N3	0.7695 (5)	0.0675 (3)	0.1584 (4)	8.4 (3)
N4	0.6735 (4)	0.1026 (3)	0.4754 (4)	6.71 (25)
H1	0.050	0.263	0.041	6.3
H2	−0.065	0.124	0.079	6.3
H3	0.093	−0.002	0.092	6.3
H4	0.309	0.061	0.056	6.3
H5	0.286	0.225	0.028	6.3
H6	0.378	0.128	0.365	6.3
H7A	0.354	−0.015	0.360	6.3
H7B	0.311	−0.015	0.232	6.3
H10	0.459	0.129	0.152	6.3
H11	0.512	0.242	0.335	6.3
H13A	0.652	0.293	0.059	6.3
H13B	0.502	0.304	0.034	6.3
H13C	0.561	0.208	0.061	6.3
H14A	0.573	0.372	0.315	6.3
H14B	0.541	0.412	0.196	6.3
H14C	0.686	0.376	0.235	6.3

[a] Esds refer to the last digit printed. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid

cyanoethylene, with the CpMo(CO)$_3$ subunit migrating to the β-carbon atom of the dienyl ligand. The coordination geometry about the molybdenum atom is approximately a distorted square pyramid with the C(20), C(19), C(9), and C(21) atoms occupying the four basal positions. The atomic coordinates and bond distances and angles are given in Tables III and IV, respectively. The bond angles Cp–Mo–C(20) (112.3 (2)°), Cp–Mo–C(21) (127.2 (2)°), Cp–Mo–C(6) (111.1 (2)°), and Cp–Mo–C(19) (127.9 (2)°) show the distortion from an ideal square pyramid. (Cp is the centroid of cyclopentadienyl group.) The Mo–C(6) bond distance (2.335 (5) Å) is comparable with that of the σ Mo–C bond (2.38 (2) Å) of the CpMo(CO)$_3$(C$_2$H$_5$) complex.[12] The C(11)—C(12) bond distance 1.312 (6) Å and the four C≡N bond distances of 1.124 (7)–1.131 (7) Å correspond to double and triplet bonds, respectively. The remaining C–C bond distances of the cyclopentane ring are consistent with those of a single bond. Particularly notable is the orientation of the vinyl double bond which lies trans to the Mo–C(6) bond. Such a stereochemical feature suggests that the reaction pathway proceeds via an ionic mechanism like that of the [3 + 2] cycloaddition of iron–η^1-allyl complexes with reactive alkenes.[13] A zwitterion M$^+$[CH$_2$=CHCH(CH=CMe$_2$)C(CN)$_2$C$^-$(CN)$_2$] is presumably the intermediate during the cycloaddition.

Table IV. Bond Distances (Å) and Angles (deg) for Compound 14[a]

Mo–C(1)	2.306 (7)	C(8)–C(9)	1.574 (6)
Mo–C(2)	2.300 (7)	C(8)–C(15)	1.483 (7)
Mo–C(3)	2.355 (6)	C(8)–C(16)	1.486 (7)
Mo–C(4)	2.381 (7)	C(9)–C(10)	1.573 (6)
Mo–C(5)	2.354 (8)	C(9)–C(17)	1.483 (7)
Mo–C(6)	2.335 (5)	C(9)–C(18)	1.492 (8)
Mo–C(19)	1.999 (6)	C(10)–C(11)	1.492 (6)
Mo–C(20)	2.006 (6)	C(11)–C(12)	1.312 (6)
Mo–C(21)	1.992 (6)	C(12)–C(13)	1.512 (8)
C(1)–C(2)	1.418 (10)	C(12)–C(14)	1.510 (7)
C(1)–C(5)	1.399 (8)	C(15)–N(1)	1.131 (7)
C(2)–C(3)	1.398 (10)	C(16)–N(2)	1.124 (7)
C(3)–C(4)	1.375 (9)	C(17)–N(3)	1.126 (7)
C(4)–C(5)	1.393 (8)	C(18)–N(4)	1.131 (7)
C(6)–C(7)	1.521 (6)	C(19)–O(1)	1.138 (6)
C(6)–C(10)	1.542 (6)	C(20)–O(2)	1.139 (7)
C(7)–C(8)	1.584 (6)	C(21)–O(3)	1.141 (7)
Mo–Cp	2.015 (6)		

Cp–Mo–C(6)	111.10 (15)	C(8)–C(9)–C(10)	103.5 (3)
Cp–Mo–C(19)	127.88 (18)	C(8)–C(9)–C(17)	112.3 (3)
Cp–Mo–C(20)	112.34 (19)	C(8)–C(9)–C(18)	109.3 (3)
Cp–Mo–C(21)	127.22 (16)	C(10)–C(9)–C(17)	112.6 (4)
C(6)–Mo–C(19)	75.88 (19)	C(10)–C(9)–C(18)	110.8 (4)
C(6)–Mo–C(20)	136.45 (20)	C(17)–C(9)–C(18)	108.2 (4)
C(6)–Mo–C(21)	79.51 (19)	C(6)–C(10)–C(9)	102.2 (3)
C(19)–Mo–C(20)	75.44 (23)	C(6)–C(10)–C(11)	115.2 (3)
C(19)–Mo–C(21)	104.9 (3)	C(9)–C(10)–C(11)	111.8 (3)
C(20)–Mo–C(21)	77.04 (21)	C(10)–C(11)–C(12)	128.9 (4)
Mo–C(6)–C(7)	112.8 (3)	C(11)–C(12)–C(13)	125.7 (4)
Mo–C(6)–C(10)	117.3 (3)	C(11)–C(12)–C(14)	120.1 (4)
C(7)–C(6)–C(10)	106.2 (3)	C(13)–C(12)–C(14)	114.3 (4)
C(6)–C(7)–C(8)	107.6 (3)	C(8)–C(15)–N(1)	178.1 (5)
C(7)–C(8)–C(9)	103.6 (3)	C(8)–C(16)–N(2)	177.5 (6)
C(7)–C(8)–C(15)	112.2 (4)	C(9)–C(17)–N(3)	177.4 (6)
C(7)–C(8)–C(16)	109.8 (4)	C(9)–C(18)–N(4)	179.4 (5)
C(9)–C(8)–C(15)	112.7 (4)	Mo–C(19)–O(1)	177.2 (4)
C(9)–C(8)–C(16)	109.0 (3)	Mo–C(20)–O(2)	178.4 (4)
C(15)–C(8)–C(16)	109.3 (4)	Mo–C(21)–O(3)	175.2 (4)

[a] Cp is the center of mass in cyclopentadienyl ring.

Comments on the Cycloaddition. The present studies together with our previous results show for the first time that the transition-metal–η^1-2,4-dien-1-yl ligand possesses a dual functionality in cycloaddition reactions with reactive alkenes. Our new compounds resemble the main-group compounds Me$_3$M(η^1-C$_5$H$_7$) (M = Si, Ge) in that both classes of compounds undergo electrophilic addition[14] and Diels–Alder reactions.[2b–d] On the other hand, they can be regarded as being a higher homologue of the allyl complexes because of the [3 + 2] cycloaddition reactivity. More interestingly, our previous studies[5] have shown that the reaction of CpFe(CO)$_2$(η^1-pentadienyl) with alkynes such as hexafluoro-2-butyne and dimethyl acetylenedicarboxylate leads to insertion products. Insertion of an alkyne molecule into the σ metal–pentadienyl bond is novel because the competitive cycloaddition[15] is known to be a facile and common process. All these results indicate that the change of dienyl structures and dienophiles vary the reaction pathway. In the light of these versatile reactivities, one might therefore reasonably anticipate that the transition-metal–η^1-dienyl complexes should possess

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greater utilization in organic reactions than their main-group metal analogues.

One interesting feature of this study is a comparison of chemical reactivity between these two types of cycloaddition. That the [4 + 2] cycloaddition appears to be more facile than the [3 + 2] reaction can be partly attributed to the presence of the vinyl group which imposes steric hindrance to the electrophilic attack of alkene on the γ-carbon of the dienyl ligand. A [3 + 2] cycloaddition, however, can be made possible if the [4 + 2] cycloaddition is hindered. In a typical Diels–Alder reaction, the dienyl ligand geometry requires a σ-*cis*-diene conformation.[11] If the ϵ-carbon of the dienyl ligand is disubstituted, the Diels–Alder reaction would encounter difficulties owing to the increasing intraligand steric hindrance in this σ-*cis*-diene geometry. In this paper, TCNE and maleic anhydride were used as the model molecules to establish the reaction pathways. In principle further expansion of the reaction chemistry of these metal–dienyl complexes with various alkenes is possible, particularly as the manganese–η^1-dienyl complexes are relatively thermally stable at moderate temperatures. These studies are currently in progress.

Experimental Section

All operations were carried out under argon in Schlenk apparatus or in a glovebox. The solvents diethyl ether, tetrahydrofuran, and pentane were dried with sodium/benzophenone and distilled before use. Chloroform was dried over phosphorus pentoxide and distilled before use. $Mn_2(CO)_{10}$ was obtained from a commercial source and used without further purification. The synthesis and spectroscopic data of 1 have been described elsewhere.[4b] 1-Chloro-2,4-hexadiene,[15] 1-chloro-5-methyl-2,4-hexadiene,[16] $CpFe(CO)_2Na$,[17] $CpMo(CO)_3Na$,[17] and $NaMn(CO)_5$[17] were prepared according to the literature. NMR spectra were recorded on a Bruker AM-400 spectrometer. Microanalyses were performed in the Microanalytic Laboratory at National Taiwan University.

(a) Synthesis of $Mn(CO)_5(\eta^1$-2,4-hexadien-1-yl) (2). A 50-mL tetrahydrofuran solution of $NaMn(CO)_5$ (2.0 g, 9.18 mmol) was stirred with 1-chloro-2,4-hexadiene (1.06 g, 9.2 mmol) at −78 °C for 4 h. The solution was warmed to 0 °C, and the solvent was removed under reduced pressure leaving a brown residue. Repeated vacuum distillation of this residues (4×10^{-3} Torr) at 23 °C into a 0 °C cold trap gave the yellow crystalline solid **2** (1.05 g, 3.8 mmol). Anal. Calcd for $C_{11}H_9MnO_5$: C, 47.85; H, 3.29. Found: C, 47.54; H, 3.36. IR spectrum ($CHCl_3$): 2140 (s), 2057 (s), 2045 (s), 2007 (s), 1979 (s) cm^{-1}; ν(C=C) 1602 cm^{-1}. Mass spectrum (12 eV): 276 (M$^+$). ^{1}H NMR spectra (400 MHz, $CDCl_3$): δ 1.70 (3 H, d, J = 6.7 Hz), 1.90 (2 H, d, J = 6 Hz), 5.49 (1 H, dq, J = 17 Hz, 6.7 Hz), 5.96 (1 H, complex m, J = 17 Hz, 6.7 Hz).

(b) Synthesis of $Mn(CO)_5CH_2CHC(CN)_2CH(CH_3)CH=CH$ (3). Tetracyanoethylene (0.25 g, 2.00 mmol) and compound **2** (0.52 g, 1.89 mmol) were dissolved in 20 mL of $CHCl_3$ and stirred at 0 °C for 2 h. After removal of the solvent, under reduced pressure, the residues were extracted with chloroform and recrystallized from chloroform/hexane to give colorless rodlike crystals (0.49 g, 1.20 mmol). Anal. Calcd for $C_{17}H_9MnN_4O_5$: C, 50.52; H, 2.24. Found: C, 50.23; H, 2.12. IR spectrum ($CHCl_3$): ν(CN) 2230 (w), 2204 (w); ν(CO) 2117 (s), 2053 (s), 2015 (s), 1975 (s), 1964 (s) cm^{-1}; ν(C=C) 1648 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (1 H, dd, H^1), 1.47 (1 H, dd, H^2), 1.55 (3 H, d, CH_3), 3.09 (1 H, dd, H^3), 3.22 (1 H, m, H^6), 5.82 (1 H, d, H^4), 5.87 (1 H, d, H^5), J_{12} = 11.2 Hz, J_{13} = 11.2 Hz, J_{23} = 1.2 Hz, J_{45} = 11.4 Hz, J_{6-CH3} = 7.3 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.4 (CH^{1}CH^2), 17.8 (CH_3), 37.6 (CH^3), 45.2 ($C(CN)_2$), 47.3 (CH^6), 110.1, 110.3, 111.8, 111.9 (CN), 125.7 (CH^5), 127.1 (CH^4), 210.8 (CO).

(c) Synthesis of $Mn(CO)_5(CH_2CHCHCOOCOCHCH_2CH=CH)$ (5). Maleic anhydride (0.49 g, 5.0 mmol) and 1 (1.31 g) were dissolved in 20 mL of $CHCl_3$ and stirred at 0 °C for 2 h. After removal of the solvent under reduced pressure, the extract was dissolved in $CHCl_3$, followed by addition of ether to give a yellow precipitate. Attempts to crystallize the precipitate were unsuccessful owing to its facile carbonylation to **7**. Elemental analyses indicate the purity of this yellow precipitate. Anal. Calcd for $MnC_{14}H_9O_8$: C, 46.69; H, 2.51. Found: C, 46.84; H, 2.68. IR spectrum ($CHCl_3$): ν(CO) 2115 (s), 2045 (s), 2007 (s), 1990 (s), 1945 (s), 1775 (s) cm^{-1}; ν(C=C) 1654 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (1 H, dd, H^1), 1.27 (1 H, dd, H^2), 2.27 (1 H, dd, H^8), 2.64 (1 H, m, H^3), 2.67 (1 H, m, H^9), 3.32 (1 H, m, H^7), 3.40 (1 H, dd, H^6), 5.93–5.99 (2 H, complex m, H^4 + H^5), J_{12} = 11.2 Hz, J_{13} = 11.2, J_{23} = 2.8 Hz, J_{78} = 7.8 Hz, J_{89} = 14 Hz, J_{36} = 7.8 Hz, J_{67} = 7.5 Hz. ^{13}C NMR (400 MHz, $CDCl_3$): δ 6.76 (CH^{1}H^2), 23.50 (CH^{8}H^9), 41.05 (CH^7), 41.63 (CH^6), 48.90 (CH^3), 127.6 (CH^5), 135.2 (CH^4), 171.5, 174.5 (COOCO), 209.1, 212.3 (CO).

(d) Synthesis of $Mn(CO)_5(CH_2CHCHCOOCOCHCH(CH_3)CH=CH)$ (6). This complex was similarly prepared from the reaction between maleic anhydride and **2**; the yield was 75%. Anal. Calcd for $MnC_{15}H_{11}O_8$: C, 48.16; H, 2.96. Found: C, 48.42; H, 2.78. IR spectrum ($CHCl_3$): ν(CO) 2110 (s), 2047 (s), 2009 (s), 1985 (s), 1960 (s), 1775 (s) cm^{-1}; ν(C=C) 1652 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (1 H, dd, H^1), 1.41 (3 H, d, CH_3), 1.52 (1 H, dd, H^2), 2.50 (1 H, m, H^3), 2.59 (1 H, m, H^8), 3.27 (1 H, m, H^7), 3.32 (1 H, m, H^6), 5.79 (1 H, br d, H^5), 5.86 (1 H, br d, H^4), J_{12} = 11.5 Hz, J_{13} = 2.8 Hz, J_{23} = 11.4 Hz, J_{45} = 9.0 Hz. ^{13}C NMR (400 MHz, $CDCl_3$): δ 7.3 (CH^{1}H^2), 16.1 $(CH_3)_7$, 30.4 (CH^8), 42.5 (CH^7), 47.0 (CH^6), 50.2 (CH^3), 134.7 (CH^5), 135.0 (CH^4), 171.2, 171.3 (COOCO), 212.5 (CO).

(e) Synthesis of $(CO)_4MnCOCH_2CHCHCOOCOCHCH_2CH=CH$ (7). Complex **5** was dissolved in $CHCl_3$. Colorless crystals were obtained after the solution was allowed to stand at 23 °C for 2 days; the yield was 92%. Anal. Calcd for $MnC_{14}H_9O_8$: C, 46.69; H, 2.52. Found: C, 46.84; H, 2.73. IR spectrum ($CHCl_3$): ν(CO) 2115 (s), 2039 (s), 2015 (s), 1919 (s), 1775 (m), 1725 (m), 1637 (m) cm^{-1}; ν(C=C) 1654 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (1 H, m, H^9), 2.69–2.77 (2 H, complex m, H^3 + H^8), 3.22 (1 H, dd, H^1), 3.37 (1 H, dd, H^7), 3.61 (1 H, dd, H^6), 3.79 (1 H, dd, H^2), 5.63 (1 H, m, H^4), 5.98 (1 H, m, H^5), J_{12} = 18.4 Hz, J_{13} = 4.8 Hz, J_{23} = 10.0 Hz, J_{36} = 7.2 Hz, J_{67} = 10.0 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.1 (CH^{8}H^9), 30.7 (CH^3), 40.8 (CH^7), 42.2 (CH^6), 66.6 (CH^{1}H^2), 126.6, 132.5 (CH^4 + CH^5), 174.1 (COOCO), 208.8 (CO), 258.4 (MnCOCH^{1}H^2).

(f) Synthesis of $(CO)_4MnCOCH_2CHCHCOOCOCHCH(CH_3)CH=CH_2$ (8). Complex **6** was dissolved in $CHCl_3$. Colorless crystals were obtained after the solution was allowed to stand at 23 °C for 2 days; the yield was 93%. Anal. Calcd for $MnC_{15}H_{11}O_8$: C, 48.14; H, 2.96. Found: C, 48.36; H, 3.04. IR spectrum ($CHCl_3$): ν(CO) 2115 (s), 2015 (s), 1999 (s), 1919 (s), 1775 (m), 1715 (m), 1639 (m) cm^{-1}; ν(C=C) 1652 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (3 H, d, CH_3), 2.43 (1 H, m, H^8), 2.75 (1 H, m, H^3), 3.23 (1 H, dd, H^1), 3.25 (1 H, m, H^7), 3.59 (1 H, m, H^6), 3.83 (1 H, dd, H^2), 5.56 (1 H, m, H^5), 5.72 (1 H, m, H^4), J_{8-CH3} = 1.4 Hz, J_{12} = 18 Hz, J_{13} = 2.0 Hz, J_{23} = 10.2 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.40 (CH_3), 30.4 (CH^8), 31.4 (CH^3), 43.5 (CH^7), 46.0 (CH^6), 66.6 (CH^{1}H^2), 131.6, 135.5 (CH^4 + CH^5), 171.3, 172.3 (COOCO), 209.1 (CO), 258.39 (MnCOCH^{1}H^2).

(g) Synthesis of $Mn(CO)_5(\eta^1$-5-methyl-2,4-hexadien-1-yl) (9). This complex was prepared similarly from the reaction between $NaMn(CO)_5$ and 1-chloro-5-methyl-2,4-hexadiene; the yield was 42%. Anal. Calcd for $C_{12}H_{11}MnO_5$: C, 49.67; H, 3.81. Found: C, 49.82; H, 3.94. IR spectrum ($CHCl_3$): ν(CO) 2103 (s), 2061 (s), 2046 (s), 2010 (s), 1965 (s) cm^{-1}; ν(C=C) 1600 (s) cm^{-1}. Mass spectrum (12 eV): 290 (M$^+$). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): 1.80 (3 H, s, CH_3), 1.82 (3 H, s, CH_3), 2.07 (d, 2 H, J = 7.0 Hz), 5.53 (1 H, dt, J = 1.5 Hz, J = 7.0 Hz), 5.77 (1 H, d, J = 10 Hz), 6.22 (1 H, dd, J = 15 Hz, J = 10 Hz).

(h) Synthesis of $CpFe(CO)_2(\eta^1$-5-methyl-2,4-hexadien-1-yl) (10). A solution of $CpFe(CO)_2Na$ (1.5 g, 8.4 mmol) in 50 mL of

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Table V. Crystal and Diffraction Data for 4 and 14

	4	14
space group	*Pbca*	$P2_1/n$
a, Å	13.353 (3)	10.760 (8)
b, Å	19.010 (4)	15.898 (6)
c, Å	14.437 (3)	12.57 (4)
β, °		96.97 (14)
v, Å^3	3664.63	2134.54
cryst size, mm	0.10 × 0.45 × 0.65	0.12 × 0.50 × 0.60
cryst color	red	red
wavelength (Mo Kα), Å	0.7093	0.7093
abs coeff μ_2 cm^{-1}	7.2	6.3
abs correctn	ψ rotation	ψ rotation
scan parameter	$0.80 + 0.35 \tan \theta$	$0.70 + 0.35 \tan \theta$
scan type	$\omega/2\theta$	$\omega/2\theta$
2θ range, deg	2.5–50	2.5–50
no. of unique reflctns	3218	3749
no. of reflctns with $I > 3\sigma(I)$	1805	2898
no. of variables	281	262
final R_F	3.7	3.9
final R_w	2.4[a]	4.3[b]
final E_{map}(max), e Å^{-3}	0.37	0.62
goodness of fit, S[c]	1.869	2.404

[a] $w = 1/(\sigma^2(F_o))$. [b] $w = 1/[\sigma^2(F_o) + (0.01F_c)^2]$. [c] $s = [\sum w|F_o - F_c|^2/(N_o - N_c)]^{1/2}$, where N_o is the number of observations and N_c is the number of variables.

tetrahydrofuran was stirred with 1-chloro-5-methyl-2,4-hexadiene (1.13 g, 8.7 mmol) at 0 °C for 3 h. After removal of the solvent, the residues were chromatographed on a neutral alumina column, using pentane as the eluting solvent. A yellow band was developed, collected, and evaporated to dryness to give an orange red-oil (1.12 g, 4.1 mmol). Anal. Calcd for $C_{14}H_{16}FeO_2$: C, 61.79; H, 5.92. Found: C, 61.84; H, 6.04. IR spectrum ($CHCl_3$): ν(CO) 2010 (s), 1960 (s) cm^{-1}; ν(C=C) 1623 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.74 (3 H, s, CH_3), 1.76 (3 H, s, CH_3), 2.07 (d, 2 H, J = 8.2 Hz), 4.40 (5 H, s, C_5H_5), 5.90–5.94 (2 H, complex m), 6.34 (dt, 1 H, J = 16.8 Hz, J = 8.2 Hz).

(i) Synthesis of CpMo(CO)$_3$(η^1-5-methyl-2,4-hexadien-1-yl) (11). A solution of CpMo(CO)$_3$Na (1.57 g, 50 mmol) in 50 mL of tetrahydrofuran was stirred with 1-chloro-5-methyl-2,4-hexadiene (0.66 g, 5.1 mmol) at 0 °C for 3 h. After removal of the solvent, the residues were chromatographed through a neutral alumina column, using pentane as the eluting solvent. A yellow band was developed, collected, and evaporated to dryness to give a yellow solid (1.19 g, 3.6 mmol). Anal. Calcd for $C_{15}H_{16}MoO_3$: C, 54.76; H, 4.86. Found: C, 54.82; H, 4.92. IR spectrum ($CHCl_3$): ν(CO) 2010 (s), 1960 (s), 1934 (s) cm^{-1}; ν(C=C) 1615 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.68 (3 H, s, CH_3), 1.69 (3 H, s, CH_3), 2.46 (3 H, d, J = 8.4 Hz), 4.44 (5 H, s, C_5H_5), 5.91 (2 H, complex m), 6.23 (1 H, dt, J = 16 Hz, J = 8.4 Hz).

(j) Synthesis of (CO)$_5$Mn(CHCH(CH=CMe$_2$)C(CN)$_2$C(CN)$_2$CH$_2$) (12). A solution of **9** (1.50 g, 5.66 mmol) and in 50 mL of tetrahydrofuran and tetracyanoethylene (0.74 g, 5.80 mmol) was stirred at 0 °C for 2 h. After removal of the solvent, the residues were extracted with chloroform and recrystallized at −20 °C to give a greenish yellow crystalline solid (1.00 g, 2.40 mmol). Anal. Calcd for $MnC_{18}H_{11}N_4O_5$: C, 51.69; H, 2.65. Found: C, 49.02; H, 2.34. (The carbon analysis is unsatisfactory because of the sensitivity of the compound to air.) IR spectrum ($CHCl_3$): ν(CN) 2230 (w) cm^{-1}; ν(CO) 2230 (s), 2115 (s), 2020 (s), 1985 (s), 1975 (s) cm^{-1}; ν(C=C) 1660 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.87 (3 H, s, CH_3), 1.89 (3 H, s, CH_3), 1.97 (1 H, s, H^1), 2.81 (1 H, dd, H^2), 3.21 (1 H, dd, H^3), 3.59 (1 H, dd, H^4), 5.09 (1 H, d, H^5), J_{12} = 11 Hz, J_{23} = 14 Hz, J_{14} = 11.2 Hz, J_{45} = 11.2 Hz. ^{13}C NMR (400 MHz, $CDCl_3$): δ 17.1 (CH^1), 20.8 (CH_3), 26.1 (CH_3), 44.8, 44.2 ($C(CN)_2C(CN)_2$), 51.3 (CH^2H^3), 61.4 (CH^4), 111.9, 113.4, 114.2, 114.5 (CN), 118.6 (CH^5), 146.1 ($C(CH_3)_2$), 209.5 (CO).

(k) Synthesis of CpFe(CO)$_2$(CHCH(CH=CMe$_2$)C(CN)$_2$C(CN)$_2$CH$_2$) (13). This complex was prepared similarly from the reaction between CpFe(CO)$_2$Na and 1-chloro-5-methyl-2,4-hexadiene. Pale yellow crystals were obtained in 42% yield after recrystallization from a saturated chloroform solution. Anal. Calcd for $C_{20}H_{16}FeO_2N_4$: C, 60.02; H, 4.03. Found: C, 60.42; H, 4.21. IR spectrum ($CHCl_3$): ν(CN) 2280 (w), 2228 (w) cm^{-1}; ν(CO) 2020 (s), 1962 (s) cm^{-1}; ν(C=C) 1645 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.54 (3 H, s, CH_3), 1.58 (3 H, s, CH_3), 2.46 (1 H, m, H^1), 2.60 (1 H, dd, H^2), 3.05 (1 H, dd, H^3), 3.36 (1 H, dd, H^4), 3.78 (5 H, s, C_5H_5), 5.07 (1 H, d, H^5), J_{12} = 14.1 Hz, J_{13} = 12.5 Hz, J_{23} = 9.0 Hz, J_{14} = 10.1 Hz, J_{45} = 11.5 Hz. ^{13}C NMR (400 MHz, $CDCl_3$): δ 18.8 (CH_3), 19.3 (CH_3), 25.7 (CH^1), 51.4 (CH^2H^3), 61.4 (CH^4), 85.2 (C_5H_5), 111.1, 112.3, 112.7, 113.1 (CN), 120.1 (CH^5), 114.0 ($C(CH_3)_2$), 214.9, 215.4 (CO).

(l) Synthesis of CpMo(CO)$_3$(CHCH(CH=CMe$_2$)C(CN)$_2$C(CN)$_2$CH$_2$) (14). This complex was prepared similarly from the reaction between CpMo(CO)$_3$Na and 1-chloro-5-methyl-2,4-hexadiene. Pale yellow crystals were obtained in 39% yield after recrystallization from a standard chloroform solution. Anal. Calcd for $C_{21}H_{16}MeO_3N_4$: C, 53.86, H, 3.44. Found: C, 54.01, H, 3.52. IR spectrum ($CHCl_3$): ν(CN) 2250 (w) cm^{-1}; ν(CO) 2010 (s), 1950 (s) cm^{-1}, 1930 (s) cm^{-1}; ν(C=C) 1670 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.81 (s, 3 H, CH_3), 1.86 (s, 3 H, CH_3), 2.71 (1 H, dd, H^2), 2.76 (1 H, m, H^1), 3.12 (1 H, dd, H^3), 3.63 (1 H, dd, H^4), 5.07 (1 H, d, H^5), 5.40 (5 H, s, C_5H_5), J_{12} = 12.3 Hz, J_{13} = 7.8 Hz, J_{23} = 11.9 Hz, J_{14} = 10.4 Hz, J_{45} = 10.1 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8 (CH^1), 45.0, 52.0 ($C(CN)_2C(CN)_2$), 51.7 (CH^2H^3), 81.2 (CH^4), 112.7, 112.6, 111.9, 111 (CN), 120.2 (CH^5), 143.4 (CMe_2).

(m) X-ray Diffraction Study of 4 and 14. Data were collected at room temperature on a CAD diffractometer, using graphite-monochromated Mo Kα radiation. All data reduction and structural refinement were performed by means of the NRCC-SDP-VAX package. Crystal data, details of data collection, and structural analysis are summarized in Table V.

The structures of the two compounds were solved by the Patterson method. All non-hydrogen atoms were refined with anisotropic parameters. The hydrogen atoms of **4** were refined isotropically, and the hydrogen atoms of **14** were added at idealized positions and included in the structure factor calculation.

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Registry No. 1, 89922-56-5; 2, 119480-67-0; 3, 112284-96-5; 4, 119480-68-1; 5, 119480-69-2; 6, 119480-70-5; 7, 119480-72-7; 8, 119480-71-6; 9, 119480-73-8; 10, 119480-74-9; 11, 119503-04-7; 12, 119480-75-0; 13, 119480-76-1; 14, 119480-77-2; TCNE, 670-54-2; 1-chloro-2,4-hexadiene, 34632-89-8; 1-chloro-5-methyl-2,4-hexadiene, 116530-74-6; maleic anhydride, 108-31-6.

Supplementary Material Available: Tables of thermal parameters and bond distances and angles for 4 and 14 (4 pages); listings of observed and calculated structure factors for 4 and 14 (48 pages). Ordering information is given on any current masthead page.