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Vilsmeier−Haack−Arnold Acylation of the Reductively Activated Benzene Ligand in $[Mn(CO)_3(\eta^4\text{-}C_6H_6)]^-$

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The major product from the reaction of the enoliminium ester $[Me_2CHC(OSO_2CF_3){=}NMe_2]^+$ (**5**$^+$) with $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ (**2**$^-$) is $[Mn(CO)_3\{\eta^5\text{-}C_6H_6C(^iPr){=}NMe_2\}]^+$ (**6**$^+$; X-ray), in which an iminium ion has been added to the reductively activated benzene ligand in **2**$^-$. Minor products include $[\{Mn(CO)_3(\eta^5\text{-}C_6H_6)\text{-}exo\}_2C(^iPr)NHMe_2]CF_3SO_3$ (**8**(CF_3SO_3); X-ray) and $[\{Mn(CO)_3(\eta^5\text{-}C_6H_6)\text{-}exo\}_2C(^iPr)NMe_2]$ (**7**), with two $Mn(CO)_3$ groups attached to the enoliminium ester derived backbone. The mechanistic relationship between the reactions that yield to formation of **6**$^+$, **8**$^+$, and **7** are unclear, since an increase in the ratio of **2**$^-$ to **6**$^+$ does not increase the yield of **7**, and reaction of **2**$^-$ with the keteniminium salt prepared by reaction of **5**$^+$ with collidine leads directly to **6**$^+$. Hydrolysis of **6**(PF_6) generates $[Mn(CO)_3\{\eta^5\text{-}C_6H_6C(^iPr){=}O\}]$ (**9**), in which the benzene ligand in **2**$^-$ has been acylated.

Introduction

Vilsmeier−Haack−Arnold reaction conditions, in which a disubstituted amide is converted into an electrophile by reaction with an acid halide such as $POCl_3$ or phosgene, are well established to promote formylation or acylation of activated aromatic rings.[1] It has also been reported that the use of triflic anhydride as the activating reagent can extend the scope of the reaction to include the formylation of polyaromatic hydrocarbons and mildly activated benzene derivatives,[2] but the reaction has never, to the best of our knowledge, been extended to benzene itself. We have previously reported that the benzene in $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]PF_6$ (**1**(PF_6)) can be activated toward a range of carbon-centered electrophiles by two-electron reduction,[3] and we now wish to report that the ligand in $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ (**2**$^-$), the activated η^4-benzene complex formed under these conditions, can be acylated under the Martínez variation of Vilsmeier−Haack−Arnold conditions.

Experimental Section

General Procedures. All reactions and manipulations (unless otherwise indicated) were carried out under a dry, oxygen-free nitrogen atmosphere, using standard Schlenk techniques or a drybox. Air- and moisture-sensitive reagents were handled by standard syringe and cannula techniques. All solvents were freshly distilled and deoxygenated before use. Fresh 0.2 M solutions of potassium naphthalenide (KNap) in THF were prepared by direct reaction of freshly cut potassium with naphthalene (1.5 equiv) in THF over 12 h. The dark green potassium naphthalenide was stored under nitrogen in a Suba-sealed Schlenk tube at −78 °C.[4] IR spectra were recorded on Perkin-Elmer Model 783 and Perkin-Elmer BX FT-IR spectrophotometers. Solution samples were examined in sealed sodium chloride cells. All ^1H NMR spectra were obtained on a Bruker AF300 at 300 MHz. ^{13}C NMR spectra were recorded on a Bruker AF300 at 75 MHz or a Bruker AF500 at 125 MHz. Detailed NMR assignments are available in the Supporting Information. Elemental analyses (C, H by combustion) were performed by Atlantic Microlab, Norcross, GA.

Single-Crystal X-ray Diffraction Studies. X-ray crystal structures were determined for $[Mn(CO)_3\{\eta^5\text{-}C_6H_6C(^iPr){=}NMe_2\}]PF_6$ (**6**(PF_6)), $[\{Mn(CO)_3(\eta^5\text{-}C_6H_6)\}_2C(^iPr)NHMe_2]\text{-}CF_3SO_3$ (**8**(CF_3SO_3)), and $[Mn(CO)_3\{\eta^5\text{-}C_6H_6C(^iPr){=}O\}]$ (**9**) using a single crystal on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation. The parameters used during the collection of diffraction data are summarized in Table 1. Crystals were adhered to fine glass fibers with epoxy cement and placed in a cold N_2 stream (150.0(2) K) for data collection.

Unit-cell parameters, systematic absences, and photographic evidence indicated that **6**(PF_6), **8**(CF_3SO_3), and **9** were uniquely assignable to centrosymmetric space groups $Pbca$, $P2_1/c$, and $P2_1/n$, respectively. For each structure, unit-cell dimensions were derived from the least-squares fit of the angular settings of 999 strong reflections from the data collection. Data were corrected for absorption using the Bruker AXS program SADABS.

Each structure was solved by direct methods which located the positions of the non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and refined isotropically. Compounds **6**(PF_6) and **8**(CF_3SO_3) each contain one molecule in the asymmetric unit with no crystallographically imposed symmetry. Compound **9**

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Table 1. Crystal and Data Collection and Refinement Parameters for 6(PF_6), 8(CF_3SO_3), and 9

	6(PF_6)	**8**(CF_3SO_3)	**9**
formula	$C_{15}H_{19}F_6MnNO_3P$	$C_{25}H_{25}F_3Mn_2NO_9S$	$C_{13}H_{13}MnO_4$
mol wt	461.22	682.40	288.17
cryst color	yellow	yellow	yellow
cryst dimens (mm)	0.32 × 0.16 × 0.14	0.35 × 0.20 × 0.20	0.48 × 0.36 × 0.18
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	$P2_1/n$
unit cell dimens			
a (Å)	10.6997(5)	11.8413(8)	13.1832(6)
b (Å)	15.2580(7)	10.7915(8)	10.0304(4)
c (Å)	22.8091(10)	22.0198(16)	19.5001(8)
α (deg)	90	90	90
β (deg)	90	93.287(2)	90.7730(10)
γ (deg)	90	90	90
V (Å^3)	3723.7(3)	2809.2(3)	2578.32(19)
Z	8	4	8
D_c (g cm^{-3})	1.645	1.613	1.485
μ (mm^{-1})	0.868	1.045	1.026
F(000)	1872	1388	1184
radiation	Mo Kα (λ = 0.710 730 Å)		
temp (K)	150(2)		
scan type	$\omega-2\theta$		
θ range (deg)	2.49−27.50	1.72−27.50	2.53−25.01
h,k,l range	$-13 \le h \le 13$ $-19 \le k \le 19$ $-29 \le l \le 29$	$-15 \le h \le 15$ $-14 \le k \le 14$ $-28 \le l \le 28$	$-19 \le h \le 19$ $-15 \le k \le 15$ $-27 \le l \le 28$
no. of rflns measd	34 435	26 873	32 823
no. of unique rflns	4268 (R(int) = 0.0803)	6449 (R(int) = 0.0958)	9105 (R(int) = 0.0210)
completeness to θ (%)	100.0 (θ = 27.50°)	100.0 (θ = 27.50°)	97.8 (θ = 27.50°)
max and min transmission	0.8881 and 0.7686	0.8182 and 0.7111	0.8368 and 0.6386
refinement method	full-matrix least squares on F^2		
no. of data/restraints/params	4268/0/320	6449/0/454	9105/0/429
goodness of fit on F^2	1.125	1.448	1.024
final R indices ($I > 2\sigma(I)$)	R1 = 0.0399 wR2 = 0.1002	R1 = 0.1068 wR2 = 0.2061	R1 = 0.0326 wR2 = 0.0833
R indices (all data)	R1 = 0.0482 wR2 = 0.1041	R1 = 0.1373 wR2 = 0.2157	R1 = 0.0409 wR2 = 0.0882
largest diff peak and hole (e Å^{-3})	0.773 and −0.329	1.394 and −0.729	0.772 and −0.234

contains two chemically similar but crystallographically independent molecules in the asymmetric unit.

Final difference Fourier syntheses showed only chemically insignificant electron density (largest difference peaks less than 1.0 Å from Mn). An inspection of F_o vs F_c values and trends based upon sin θ, Miller index, or parity group failed to reveal any systematic error in the data. All computer programs used in the data collection and refinements are contained in the Bruker program packages Smart, Saint, and SHELXTL (version 6.10).

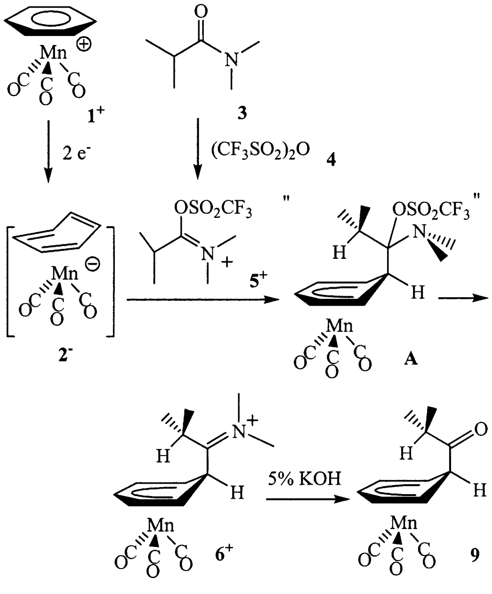
Synthesis of [{Mn(CO)$_3$(η^5-C_6H_6)}$_2$C(^{i}Pr)NMe$_2$] (7), [Mn(CO)$_3${η^5-C_6H_6C(^{i}Pr)=NMe$_2$}]PF$_6$ (6(PF$_6$)), and [Mn(CO)$_3${η^5-C_6H_6C(^{i}Pr)=NMe$_2$}]CF$_3$SO$_3$ (6(CF$_3$SO$_3$)). A solution of 0.2 M KAnt/THF 8.7 mL (1.74 mmol) was added to a slurry of 0.30 g (0.83 mmol) of [Mn(η^6-C_6H_6)(CO)$_3$]PF$_6$ in 15 mL of THF at −78 °C to give a yellow anionic solution. After the mixture was stirred for 15 min, the product from the reaction of 0.12 mL (0.93 mmol) of *N,N*,2-trimethylpropionamide ($CH_3CHC(O)N(CH_3)_2$) and 0.15 mL (0.91 mmol) of triflic anhydride ($(CF_3SO_2)_2O$) in Et$_2$O was transferred into the yellow anionic slurry at −78 °C (the white solid obtained in ether was dissolved in THF and transferred). After 1 h of stirring, the solution was warmed to ambient temperature and the solvents were removed under vacuum. The residue was extracted with pentane twice (50 mL × 2) and then Et$_2$O twice (50 mL × 2). The residue was partially redissolved in DME (30 mL × 2) and the solution filtered. Pale yellow precipitate not soluble in DME was dried under vacuum to give ([Mn(CO)$_3${η^5-C_6H_6−C(^{i}Pr)=NMe$_2$}]PF$_6$ (**6**(PF$_6$), 0.040 g, 0.087 mmol, yield 10%). IR spectrum (THF): ν_{CO} 2027 (s), 2018 (s), 1937 (vs, br) cm^{-1}; $\nu_{C=N}$ 1653 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{19}F_6MnNO_3P$: C, 39.04; H, 4.15. Found: C, 38.76; H, 4.07. ^{1}H NMR (acetone-d_6): δ 6.16 (m, 1H), 5.45 (t, 2H), 4.48 (t, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.57 (t, 2H), 3.50 (m, 1H), 1.31 (d, 6H). ^{13}C{^{1}H} NMR (acetone-d_6): δ 221.8 (CO), 193.5 (C=N), 98.9 (CH), 81.5 (CH), 51.0 (CH), 46.5 (CH$_3$), 45.8 (CH$_3$), 41.1 (CH), 30.7 (CH), 16.9 (CH$_3$).

The DME solution was dried under vacuum, and the residue was extracted by CH$_2$Cl$_2$ to obtain a yellow solution. The CH$_2$Cl$_2$ solution was concentrated to 5 mL and layered with 15 mL of toluene to form the yellow crystalline solid [Mn(CO)$_3$-{η^5-C_6H_6C(^{i}Pr)=NMe$_2$}]CF$_3$SO$_3$ (**6**(CF$_3$SO$_3$); 0.12 g, 26 mmol, yield 31%). ^{1}H NMR (acetone-d_6): δ 6.14 (s, 1H), 5.42 (s, 2H), 4.63 (s, 1H), 3.74 (s, 3H), 3.65 (s, 3H), 3.55 (m, 2H) 3.48 (s, 1H), 1.29 (d, 6H). ^{13}C{^{1}H} NMR (acetone-d_6): δ 221.8 (CO), 193.2 (C=N), 98.8 (CH), 81.5 (CH), 51.2 (CH), 45.8 (CH$_3$), 45.8 (CH$_3$), 41.0 (CH), 30.6 (CH), 16.9 (CH$_3$).

The pentane solution was concentrated and recrystallized at 0 °C for 6 days to give [{Mn(CO)$_3$(η^5-C_6H_6)}$_2$C(^{i}Pr)NMe$_2$] (**7**; 13 mg, 0.024 mmol, yield 3%). ^{1}H NMR (acetone-d_6): δ 5.98 (t, 2H), 5.16 (t, 2H), 5.10 (t, 2H), 3.49 (m, 4H), 3.24 (t, 2H), 2.40 (s, 6H), 1.83 (m, 1H), 0.96 (d, 6H). ^{13}C{^{1}H} NMR (acetone-d_6): δ 223.6 (CO), 99.0 (CH), 98.9 (CH), 78.9 (CH), 70.9 (C), 62.7 (CH), 62.3 (CH), 41.0 (N*Me*$_2$), 38.6 (CH), 19.6 (CH*Me*$_2$).

Crystallization of [{Mn(CO)$_3$(η^5-C_6H_6)}$_2$C(^{i}Pr)NHMe$_2$]-CF$_3$SO$_3$ (8(CF$_3$SO$_3$)) and [Mn(CO)$_3${η^5-C_6H_6C(^{i}Pr)=NMe$_2$}]-PF$_6$ (6(PF$_6$)). A solution of 0.2 M KNap/THF (8.2 mL, 1.64 mmol) was added to a slurry of 0.29 g (0.80 mmol) of [Mn(η^6-C_6H_6)(CO)$_3$]PF$_6$ in 20 mL of THF at −78 °C to give a brown anionic solution. After the mixture was stirred for 15 min, the product from the reaction of 0.097 g (0.97 mmol) of *N,N*,2-trimethylpropionamide ($CH_3CHC(O)N(CH_3)_2$) and 0.16 mL (0.95 mmol) of triflic anhydride ($(CF_3SO_2)_2O$) in 5 mL of Et$_2$O was transferred into the anionic slurry at −78 °C. The mixture was warmed slowly to ambient temperature after 15 min of stirring at −78 °C. The solvent was removed under vacuum, and the residue was washed with pentane (30 mL × 2). Then the residue was extracted partially into Et$_2$O (30 mL × 2) and

Scheme 1



then extracted partially into THF. Yellow crystals of [{Mn(CO)$_3$-{η^5-C$_6$H$_6$}$_2$C(^{i}Pr)NHMe$_2$]CF$_3$SO$_3$ (20 mg, 0.043 mmol, yield 10%) were formed from concentrated Et$_2$O solution at 0 °C over 5 days. ^{1}H NMR (acetone-d_6): δ 6.15 (t, 2H), 5.45 (m, 4H), 3.66 (m, 7H), 3.09 (s, 6H), 2.17 (m, 1H), 1.19 (d, 6H).

Crystals of [Mn(CO)$_3${η^5-C$_6$H$_6$C(^{i}Pr)=NMe$_2$}]PF$_6$ (83 mg, 0.18 mmol, yield 23%) precipitated out from THF/Et$_2$O slow-diffusion solvents at 0 °C over 5 days.

Synthesis of [Mn(CO)$_3${(η^5-C$_6$H$_6$)C(^{i}Pr)=O}] (9). A THF solution of 20 mg (0.046 mmol) of [Mn(CO)$_3${η^5-C$_6$H$_6$C(^{i}Pr)=NMe$_2$}]PF$_6$ was mixed and stirred with 5% KOH/H$_2$O solution at ambient temperature for 2 h. Solvents were dried under vacuum. Product was extracted into pentane (20 mL × 2) and recrystallized from concentrated pentane solution at 0 °C over 5 days to give yellow crystals of [Mn(CO)$_3${(η^5-C$_6$H$_6$)-C(^{i}Pr)=O}] (**9**; 7 mg, 0.024 mmol, yield 53%). ^{1}H NMR (acetone-d_6): δ 5.87 (t, 1H), 5.17 (t, 2H), 3.50 (t, 1H), 3.38 (t, 2H), 2.75 (m, 1H), 0.90 (d, 6H). ^{13}C{^{1}H} NMR (acetone-d_6): δ 223.8 (Mn–*C*O), 211.0 (*C*O), 99.4 (CH), 81.3 (CH), 52.6 (CH), 45.0 (CH), 35.1 (CH), 18.7 (CH$_3$). IR spectrum (pentane): ν_{CO} 2024.1 (s), 1945.8 (vs) 1665.9 (w) cm^{-1}.

Results and Discussion

Iminium addition to **2**$^-$ (Scheme 1) was achieved under conditions in which an enoliminium ester was preformed by mixing *N,N,*2-trimethylpropionamide (Me$_2$CHC(O)NMe$_2$; **3**) and triflic anhydride ((CF$_3$SO$_2$)$_2$O; **4**) in a 1:1 ratio to form [Me$_2$CHC(OSO$_2$CF$_3$)=NMe$_2$]$^+$ (**5**$^+$) in Et$_2$O. The mixture was transferred into a solution of **2**$^-$ at −78 °C to give a mixture with an IR spectrum (ν_{CO}, THF) with carbonyl absorptions at 2027 (m), 2018 (m), and 1937 (s, br), consistent with the presence of an Mn(CO)$_3$ unit as an uncharged metal center, together with a $\nu_{C=N}$ peak in THF at 1653 (m) cm^{-1}. The solvents were removed under reduced pressure, and minor products were extracted into pentane and Et$_2$O. The major product in the insoluble residue was shown to be [Mn(CO)$_3${η^5-C$_6$H$_6$C(^{i}Pr)=NMe$_2$}]$^+$ (**6**$^+$) after extraction of the spectroscopically characterized (^{1}H NMR) CF$_3$SO$_3$$^-$ salt into DME in 30% yield. This left an additional spectroscopically and analytically pure 10% yield of the PF$_6$$^-$ salt of **6**$^+$.

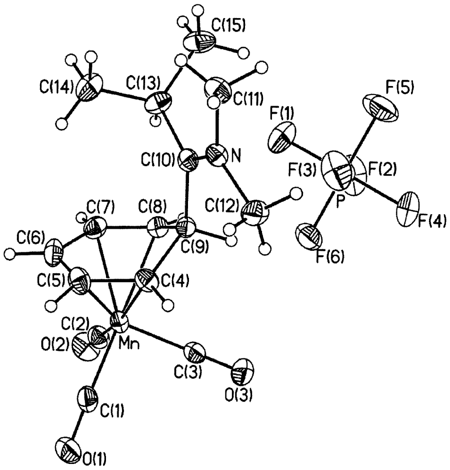


Figure 1. Molecular structure of **6**$^+$ in **6**(PF$_6$).

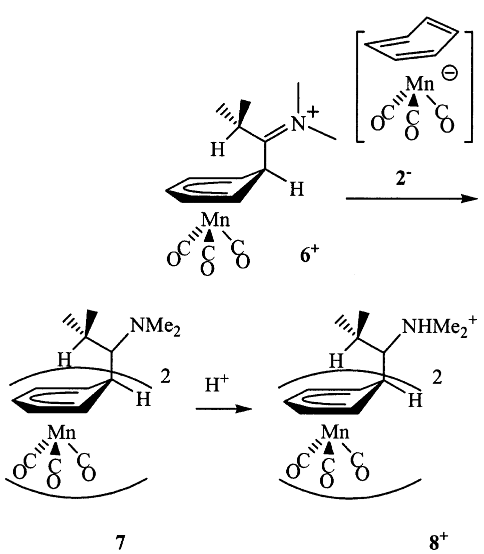
Table 2. Selected Bond Lengths (Å) and Angles (deg) in [Mn(CO)$_3${η^5-C$_6$H$_6$C(^{i}Pr)=NMe$_2$}]$^+$ (6$^+$)

Mn–C(3)	1.797(2)	N–C(11)	1.476(3)
Mn–C(1)	1.801(2)	C(4)–C(5)	1.400(3)
Mn–C(2)	1.808(2)	C(4)–C(9)	1.520(3)
Mn–C(6)	2.132(2)	C(5)–C(6)	1.404(3)
Mn–C(5)	2.134(2)	C(6)–C(7)	1.417(3)
Mn–C(7)	2.134(2)	C(7)–C(8)	1.392(3)
Mn–C(4)	2.197(2)	C(8)–C(9)	1.511(3)
Mn–C(8)	2.2096(19)	C(9)–C(10)	1.532(3)
N–C(10)	1.288(2)	C(10)–C(13)	1.514(3)
N–C(12)	1.473(3)		
C(10)–N–C(12)	124.11(17)	C(4)–C(9)–C(10)	114.13(16)
C(10)–N–C(11)	124.71(17)	N–C(10)–C(13)	123.06(18)
C(12)–N–C(11)	111.18(16)	N–C(10)–C(9)	118.29(17)
C(8)–C(9)–C(4)	102.64(15)	C(13)–C(10)–C(9)	118.65(16)
C(8)–C(9)–C(10)	116.44(16)		

A single-crystal X-ray diffraction study of crystals of **6**(PF$_6$) grown in THF/Et$_2$O (Figure 1; see Table 2 for selected bonds and angles) confirmed that **6**$^+$ has an exo iminium substituent on the cyclohexadienyl ligand. The rotation of the iminium substituent about C(9)–C(10) presumably minimizes steric interactions between the isopropyl group and the cyclohexadienyl ligand.

Formation of **6**$^+$ as the product of these reactions is consistent with nucleophilic addition to the unsaturated carbon of an intermediate enoliminium ester to give **A** followed by loss of the triflate anion (Scheme 1).

Scheme 2



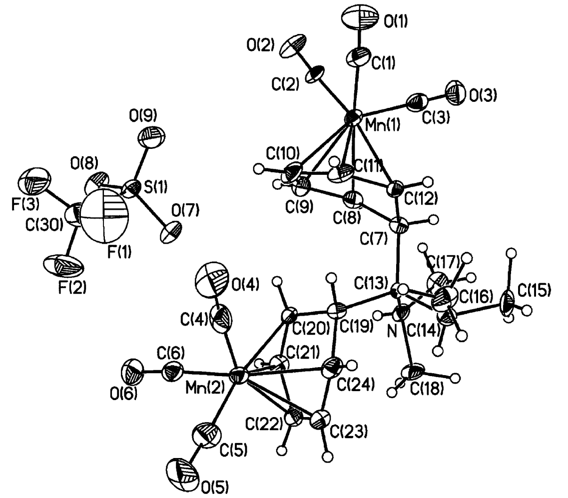


Figure 2. Molecular structure of 8^+ in $8(CF_3SO_3)$.

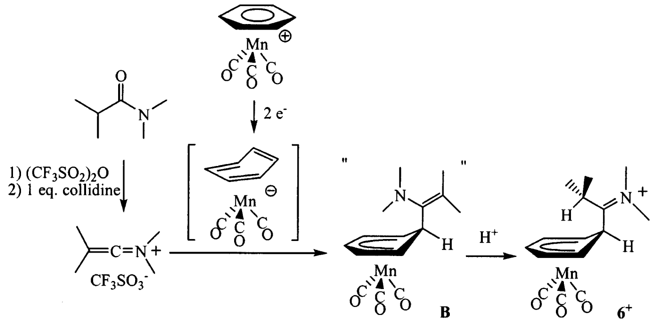
Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[\{Mn(CO)_3(\eta^5\text{-}C_6H_6)\}_2C(^iPr)NHMe_2]^+$ (8^+)

Mn(1)−C(3)	1.797(7)	Mn(2)−C(24)	2.234(7)
Mn(1)−C(2)	1.803(7)	C(7)−C(12)	1.507(8)
Mn(1)−C(1)	1.816(7)	C(7)−C(8)	1.549(9)
Mn(1)−C(10)	2.103(7)	C(7)−C(13)	1.564(8)
Mn(1)−C(11)	2.128(7)	C(8)−C(9)	1.396(9)
Mn(1)−C(9)	2.137(6)	C(9)−C(10)	1.407(9)
Mn(1)−C(8)	2.223(6)	C(10)−C(11)	1.414(10)
Mn(1)−C(12)	2.229(6)	C(11)−C(12)	1.420(8)
Mn(2)−C(5)	1.806(7)	C(13)−C(19)	1.610(8)
Mn(2)−C(6)	1.806(7)	C(19)−C(24)	1.526(8)
Mn(2)−C(4)	1.811(8)	C(19)−C(20)	1.529(8)
Mn(2)−C(21)	2.118(6)	C(20)−C(21)	1.402(8)
Mn(2)−C(22)	2.129(6)	C(21)−C(22)	1.414(9)
Mn(2)−C(23)	2.150(6)	C(22)−C(23)	1.420(9)
Mn(2)−C(20)	2.210(6)	C(23)−C(24)	1.400(9)
C(12)−C(7)−C(8)	101.2(5)	C(24)−C(19)−C(20)	103.0(5)
C(12)−C(7)−C(13)	117.4(5)	C(24)−C(19)−C(13)	119.8(5)
C(8)−C(7)−C(13)	116.5(5)	C(20)−C(19)−C(13)	118.1(5)
C(7)−C(13)−C(19)	110.3(4)		

The minor product that had been extracted into ether following the reaction of 2^- with an enoliminium ester was identified by comparison with a sample that had been isolated in a variation on this procedure in which the mixture obtained from the reaction of 2^- with $Me_2CHC(OSO_2CF_3){=}NMe_2$ (5^+) in Et_2O was dried under vacuum, washed with pentane, and then triturated with Et_2O. Crystals obtained from the concentrated Et_2O solution at 0 °C were shown to contain $[\{Mn(CO)_3(\eta^5\text{-}C_6H_6)\text{-}exo\}_2C(^iPr)NHMe_2]CF_3SO_3$ ($8(CF_3SO_3)$; 10% yield) (Scheme 2), in which two cyclohexadienyl Mn fragments are attached to an organic backbone derived from a single molecule of the enoliminium ester 5^+, by a single-crystal diffraction study (Figure 2; see Table 3 for selected bonds and angles). The diffraction studies are consistent with ^1H NMR spectra, and the combustion analysis is in acceptable agreement. The unusual and crowded connectivity is also seen in the neutral pentane-soluble compound formulated as $[\{Mn(CO)_3(\eta^5\text{-}C_6H_6)\text{-}exo\}_2C(^iPr)NMe_2]$ (**7**, 3% yield) (Scheme 2) on the basis of ^1H and ^{13}C NMR spectra.

It is tempting to assume that **7** is simply the product of the addition of a second equivalent of 2^- to 6^+ as shown in Scheme 2, but the complete mechanistic picture is more complex than the combination of the reactions in Schemes 1 and 2—this combination would predict that 2 equiv of 2^- would react with 1 equiv of 5^+ to give **7** as the major product, but excess 2^- does not increase the yield of **7** (IR), whether a solution of 2^- in THF is transferred into a slurry of 5^+ in Et_2O or a slurry of 5^+ in Et_2O is transferred into a solution of 2^- in THF at −78 °C.

Scheme 3



Multiple reaction pathways are probably in action in parallel, and this argument is supported by an experiment in which 5^+ was treated with collidine under conditions reported to convert 5^+ to a keteniminium salt.[5] We expected that addition of the keteniminium species to 2^- would provide access to the enamine **B** (Scheme 3), in a reaction complementary to the formation of 6^+. In practice, however, reaction of a solution of 2^- at −78 °C with keteniminium salt prepared by the literature procedure in which 1 equiv of collidine was added to a mixture (1:1 ratio) of **3** and **4** in Et_2O[5] gave a solution with an IR spectrum identical with that of 6^+. A control experiment showed that addition of collidine had no impact on IR spectra of a solution of 6^+ made in situ at −78 °C, even when the mixture had been warmed to ambient temperature. We conclude that addition of the keteniminium species to 2^- did provide access to the enamine **B** but that this abstracts a proton back from collidinium. This leads us to further conclude that we cannot determine whether 6^+ is ever formed through **A** or is always formed via the keteniminium.

Hydrolysis of $6(PF_6)$ to generate the final acylation product $[Mn(CO)_3\{\eta^5\text{-}C_6H_6C(^iPr){=}O\}]$ (**9**) was carried out in THF by addition of 5 equiv of 5% KOH/H_2O solution at ambient temperature and leaving the stirred mixture for 2 h under nitrogen protection (Scheme 1).

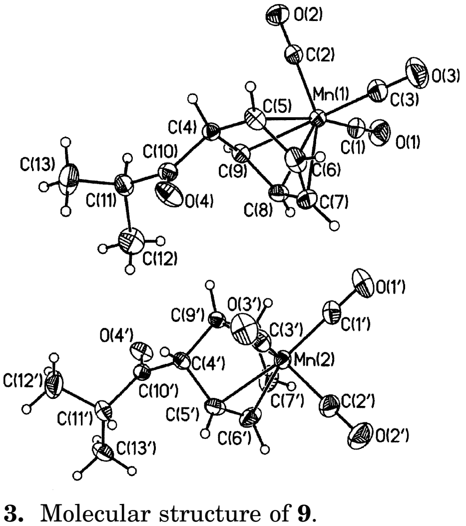


Figure 3. Molecular structure of **9**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[Mn(CO)_3\{\eta^5\text{-}C_6H_6C(^iPr){=}O\}]$ (9)

Mn(1)−C(2)	1.8011(11)	C(4)−C(9)	1.5131(14)
Mn(1)−C(3)	1.8038(13)	C(4)−C(10)	1.5231(14)
Mn(1)−C(1)	1.8084(12)	O(4)−C(10)	1.2121(14)
Mn(1)−C(7)	2.1381(12)	C(5)−C(6)	1.3946(17)
Mn(1)−C(6)	2.1383(12)	C(6)−C(7)	1.420(2)
Mn(1)−C(8)	2.1427(12)	C(7)−C(8)	1.421(2)
Mn(1)−C(9)	2.2165(11)	C(8)−C(9)	1.3946(16)
Mn(1)−C(5)	2.2225(11)	C(10)−C(11)	1.5200(16)
C(4)−C(5)	1.5024(15)		
C(5)−C(4)−C(9)	103.68(8)	O(4)−C(10)−C(11)	120.99(10)
C(5)−C(4)−C(10)	114.38(9)	O(4)−C(10)−C(4)	120.96(10)
C(9)−C(4)−C(10)	112.25(8)	C(11)−C(10)−C(4)	118.05(9)

The acyl **9** was extracted into pentane (IR ν_{CO} 2024.1 (s), 1945.8 (vs) 1665.9 (w) cm^{-1}) and recrystallized in 53% yield from a concentrated pentane solution at 0 °C over 5 days. A single-crystal diffraction study confirmed the formation of a ketone with the connectivity shown in Figure 3 and structural parameters as summarized in Table 4.

Conclusion

We conclude that the benzene ligand in $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$ (**2**$^-$) is sufficiently activated to be acylated under the Matínez variation of Vilsmeier−Haack−Arnold conditions. The mechanism of the reaction has not been established and may involve multiple pathways, but the reaction of **2**$^-$ with 1:1 mixtures of amides and triflic anhydride is likely to provide a general route to derivatives of **2**$^-$ in which the benzene ligand has been functionalized.

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Supporting Information Available: Detailed ^1H and ^{13}C NMR assignments for **6**(PF_6), **7**, **8**(CF_3SO_3), and **9** and full tables of X-ray crystallographic data for **6**(PF_6), **8**(CF_3SO_3), and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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