(η^5-Cyclopentadienyl)manganese Dicarbonyl η^3-Allyl Cations

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A range of Mn(III) π-allyl cations of the form (η^5-cyclopentadienyl)manganese dicarbonyl-η^3-allyl$^+PF_6^-$ has been prepared and characterized by IR and ^{1}H NMR. These compounds are available through two convenient synthetic avenues involving coordination and subsequent dehydration of allylic alcohols or protonation of 1,3-dienes.

Introduction

Complexation and attendant activation of allylic fragments continue to command considerable attention from structural, mechanistic, and synthetic vantages.[1] Organometallic complexes of the form $CpM(L)_n(\eta^3\text{-allyl})$ are of particular merit in this regard as they incorporate symmetry which can lead to stereospecific elaboration.[2] We report here the preparation and characterization of a wide range of allylic cations of the form η^5-$C_5H_5Mn(CO)_2(\eta^3\text{-allyl})^+PF_6^-$.[3]

The 16-electron fragment $C_5H_5Mn(CO)_2$,[4] derived from cymantrene,[5] enjoys ready accessibility,[6] versatility, and reactivity, being capable of coordination to a variety of inorganic and organic two-electron-donor ligands.[7] Both the preparative and reaction chemistries of the derived compounds have, however, been confined principally to those of alkene,[8] diene,[9] alkyne,[10] carbene,[11] vinylidene,[12] and carbyne[13] fragments. Indeed the electron donor/acceptor ability of $CpMn(CO)_2$ and the accompanying stability of $CpMn(CO)_2(L)$ complexes lends particular emphasis to structural studies, and a wide variety of bonding types have been stabilized by virtue of coordination to this moiety. Viewed in terms of $CpMn(CO)_2$ complexation, we anticipated that the combination of forward, L → M, ψ_1 to d_{z^2} (LUMO), and back-bonding, M → L, d_{yz} (HOMO) to ψ_2, would permit preparation and isolation of such allylic species. Alternatively, one can consider that it is the LUMO level of d^4 Mn(III), (a″ symmetry) that is stabilized by interaction with ψ_2 of an allylic anion.[14]

Results and Discussion

Preparation. Until recently the π-allyl complexes **1** were unknown. Facile entry to these compounds is gained by photodecarbonylation (365 nm) of cymantrene[15] or methylcymantrene followed by π complexation of a precursor allylic alcohol or acetate ester (Scheme I) and protonolysis.[16] Cations **1** are obtained in poor-to-good yield. Following our initial report,[3] similar studies were reported,[17] and it was further disclosed that hydride abstraction from neutral $CpMn(CO)_2(\eta^2\text{-}H_2C{=}CHCH_3)$ can provide **1a** in 14% yield.[17] In addition, $CpMn(CO)_2(\eta^2\text{-}C_8H_8)$ has been reported to react with Ph_3C^+, though apparently not with protons. However, the product, produced via electrophilic addition, could not be isolated or fully characterized.[18] Finally, the reported thermal rearrangement of the σ-allyl η^5-$CH_3C_5H_4Mn(CO)_2(SiPh_3)(\eta^1\text{-}CH_2CH{=}CH_2)$ to the dihapto-bonded η^5-$CH_3C_5H_4Mn(CO)_2(\eta^2\text{-}H_2C{=}CHCH_2SiPh_3)$ may implicate an η^3-allylic intermediate.[19]

The reaction outlined in Scheme I can be conducted with both acyclic and cyclic allylic alcohols. Complexation is tolerant of considerable structural variation, and we have utilized both terminal and internal alkenols. Subsequent protonation of the intermediate π complex liberates the cation. It is not necessary to isolate the alkene complex, and on a preparative scale this process is conveniently conducted in one "pot". We have found Et_2O to be a decidedly more useful solvent than THF in this procedure.[20] This reasonable derives both from the relative stability of the THF adduct and the relative solubility of the product cations in THF. In Et_2O a much more labile solvent adduct is initially produced,[21] alkene (or diene)

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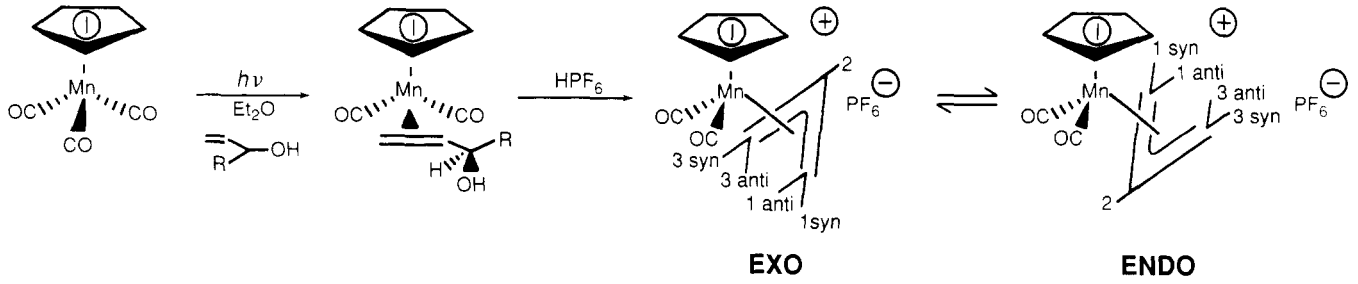
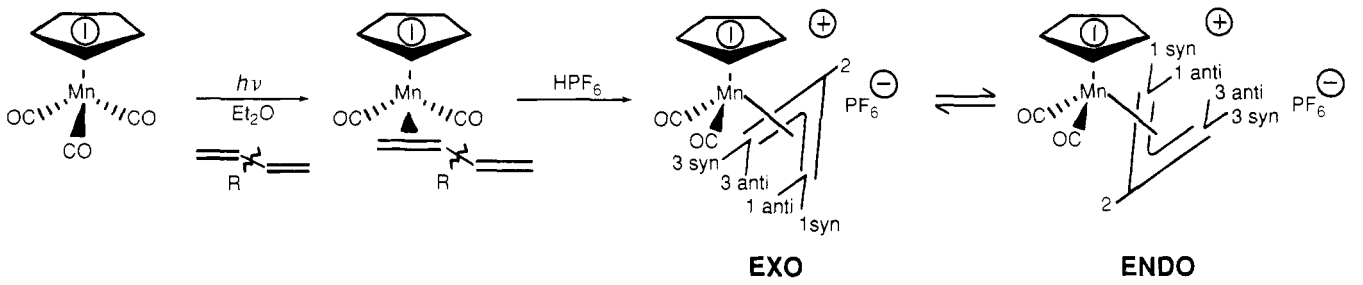
Scheme I



1

	R_1		R_2	R_3	
	syn	anti		syn	anti
1a	H	H	H	H	H
1b	H	H	CH_3	H	H
1c	CH_3	H	H	H	H
1d	CH_3CH_2	H	H	H	H
1e	C_6H_5	H	H	H	H
1f	CH_2=CH	H	H	H	H
1g	CH_3	CH_3	H	H	H
1h	CH_3	H	H	CH_3	H
1i	H	CH_2OH	H	H	H

Scheme II



1

	R_1		R_2	R_3	
	syn	anti		syn	anti
1c	CH_3	H	H	H	H
1d	CH_3CH_2	H	H	H	H
1g	CH_3	CH_3	H	H	H
1h	CH_3	H	H	CH_3	H
1j	CH_3	H	CH_3	H	H
1k	CH_3	CH_3	CH_3	H	H
1l	H	CH_2	H	H	CH_2
1m	H	CH_2	H	H	CH_2

coordination is fast, and subsequent proton-initiated dehydration, or addition in the case of dienes, leads to rapid and complete precipitation of the product, typically within 15–30 min. Although this developing heterogeneity limits photoconversion, in an unstirred reactor the salt sinks to the bottom and photolysis can effectively continue for upward of an hour. Under such conditions we typically obtain ca. 20–40% photoconversion. Product yields are usually 10–50% and can be higher if subsequent photocycles are employed. Recycle of cymantrene or methylcymantrene is readily accomplished upon neutralization of the soluble fraction. We view this preparative process as a metal-assisted dehydration rather than a dehydroxylation since, in the absence of protons, the alkene complex $CpMn(CO)_2(\eta^2\text{-}H_2C{=}CHCH_2OH)$ is stable.[17]

A second and complementary preparative pathway lies in the protonation of a suitable η^2-diene intermediate (Scheme II).[22] Again it is not necessary to isolate this complex, and rapid in situ protonation efficiently produces the desired cations.

Table I summarizes the results of the conversion of representative allylic alcohols. In Table II is summarized the conversion of dienes.

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Table I. $CpMn(CO)_2$-η^3-Allyl Cations via Allylic Alcohols

allyl alcohol	cation	yield,[a] %
2-propen-1-ol	**1a**	65
	1a[b]	38 at 40% C
2-methyl-2-propen-1-ol	**1b**	45
3-buten-2-ol	**1c**	NA
1-penten-3-ol	**1d**	34
cis-2-penten-1-ol	**1d** (anti)	15
3-phenyl-2-propen-1-ol	**1e**	8
	1e[c]	9
1-phenyl-2-propen-1-ol	**1e**	9
1,4-pentadien-3-ol	**1f**	22
2-methyl-3-buten-2-ol	**1g**	100 at 17% C
3-methyl-2-buten-1-ol	**1g**	56
3-penten-2-ol	**1h**	35 at 55% C
cis-2-butene-1,4-diol	**1i**[d]	10

[a] Yield based on 100% conversion unless specified. [b] Prepared from allyl acetate. [c] Prepared from cinnamyl acetate. [d] Signifies the η^5-$CH_3C_5H_4$ complex.

Table II. $CpMn(CO)_2$-η^3-Allyl Cations via Diene Conversion

diene	cation	yield,[a] %
1,3-butadiene	*syn*-1-methyl (**1c**)	91 at 22% C
1,3-butadiene	*syn*-1-methyl (**1c**)[b]	15
1,3-pentadiene	*syn,syn*-1,3-dimethyl (**1h**) *syn,anti*-1,3-dimethyl (**1h**) *syn*-1-ethyl (**1d**)	25 at 41% C
2-methyl-1,3-butadiene	*syn*-1,2-dimethyl (**1j**)	33
2-methyl-1,3-butadiene	*syn*-1,2-dimethyl (**1j**)[b]	38 at 43% C
2,3-dimethyl-1,3-butadiene	1,1,2-trimethyl (**1k**)	26
1,3-cyclopentadiene	cyclopentenyl (**1l**)[b]	9
1,3-cyclohexadiene	cyclohexenyl (**1m**)	58 at 29% C

[a] Yield based on 100% conversion unless specified. [b] Signifies the η^5-$CH_3C_5H_4$ complex.

Characterization. Cations **1**, while hydroscopic, are generally oxidatively and thermally stable, cream yellow solids and were characterized by ^1H NMR (Table III) and IR (Table IV) spectroscopy as well as, in most cases, by elemental analysis (Table V). These compounds are often isolated as the hydrates or acetone solvates.

Comparison of the chemical shifts for a series of salts suggests that the exo conformation is realized for **1a** and 1-substituted analogues while cation **1b** prefers the endo conformation. We note that these assignments are based on arguments that are not necessarily general and in the absence of structural data must be considered tentative. The NMR parameters for $CpRe(CO)(H)(\eta^3$-allyl), for example, reveal an anomalous shielding of H_A in the endo conformation.[23] Similarly, at equilibrium, $CpRu(CO)_2$-(η^3-2-methylallyl) evidences an exo/endo ratio of 50.[24] The structure of the latter exo conformer reveals the dihedral angle between the cyclopentadienyl ring plane and the allyl ring plane to be a mere 16.5°. Relevant proton chemical shifts for cations **1** are provided in Table III. Although a systematic study has not yet been conducted, it does not appear that methylcymantrene (MeCp) elicits a major effect. That is, the NMR parameters observed for **1a**–Cp and **1a**–MeCp are nearly coincident. Of particular note are the anti hydrogens, H_A, whose chemical shifts, diagnostic of conformation,[2] do not evidence an appreciable upfield shift on going from Cp to MeCp. Similarly, in the 2-methallyl complexes **1b**–Cp and **1b**–MeCp, H_A is found 1.18 and 1.07 ppm upfield of that in the corresponding allyl complex **1a**. We intend to prepare representative $C_5(CH_3)_5$ and indenyl complexes to confirm this point.

Primary, secondary, and tertiary allylic alcohols all function equally well. In this regard the 1,1-dimethylallyl cation (**1g**) is accessed with comparable facility[35] from both 3-methyl-2-buten-1-ol and 2-methyl-3-buten-2-ol. This complex assumes the exo conformation as indicated by the chemical shift of H_A at 2.76 and H_S at 4.42 ppm, respectively.

Complexation of secondary allylic alcohols occurs from both enantiotopic faces and leads to the production of a mixture of the configurationally isomeric syn and anti 1-substituted cations. This result is accommodated by irreversible, kinetically controlled complexation and requires that dehydration proceed stereospecifically, presumably from a trans-antiperiplanar disposition of the metal and (protonated) hydroxyl group. The syn isomer **1c** is distinguished by the appearance of a methyl doublet at 2.22 ppm, while the configurationally isomeric anti isomer displays a high-field doublet at 1.26 ppm. The chemical shift of H_A at 2.93 ppm suggests an exo conformation for the syn isomer.

For 1-substituted allyl cations the syn–anti isomer ratio is a function of allyl substituent, suggesting either that the stability of the incipient carbocation is determinant or that face selection operates. We view the latter as unlikely at this stage, although we cannot rule out a directive effect of the hydroxyl function. The syn/anti ratio increases from ca. 1.6 to 6.7 on going from $R_1 = CH_3$ (**1c**) to $R_1 = C_6H_5$ (**1e**). The vinyl cation (η^3-pentadienyl) (**1f**) is formed exclusively as a single isomer, which we designate as the exo–syn geometry. This assignment is based on the observed chemical shifts of the syn and anti hydrogens, which are coincident with those found in **1a**, and on spin decoupling experiments, which reveal the anti hydrogen at C_3, $H_{A'}$, to be a pseudotriplet resulting from coupling to both the C_2 hydrogen, H_C, and the C_4 hydrogen, H_X, with $J_{A'-C} = J_{A'-X} = 9.6$ Hz. The isoelectronic $CpFe(CO)(\eta^3$-pentadienyl) complex evidences rapid endo ↔ exo equilibration ($K_{X/N} > 100$ at equilibrium) and a syn configuration at C_3 as revealed in the $J_{A'-X}$ coupling of 11 Hz.[25] In contrast, $Mn(dmpe)_2(\eta^3$-pentadienyl) reportedly evidences syn–anti equilibration (syn/anti = 1.5) although the mechanism is obscure,[26] and $Mn(CO)_3(PMe_3)(\eta^3$-pentadienyl) has been shown to adopt an anti configuration with nonsymmetric allyl coordination.[27]

The major isomer appears to be exo for **1c** (R = CH_3), **1d** (R = Et), **1e** (R = Ph), and **1f** (R = vinyl) as judged by the chemical shift of the C_3 anti hydrogen at 3.30, 3.30, 4.34, and 3.97 ppm, respectively.

Preparation of the pure syn crotyl complexes, i.e., *syn*-**1c**, is easily accomplished by protonation[3,22] of an η^2-diene precursor.[9] This process presumably occurs from the favored η^2-s-trans geometry and proceeds by electrophilic attack at the uncomplexed double bond of the coordinated diene. Deuteration experiments are in progress to assess this mechanism. The exo,syn geometry is suggested by the chemical shift of $H_{A'}$, which, at 3.30 ppm, is 1 ppm upfield of the $H_{S'}$ signal in the anti isomer. Control of the configuration at C_1 is, however, dependent on the site of π coordination. Initial results with 2-methyl-1,3-butadiene (isoprene) and 1,3-pentadiene (piperylene) confirm that a mixture of isomers is obtained. In the latter case the

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Table III. ^{1}H NMR Data on $CpMn(CO)_2$-η^3-Allyl Cations (Chemical Shifts in ppm, Solvent Acetone-d_6[a])

cation	C_5H_5	H_C	H_S	H_A	R groups and substituents
allyl (**1a**)	5.83	5.95	4.48 d (J = 6.9)	2.43 d (J = 11.4)	
allyl (**1a**[b])	5.72	5.70	4.36 (J = 7.0)	2.36 (J = 13.0)	CH_3 2.20
2-Me (**1b**)	5.80		4.37 s	3.61 s	CH_3 1.80
2-Me (**1b**[b])	5.67		4.64 s	3.43 s	CH_3 1.83 s, CH_3 2.23 s
1-Me[c] (*syn*-**1c**)	5.79	5.79	4.27 dd (J = 6.5, 1.5)	2.93 d (J = 11)	H_A, 3.30 m, CH_3 2.22 d (J = 7)
1-Me[d] (*anti*-**1c**)	5.77		4.58 dd (J = 6.5, 1.0)		H_S, 4.30, CH_3 1.26 d (J = 7)
1-Et[e] (**1d**)	5.85		4.35 d (J = 6.0)	2.2	H_A, 3.30 m, CH_2[f] 2.40 dq, 2.48 dq CH_3 1.32 t (J = 7.6)
1-Ph[g] (*syn*-**1e**)	5.69	6.69	4.65 (J = 6.2)	2.53 (J = 10.4)	H_A, 4.34 (J = 11.8), Ph 7.72 (2), 7.50 (3)
1-Ph[g] (*anti*-**1e**)	5.87				
1-vinyl[h] (*syn*-**1f**)	5.81	5.95 m	4.43 br d	2.41 d (J = 9.6)	H_A, 3.97 dd, (J = 9.6), H_X 6.55 m, H_C 5.69 d (J = 8.9), H_T 5.95 d (J = 16.5)
1,1-diMe (**1g**)	5.70	5.58 dd (J = 12.0, 6.5)	4.42 dd (J = 6.5, 1.5)	2.76 dd (J = 12.0, 1.5)	CH_3 syn 2.33, anti 1.55
1,2-dimethyl (**1j**)	5.84		4.35	2.8	H_A, 3.4, CH_3 2.3, 1.85, 1.30
1,3-dimethyl[i], (*syn,syn*-**1h**)	5.77	5.71		3.08 dq (J = 11.5), 3.75 dq (J = 11.5)	CH_3 syn 2.18 d (J = 6.5), 2.20 d (J = 5.0)
1,3-dimethyl[i] (*syn,anti*-**1h**)	5.81		4.35 dq	3.90 dq	CH_3 syn 2.25 d (J = 6.4), anti 1.35 d (J = 7.6)
cyclohexenyl (**1m**)	5.76	6.06 t (J = 6.0)	5.66 m		

[a] Referenced to acetone at 2.04 ppm. Spectra recorded at ambient temperature unless specified. [b] Signifies the η^5-$CH_3C_5H_4$ complex. [c] Prepared from 1,3-butadiene. Assignments suggested by spin decoupling at 200 MHz. [d] Prepared as a syn–anti mixture from 3-buten-2-ol. Assignments suggested by spin decoupling at 200 MHz. [e] All resonances are broad at 36 °C. [f] Diastereotopic methylenes. [g] Spectra recorded at −18 °C on the cation derived from cinnamyl alcohol. [h] Assignments confirmed by spin decoupling at 400 MHz. [i] Assignments suggested by spin decoupling at 400 MHz.

Table IV. IR Spectra (cm^{-1}) of $CpMn(CO)_2$-η^3-Allyl Cations

cation	ν_{CO},[a,b] cm^{-1}
1a (allyl)	2030, 1985; 2035, 1999
1a[c] (allyl)	2030, 1985; 2032, 1999
1b (2-Me)	2043, 2003; 2046, 2006
1b[c] (2-Me)	2045, 2004; 2045, 2004
1c (1-Me)[d]	2026, 1997, 1987; 2031, 1997
1c (1-Me (syn))	2007, 1997, 1987; 2031, 1997
1d (1-Et[d])	2023 (maj), 2017 (sh), 1997 (sh), 1992 (maj)
1d (1-Et[d] (anti))	2020, 1991
1e (1-Ph)	2035 (maj), 2022 (min), 1996 (min), 1988 (maj)
1e (1-Ph[e])	2022 (maj), 2012 (min), 1992 (maj), 1974 (min)
1f (1-vinyl)	2022, 1988
1g (1,1-diMe)	2016, 1977; 2025, 1987
1h (1,3-diMe[d])	2014, 2008, 1978; 2024, 1991
1i (1-CH_2OH[c] (anti))	2025, 1985
1j[f] (1,2-dimethyl)	2010, 1985, 1976
1k (1,1,2-triMe)	2023 (min), 2000 (maj), 1980 (min), 1957 (maj)
1l[c] (cyclopentenyl)	2003, 1963, 1951 (sh)
1m (cyclohexenyl)	2006, 2003, 1986 (sh) 1976, 1967; 2031, 1999

[a] 0.5% (w/w) in CsI matrix. [b] Acetone solution. [c] Signifies the η^5-$CH_3C_5H_4$ complex. [d] Mixture of syn–anti isomers via 1-penten-3-ol. The anti isomer was prepared from *cis*-2-penten-1-ol. [e] Prepared from 1-phenyl-2-propen-1-ol. [f] Mixture with **1g**.

Table V. Elemental Analysis

	calcd; found	
cation	C	H
1a·$^1/_2$acetone	34.41; 34.45	3.24; 3.44
1b	35.13; 34.50	3.22; 3.11
1c (syn)	35.13; 35.93	3.22; 3.45
1e·$2H_2O$	40.53; 40.39	3.82; 3.16
1f·$3H_2O$	32.60; 31.93	4.10; 2.79
	32.60; 31.29[a]	4.10; 2.82[a]
1g·2HPF	21.13; 22.12	2.36; 2.19
1j + **1g** (mixture)	36.95; 37.39	3.62; 3.76
1m	38.73; 38.27	3.50; 3.37

[a] These results were not improved after drying in vacuo at 100 °C/3 h.

major product, interestingly, is that derived from complexation at the more substituted C=C bond. This reasonably results from the increased donor ability of internal double bonds. Thus from piperylene (mixture of isomers) is produced as a mixture of the three cations, *syn,syn*-**1h**, *syn,anti*-**1h**, and **1d**, in the relative ratio 5:1:0.8. Cation **1h** has been previously prepared[3] as a syn–anti mixture (syn–syn/syn–anti ratio = 5.5) from 3-penten-2-ol. The infrared spectra of the product mix in the two cases are, not surprisingly, very similar, displaying ν_{CO} at 2014, 2008, and 1978 cm^{-1}. The small amount of the *syn*-1-ethyl cation **1d** formed from piperylene reflects limited bonding at the

terminal position. The assignment of the major conformer rests on the position of $H_{A'}$, which at 3.08 ppm is similar to that in **1c**, 3.30 ppm, and on the chemical shift of the methyl signal at 2.25 ppm (compare the syn methyl in **1g** at 2.33 ppm). While exo–endo equilibration of **1h** has been observed at 100 °C (CD_3NO_2) the syn,syn and syn,anti configurational isomers do not interconvert.[3]

We have not been able to obtain entirely satisfactory NMR spectra of the isoprene-derived product. Preliminary results, particularly methyl resonances at 1.44 and 2.31 ppm, along with signals at 1.30 and 1.85 ppm indicate that the product mix is comprised of **1g** and the isomeric *syn*-1,2-dimethylallyl species **1j**. The NMR spectrum (36 °C) is consistent with the presence of two conformational isomers for **1j** in approximately a 3:1 ratio. Thus in 2-methyl-1,3-butadiene the preference for binding at C_1–C_2, leading to *exo*- and *endo*-**1j**, over that at C_3–C_4 leading to **1g** is approximately 4:1. This is comparable to the ca. 7:1 selectivity observed for formation of **1h** over **1d**. In stark contrast, coordination of piperylene to Fp^+ is accomplished exclusively at C_1–C_2.[28] Interestingly, earlier studies have suggested preferential coordination of $CpMn(CO)_2$ at the terminal or at the nonconjugated site in 1,3,5-cycloheptatriene or 1,3,6-cyclooctatriene, respectively.[18]

As indicated, cyclic dienes are also suitable substrates, with cyclopentadiene and 1,3-cyclohexadiene providing **1l** and **1m**, respectively. However, both 1,2,3,4,5-pentamethylcyclopentadiene and cycloheptatriene are poor ligands and provide, at best, only a trace of cationic material. The limited reactivity of the former may reflect a steric bias. In the latter case secondary photolysis may compete with protonation. On photolysis, cymantrene is reported to provide an η^6-cycloheptatriene complex, and both η^2- and η^6-cyclooctatetraene complexes are known.[29]

The infrared spectra of cations **1** are distinguished by the expected high-frequency shift of carbonyl absorption (ca. 2025, 1990 cm^{-1}), which may be compared with that of $CpMn(CO)_3$ (2014, 1936 cm^{-1}),[30] $CpMn(CO)_2NO^+PF_6^-$ (2125, 2075 cm^{-1}),[31] and $CpMn(CO)_2{\equiv}CPh^+BCl_4^-$ (2083, 2047 cm^{-1}).[13] Consistent with a formal Mn(III) oxidation state, these salts evidence carbonyl absorption at frequencies slightly higher than those recently reported for the η^6-arene $Mn^I(CO)_2(\eta^2$-olefin) cations, viz., 2012 and 1971 cm^{-1}.[32] The CO band positions imply limited π-acid acceptor ability by the η^3-allyl ligand and suggest appreciable electrophilicity. Even in the (formally) Mn(I) complex, $Mn(CO)_4(\eta^3$-$C_3H_5)$, the low electron density observed in the XPS spectrum suggests only weak back bonding.[33]

Infrared stretching frequencies are provided in Table IV.

We have noticed that dispersive IR spectra recorded in CsI or KBr pellets display time-dependent changes. In all salts examined to date, new absorption features at ca. 1950, 1930, and 1880 cm^{-1} arise soon after pressing. The 1950- and 1880-cm^{-1} bands are transient, giving way to that at 1930 cm^{-1}, which steadily increases in intensity at the expense of the bands due to cation. It is tempting to tentatively ascribe this new absorption to the carbonyl displacement product η^5-$C_5H_5Mn(CO)(X)(\eta^3$-allyl), although rather surprisingly this complex is not produced under a variety of conditions from reaction of cation **1a** and NaI or $(C_7H_{15})_3NCH_3^+I^-$.[34] Prolonged contact with halide salt matrixes produces, via reductive processes, $CpMn(CO)_3$.

Attempts to obtain solution spectra of these salts in acetone are not uniformly successful and reveal exceptional reactivity with an increasing propensity for reaction shown by the more heavily alkylated congeners. Thus, to date, we have been unable to obtain IR (or ^1H NMR) spectra of the 1,1,2-trimethylallyl cation (**1k**) in acetone, dissolution immediately providing a species displaying carbonyl absorption indicative of a neutral π-olefin complex. Similarly reaction of acetone with the 1,1-dimethyl cation **1g** appears complete within 1 h at room temperature. These findings suggest that heightened reactivity may be induced by steric compression and/or nonsymmetric allyl coordination and that these systems will serve as useful electrophilic partners in organomanganese-mediated carbon–carbon construction sequences.

We are actively exploring the preparative and reaction chemistry of these cations with particular emphasis on diastereoselective complexation and electrophilic reactivity.

Experimental Section

General Comments. Synthetic manipulations were conducted under nitrogen where indicated. Cyclopentadienylmanganese tricarbonyl was purchased from Strem Chemicals. Organic reagents were commercial and used as received. Photolyses were conducted in a water-cooled, inverted, wide-bore Pyrex condenser. Irradiation was via a Blak-Ray Model 8-100A lamp (Ultraviolet Products, San Gabriel, CA) at 365 nm, $I = 2 \times 10^3$ mW/cm^2 at ca. 6 cm.

Infrared spectra were recorded on Perkin-Elmer 1430 ratio recording spectrometer. Proton magnetic resonance spectra were obtained on a JEOL JNM PMX 60, a Varian T-60, or Varian XL-400 spectrometer.

Analysis were performed by Robertson Laboratory, Inc., Madison, NJ.

General Procedure for Preparation of (η^5-Cyclopentadienyl)manganese Dicarbonyl η^3-Allyl Hexafluorophosphate Salts. To a 0.05 M solution of cyclopentadienylmanganese tricarbonyl (1.00 g, 5 mmol) in diethyl ether (100 mL) contained in a wide-bore inverted Pyrex condenser fitted with a thermocouple and N_2 inlet was added the appropriate allylic alcohol or diene (10 mmol) and hexafluorophosphoric acid (60 wt%, aqueous, 1.5 mL, 10 mmol). The resulting homogeneous yellow-green solution was purged with nitrogen, stirred briefly, and then irradiated without stirring or agitation at 15–25 °C for approximately 1 h. Usually precipitation commenced within 15–30 min, depending on the substrate. The resulting flocculent solid is allowed to settle, the mix filtered, and the yellow-cream product washed with ether (3 × 10 mL). The salt may be purified by rapid precipitation from acetone/ether at 0 °C. The filtrate may be recycled for higher yield or, after neutralization (Na_2CO_3), filtered for recovery of starting material.

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