ORGANOMETALLICS

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Organometallics, **1990**, 9 (6), 1936-1942• DOI: 10.1021/om00156a038 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

$(CO)_3PMe_3$, 12276-38-9; *cis*-$CpV(CO)_2(PMe_3)_2$, 62414-52-2; *trans*-$CpV(CO)_2(PMe_3)_2$, 62414-53-3; $CpV(C_4Ph_4)PMe_3$, 126949-00-6; 3,4-(*E*)-diphenyl-1,3-hexadiene, 126948-96-7; 1-hexene, 592-41-6; 2-butyl-1-methyl-1-heptene, 37549-88-5; 7-methyl-5-undecene, 126927-92-2; 2-butyl-1-octene, 5698-48-6; hexamethylbenzene, 87-85-4.

Supplementary Material Available: Full details of structure determinations and tables of positional and thermal parameters and bond distances and angles for **2**, **4**, **10**, and **14** (45 pages); listings of observed and calculated structure factors for **2**, **4**, **10**, and **14** (63 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Secondary Carbene Complexes of Manganese and Rhenium

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Received January 9, 1990

Reactions of *mer,trans*-$M(CO)_3(PPh_3)_2CHO$ (M = Mn, Re) with protonic acids or methylating agents lead to isolation of rare secondary hydroxy- and methoxycarbene complexes in high yields. The compounds have been characterized by IR and ^1H and ^{13}C NMR spectroscopy; the methoxycarbene *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^-$ has also been characterized by X-ray crystallography (space group *Pbca*, $a = 18.934$ (4) Å, $b = 19.810$ (6) Å, $c = 23.436$ (5) Å, $Z = 8$, $d_c = 1.42$ g cm^{-3}, and $R = 0.068$). Aminolysis of the methoxycarbene complexes with benzylamine produces the corresponding aminocarbene complexes in high yields. One of these, *mer,trans*-$Mn(CO)_3(PPh_3)_2(CHNHCH_2Ph)^+CF_3SO_3^-$, has been characterized by X-ray crystallography (space group $P2_1/n$, $a = 14.268$ (2) Å, $b = 16.107$ (2) Å, $c = 22.264$ (3) Å, $\beta = 104.62$ (2)°, $Z = 4$, $d_c = 1.35$ g cm^{-3}, and $R = 0.061$). Deprotonation of the aminocarbene complexes yields the corresponding iminomethyl (formimidoyl) complexes.

Introduction

Hydroxy- and alkoxycarbene complexes, M=CHOR (R = H, alkyl), are of interest because of their proposed intermediacy in catalytic reductions of CO that lead to oxygenates.[1] Few complexes of the first type have been isolated,[2] particularly those involving first-row transition elements;[3] in other cases, more labile hydroxycarbene complexes have been spectroscopically observed at low temperatures.[4] The alkoxycarbene compounds can sometimes be prepared by α-hydride abstraction from the corresponding ether complexes, $M—CH_2—OR$, although ether cleavage is frequently the competing or exclusive pathway.[5] One potentially general route to either type of compound would involve electrophilic additions to neutral metal formyl complexes. However, this method has shown only limited success,[2-4] in part because the initial electrophilic addition is often followed by rapid hydride transfer from a second molecule of the neutral formyl. We have isolated and characterized hydroxy- and methoxycarbene cationic complexes of the general formula *mer,trans*-$M(CO)_3(PPh_3)_2(CHOR)^+$ (M = Mn, Re; R = H, CH_3) by direct electrophilic additions to the corresponding neutral formyls. Also reported are the first aminolysis reactions of secondary methoxycarbene cationic complexes which lead to aminocarbene derivatives (see Chart I). Finally, deprotonations of the aminocarbene complexes afforded the corresponding iminomethyl derivatives. Structures of the manganese methoxycarbene and (benzylamino)carbene complexes have been established by X-ray crystallography.

Chart I. Secondary Carbene Complexes

mer,trans-$M(CO)_3(PPh_3)_2(CHOH)^+X^-$
1a: M = Mn, X = *p*-$CH_3C_6H_4SO_3$
b: M = Mn, X = BF_4
c: M = Re, X = *p*-$CH_3C_6H_4SO_3$

mer,trans-$M(CO)_3(PPh_3)_2(CHOCH_3)^+X^-$
2a: M = Mn, X = CF_3SO_3
b: M = Mn, X = BF_4
c: M = Re, X = CF_3SO_3

mer,trans-$M(CO)_3(PPh_3)_2(CHNHCH_2C_6H_5)^+X^-$
3a: M = Mn, X = CF_3SO_3
b: M = Mn, X = BF_4
c: M = Re, X = CF_3SO_3

Results and Discussion

Hydroxycarbene Complexes. Direct protonation of *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$ was accomplished by either *p*-toluenesulfonic acid or $HBF_4·(CH_3)_2O$; only the former was used with the corresponding rhenium complex.[6] It was necessary to prepare the manganese complex **1b** at low temperature because of its high lability; compounds **1a** and **1c** could be prepared at room temperature. All reactions were complete after a few minutes, and the complexes were isolated in better than 90% yields. The

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[1] (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

[2] (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (b) Lilga, M. A.; Ibers, J. A. *Organometallics* **1985**, *4*, 590. (c) Barratt, D. S.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1986**, *306*, C41.

[3] A preliminary account of some of this work has been published: Gibson, D. H.; Mandal, S. K.; Owens, K.; Richardson, J. F. *Organometallics* **1987**, *6*, 2624.

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[5] (a) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604. (b) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (c) Guerchais, V.; Lapinte, C.; Thepot, J.-Y.; Toupet, L. *Organometallics* **1988**, *7*, 604.

[6] For the preparations of the formyl complexes, see: Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498.

0276-7333/90/2309-1936$02.50/0

Table I. Selected NMR Spectral Properties of Carbene Complexes

	^{1}H NMR, δ^a				^{13}C NMR, δ^a		
compd	OH	CHO	NH	CHN	CHO	CHN	CO
1a							
38 °C	12.35 (s)	13.09 (s)			335.32 (s)		219.64 (t)^b 216.75 (t)
17 °C	12.70 (s)	12.86 (s)					
1b	12.62 (s)	12.62 (s)			330.94 (s)		220.30 (t) 217.62 (t)
1c							
38 °C	13.19 (s)	13.82 (s)			298.86 (s)		195.86 (t) 192.69 (t)
16 °C	13.60 (s)	13.60 (s)					
2a		12.67 (s)^b			338.64 (s)		219.94 (t) 216.63 (t)
2b		12.60 (s)^b					
2c		12.42 (s)			303.97 (s)		195.04 (t) 191.16 (t)
3a			9.98 (d)	10.26 (d)		255.33 (t)	220.27 (t) 217.69 (t)
3b			9.29 (d)	10.60 (d)		256.26 (t)	220.23 (t) 217.71 (t)
3c			10.50 (d)	10.10 (d)		227.68 (t)	194.72 (t) 191.34 (t)

[a] CD_2Cl_2 unless otherwise noted. [b] $CDCl_3$.

compounds are sensitive to moisture and are relatively labile in solution, although **1a** is more stable than **1b** and both of these are less stable than **1c**. Samples of all three compounds are stable in the solid state, at −10 °C, for periods up to 1 week. Because of their lability, the compounds have been characterized primarily by their spectral properties, which are consistent with their formulation as hydroxycarbene cationic complexes. The ^{1}H NMR spectra of **1a**–**c** show the carbene methine proton at very low field (see Table I); as with the few other compounds of this type that have been characterized,[2-4] the hydroxyl proton was not always distinct. At a probe temperature of 16 °C (and in CD_2Cl_2 solution) the methine and hydroxyl protons of rhenium complex **1c** have the same chemical shift (13.60 ppm). However, at 38 °C, there are two separate resonances: a broad singlet appears at 13.19 ppm, which is assigned to the hydroxyl proton, and a sharp singlet is seen at 13.82 ppm, which is assigned to the methine proton. Similar behavior is observed for manganese compound **1a**; however, since the spectra of **1b** can be obtained only at low temperatures, we observe only one resonance for the two protons. As shown in Table I, the carbene carbon resonances also appear at very low field, as expected for this type of carbon, with the rhenium complex showing the higher chemical shift (see the Experimental Section for complete NMR data). No high-frequency bands are seen in the IR spectra of these compounds that could be assigned to hydroxyl stretching vibrations. Only Cole-Hamilton[2c] has reported ν_{OH} for compounds of this type.

Deprotonation of **1a**–**c** occurs readily upon treatment with bases such as triethylamine, with regeneration of the corresponding formyl complex. Compound **1a** is the first secondary hydroxycarbene complex of a first-row transition element to be isolated. As with other carbene complexes prepared in this way, the main factor that limits the ability to isolate or observe a hydroxycarbene is the ease of hydride transfer from the unprotonated formyl complex to the carbene cation. With **1a**–**c** the metal centers have two strong σ-donor ligands that act to reduce the electrophilicity of the carbene and retard hydride transfer. Even when less than 1 equiv of protonic acid is employed, the hydroxycarbene cation is the only product that can be spectroscopically observed.

Methoxycarbene Complexes. Methyl trifluoromethanesulfonate and trimethyloxonium tetrafluoroborate were used to methylate the manganese and rhenium formyl complexes. Equimolar quantities of the alkylating agent and the formyl complex were mixed and allowed to stand until IR spectral data indicated that the formyl complex had been consumed; reaction times varied from a few minutes to about 1 h. The isolated compounds, formed in nearly quantitative yields, have been characterized by IR and ^{1}H and ^{13}C NMR spectroscopy, elemental analysis (**2a** and **2c**), and X-ray crystallography (**2a**); the compounds are stable in solution for several hours at room temperature and are stable in the solid state for several days at room temperature. The IR spectra of **2a**–**c** show, in addition to the expected bands for the terminal carbonyl ligands, very weak bands near 2700 cm^{-1}, which are believed to be due to the carbene C–H stretch. The ^{1}H NMR spectra of all three compounds show the carbene methine proton at very low field (12.5 ppm) as a singlet and show the hydrogens of the methoxy group at about 3.7 ppm. The carbene carbon appears at extremely low field (338.64 ppm for **2a** and 303.97 ppm for **2c**) as expected; only one conformational isomer of the carbene ligand (presumably anti as in the solid-state structure of **2a**; see below) is evident in all cases.

Single-crystal X-ray data were obtained for compound **2a** (as the CH_2Cl_2 solvate) under the conditions summarized in Table II; the unit cell was found to be orthorhombic. Refinement, described in the Experimental Section, included the location of the hydrogen atoms from a difference Fourier map. An ORTEP representation of **2a** is shown in Figure 1; bond distances and bond angles are compiled in Table III. Positional parameters are given in Table IV. The structural analysis confirms the octahedral geometry about the manganese atom and the trans relationship of the triphenylphosphine ligands. As shown in Figure 1, the compound has adopted the anti conformation about the carbene carbon–oxygen bond in the solid state. The manganese–carbene carbon bond length is 1.947 Å, which compares quite favorably with 1.950 Å found for the analogous bond in *cis*-$Mn_2(CO)_9[C(OCH_3)(C_6H_5)]$.[7]

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(7) Huttner, G.; Regler, D. *Chem. Ber.* **1972**, *105*, 1230.

Table II. Summary of Crystallographic Data for $Mn(CO)_3(PPh_3)_2(CHOCH_3)^+CF_3SO_3^- \bullet 0.8CH_2Cl_2$ (2a) and $Mn(CO)_3(PPh_3)_2(CHNHCH_2Ph)^+CF_3SO_3 \bullet CH_2Cl_2$ (3a)

	2a	3a
formula	$C_{42.8}H_{35.6}Cl_{1.6}MnF_3O_7P_2S$	$C_{49}H_{41}Cl_2MnF_3NO_6P_2S$
fw	924.63	1016.73
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/n$
a, Å	18.934 (4)	14.268 (2)
b, Å	19.810 (6)	16.107 (2)
c, Å	23.436 (5)	22.264 (3)
β, deg	90	104.62 (2)
V, Å^3	8790.1	4950.6
Z	8	4
d_c, g cm^{-3}	1.42	1.35
cryst dimens, mm	0.30 × 0.40 × 0.40	0.40 × 0.45 × 0.50
cryst descripn	yellow block, cut	yellow block, cut
μ(Mo Kα), cm^{-1}	5.9	5.2
radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
diffractometer	CAD4	CAD4
monochromator	graphite	graphite
temp, °C	23	23
scan range, deg	$0.70 + 0.34 \tan\theta$	$0.8 + 0.34 \tan\theta$
scan speed, deg min^{-1}	1–3	1–3
max θ, deg	25	25
intens decay, %	3.1	1.5
no. of unique rflns collected	7866	9027
computing	SDP/VAX	SDP/VAX
weighting formula	$[\sigma(F)^2 + (0.02F)^2 + 1.0]^{-1}$	$[\sigma(F)^2 + (0.03F)^2 + 3.0]^{-1}$
no. of variables	442	596
no. of obs rflns ($I > 3\sigma(I)$)	5129	5523
max Δ/σ	0.53	2.54
GOF	2.47	1.75
resid electron density, e Å^{-3}	0.73 (8)	1.09 (8)
agreement factors		
R	0.068	0.061
R_w	0.059	0.062

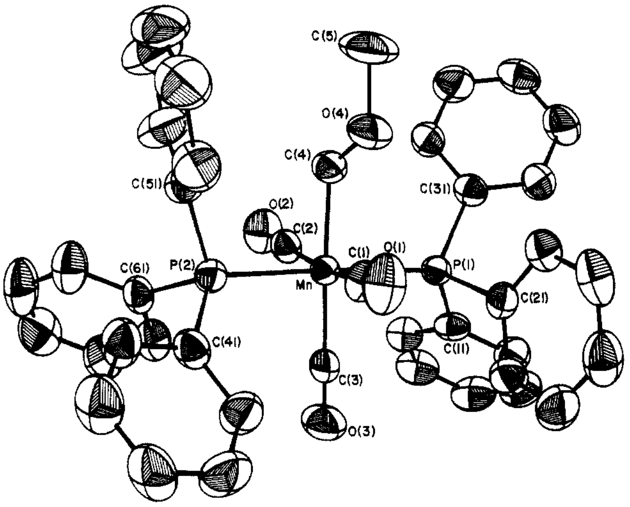

Figure 1. Molecular structure of compound **2a**. Ellipsoids are drawn at the 50% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) for Compound 2a[a]

	Bond Distances		
Mn–P1	2.326 (2)	C1–O1	1.152 (6)
Mn–P2	2.314 (1)	C2–O2	1.135 (6)
Mn–C1	1.853 (5)	C3–O3	1.144 (5)
Mn–C2	1.842 (6)	C4–O4	1.286 (6)
Mn–C3	1.847 (4)	O4–C5	1.473 (6)
Mn–C4	1.947 (4)		
	Bond Angles		
P1–Mn–P2	173.76 (6)	P1–Mn–C1	89.4 (2)
P1–Mn–C2	95.9 (1)	P1–Mn–C3	86.3 (2)
P1–Mn–C4	90.9 (2)	P2–Mn–C1	84.7 (2)
P2–Mn–C2	90.2 (1)	P2–Mn–C3	92.1 (2)
P2–Mn–C4	91.0 (2)	C1–Mn–C2	170.7 (2)
C1–Mn–C3	94.9 (2)	C1–Mn–C4	86.9 (2)
C2–Mn–C3	93.3 (2)	C2–Mn–C4	85.2 (2)
C3–Mn–C4	176.6 (2)	Mn–C1—O1	174.1 (4)
Mn–C2–O2	177.1 (4)	Mn–C3–O3	176.1 (4)
Mn–C4–O4	123.9 (4)	C4–O4–C5	119.9 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The carbene carbon–oxygen bond length in **2a** is 1.286 Å and is shorter than in the binuclear compound (1.315 Å), whereas the Mn–C–O angle in the carbene unit of **2a** is 124.6°, as compared to only 119.4° in the binuclear compound. The binuclear compound also exhibits a trans geometry about the carbene carbon–oxygen bond. The significant shortening of the carbene C–O bond in cation **2a** as compared to the analogous bond in the neutral binuclear compound can be taken as evidence of increased π-donating character of the heteroatom in **2a**. Bond lengths and bond angles in manganese carbene complexes have been shown to differ significantly, depending on the electronic nature of the substituents on the carbene carbon and the steric environment at this center;[8] it is less clear what factors determine the geometry about the carbene C–O bond. Complete tables of anisotropic thermal parameters, hydrogen atom parameters, and structure factors for **2a** are given in the supplementary material together with full tables of bond distances and angles.

Just as it is possible to deprotonate the hydroxycarbene complexes, it is also possible to dealkylate the methoxycarbenes. Complexes **2a–c** are readily dealkylated by NaI, as observed for other alkoxycarbene cations,[5a,9] to regenerate the original formyl complex.

Reaction of *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$ with $^1/_2$ equiv of methyl triflate slowly converts the formyl complex to equal quantities of **2a** and *mer,trans*-$Mn(CO)_3(PPh_3)_2CH_2OCH_3$ as reported earlier.[3] However, the hydride transfer is sufficiently slow that this reaction does not compete when equivalent quantities of formyl complex and alkylating agent are used. The related formyl complex *cis*-$Mn(CO)_4(PPh_3)CHO$ is rapidly converted to the corresponding methoxymethyl complex[3] by methyl triflate, and the reaction cannot be arrested at the carbene stage. Also, the corresponding formyl complex *mer,trans*-$Mn(CO)_3[P(OPh)_3]_2CHO$ is converted rapidly to the methoxymethyl derivative by treatment with methyl triflate; the methoxycarbene cation cannot be isolated.[10] For electronic reasons, the bis(phosphine)-substituted formyl complex should be the most nucleophilic of the three and

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[8] See: Schubert, U. *Organometallics* **1982**, *1*, 1085 and references cited therein.

[9] (a) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604.

[10] See: Kreissl, F. R. In *Transition Metal Carbene Complexes*; Seyferth, D., Ed.; Verlag Chemie: Deerfield Beach, FL, 1983.

Table IV. Positional Parameters and Their Estimated Standard Deviations for Compound 2a[a]

atom	*x*	*y*	*z*	*B*, Å^2	occ
Mn	0.74843 (4)	0.02552 (3)	0.12599 (3)	2.50 (1)	
P1	0.72456 (7)	0.01122 (6)	0.22258 (6)	2.59 (2)	
P2	0.75911 (7)	0.03841 (6)	0.02821 (6)	2.92 (3)	
O1	0.5984 (2)	0.0687 (2)	0.1065 (1)	5.61 (9)	
O2	0.9047 (2)	0.0118 (2)	0.1342 (2)	5.24 (9)	
O3	0.7283 (2)	−0.1236 (2)	0.1159 (2)	5.5 (1)	
O4	0.7184 (2)	0.1643 (2)	0.1517 (2)	5.1 (1)	
C1	0.6547 (3)	0.0487 (2)	0.1141 (2)	3.5 (1)	
C2	0.8449 (3)	0.0159 (2)	0.1323 (2)	3.2 (1)	
C3	0.7336 (3)	−0.0663 (2)	0.1192 (2)	3.1 (1)	
C4	0.7663 (3)	0.1213 (2)	0.1376 (2)	3.3 (1)	
C5	0.7378 (4)	0.2353 (3)	0.1620 (3)	7.4 (2)	
C11	0.7535 (2)	−0.0683 (2)	0.2570 (2)	3.1 (1)	
C12	0.8183 (3)	−0.0966 (3)	0.2415 (2)	4.2 (1)	
C13	0.8430 (3)	−0.1544 (2)	0.2709 (3)	4.9 (1)	
C14	0.8031 (3)	−0.1823 (3)	0.3138 (3)	5.4 (2)	
C15	0.7383 (3)	−0.1542 (3)	0.3292 (3)	5.1 (1)	
C16	0.7138 (3)	−0.0973 (3)	0.3008 (2)	4.3 (1)	
C21	0.6291 (2)	0.0111 (2)	0.2329 (2)	3.1 (1)	
C22	0.5934 (3)	0.0697 (3)	0.2477 (2)	4.0 (1)	
C23	0.5196 (3)	0.0684 (3)	0.2500 (2)	4.7 (1)	
C24	0.4831 (3)	0.0103 (3)	0.2363 (2)	5.5 (1)	
C25	0.5182 (3)	−0.0460 (2)	0.2220 (3)	5.4 (1)	
C26	0.5909 (3)	−0.0464 (2)	0.2206 (2)	3.9 (1)	
C31	0.7571 (2)	0.0742 (2)	0.2737 (2)	3.2 (1)	
C32	0.8180 (2)	0.1129 (3)	0.2612 (2)	3.6 (1)	
C33	0.8433 (3)	0.1586 (3)	0.3007 (2)	5.1 (1)	
C34	0.8107 (3)	0.1665 (3)	0.3528 (3)	5.3 (2)	
C35	0.7537 (3)	0.1272 (3)	0.3658 (2)	5.2 (1)	
C36	0.7258 (3)	0.0804 (3)	0.3266 (2)	4.3 (1)	
C41	0.6865 (3)	0.0061 (2)	−0.0162 (2)	3.2 (1)	
C42	0.6803 (3)	0.0295 (3)	−0.0724 (2)	4.8 (1)	
C43	0.6271 (3)	0.0061 (3)	−0.1069 (3)	6.0 (2)	
C44	0.5786 (3)	−0.0376 (3)	−0.0868 (2)	5.5 (1)	
C45	0.5841 (3)	−0.0621 (3)	−0.0317 (2)	6.2 (1)	
C46	0.6376 (3)	−0.0393 (2)	0.0030 (2)	4.7 (1)	
C51	0.7618 (3)	0.1287 (2)	0.0105 (2)	3.9 (1)	
C52	0.8262 (3)	0.1635 (3)	0.0160 (3)	5.8 (2)	
C53	0.8290 (4)	0.2345 (3)	0.0103 (3)	8.1 (2)	
C54	0.7676 (4)	0.2685 (3)	−0.0025 (3)	7.8 (2)	
C55	0.7028 (4)	0.2349 (3)	−0.0086 (3)	6.9 (2)	
C56	0.7005 (3)	0.1644 (3)	−0.0014 (3)	5.7 (2)	
C61	0.8363 (3)	0.0005 (2)	−0.0074 (2)	3.6 (1)	
C62	0.8635 (3)	−0.0603 (2)	0.0118 (2)	4.7 (1)	
C63	0.9152 (3)	−0.0930 (3)	−0.0168 (2)	6.4 (2)	
C64	0.9458 (3)	−0.0644 (3)	−0.0649 (2)	6.2 (1)	
C65	0.9220 (3)	−0.0016 (3)	−0.0838 (2)	6.6 (2)	
C66	0.8671 (3)	0.0296 (3)	−0.0553 (2)	5.1 (1)	
Cl1	0.5503 (4)	0.3489 (2)	0.1385 (2)	11.7 (2)	0.40
Cl2	0.5210 (6)	0.2197 (3)	0.1089 (5)	13.8 (3)	0.30
Cl3	0.4417 (5)	0.3039 (5)	0.1088 (5)	13.9 (3)	0.25
Cl4	0.585 (1)	0.280 (1)	0.1206 (8)	24.9 (7)	0.25
Cl5	0.4994 (9)	0.3592 (5)	0.1296 (6)	9.8 (5)	0.15
Cl6	0.4816 (8)	0.2274 (5)	0.0933 (4)	11.0 (3)	0.15
Cl7	0.534 (1)	0.240 (1)	0.1487 (8)	7.6 (5)	0.10
S	0.4668 (1)	0.24214 (8)	0.33334 (7)	9.39 (6)	
C6	1.0058 (5)	0.2782 (4)	0.1088 (4)	11.0 (3)*	
F1	0.5427 (3)	0.3338 (2)	0.3835 (2)	11.0 (1)	
F2	0.5030 (3)	0.2563 (3)	0.4398 (2)	14.0 (2)	
F3	0.4354 (5)	0.3252 (3)	0.4041 (3)	8.2 (2)*	0.50
F4	0.5696 (7)	0.2231 (5)	0.3822 (5)	13.0 (3)*	0.50
O5	0.4805 (5)	0.2639 (3)	0.2875 (2)	18.7 (2)	
O6	0.4304 (3)	0.1836 (2)	0.3499 (2)	8.2 (1)	
O7	0.5566 (8)	0.2064 (6)	0.3351 (5)	12.6 (4)*	0.50
O8	0.4009 (7)	0.3018 (6)	0.3479 (5)	11.4 (3)*	0.50
C7	0.4933 (7)	0.2921 (6)	0.1546 (5)	11.7 (4)*	0.80

[a] Starred values denote atoms refined isotropically, while occupancies indicate the fraction of an atom used in the disorder models. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

should be a better hydride donor as well. Again the factor which halts the sequence of electrophilic additions and hydride transfers that allows the conversion of a formyl complex into the completely reduced methyl analogue, as demonstrated first by Gladysz[2a] and illustrated in Scheme I, seems to be the hydride acceptor characteristics of the alkylated (or protonated) formyl.

Scheme I

$$\mathrm{M{-}CHO} \xrightarrow{\mathrm{H^+}} \mathrm{M{=}CHOH^+} \xrightarrow[\mathrm{-M(CO)^+}]{\mathrm{M{-}CHO}}$$

$$\mathrm{M{-}CH_2{-}OH} \xrightarrow[\mathrm{-H_2O}]{\mathrm{H^+}} \mathrm{M{=}CH_2{}^+} \xrightarrow[\mathrm{-M(CO)^+}]{\mathrm{M{-}CHO}} \mathrm{M{-}CH_3}$$

Aminocarbene Complexes. Aminolysis reactions of Fischer-type carbene complexes have been widely used to prepare the corresponding aminocarbene derivatives.[11] Good methods have been developed recently for the preparation of neutral secondary mononuclear aminocarbene complexes,[12] and Adams[13] has developed synthetic routes to cluster compounds containing secondary amino carbene ligands; however, these methods do not involve aminolysis. Few examples of cationic secondary aminocarbene complexes have been reported; some have been prepared by protonation of the corresponding iminomethyl complexes.[14] Additional secondary carbene cations were prepared by aminolysis of the corresponding thioethers;[15] however, aminolysis of a secondary alkoxycarbene complex has, to our knowledge, not been reported previously.

Compounds **2a–c** react rapidly with benzylamine to give the aminocarbene cations **3a–c**, respectively, in high yields (80–92%). The compounds are stable at room temperature and have been characterized by IR and ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray crystallography (**3a**). The IR spectra of the compounds show a weak band above 2000 cm^{-1}, a strong band at about 1950 cm^{-1}, and a shoulder at about 1940 cm^{-1}, consistent with the *mer,trans* geometry of the compounds.[17] Also, a medium-intensity band is seen in each compound at about 3250 cm^{-1}, which is assigned to the N–H stretching vibration, and a weak band is seen in the spectra of the two manganese complexes at about 2700 cm^{-1}, which is assigned to the carbene methine C–H stretch (this band is absent in **3c**). ^{1}H NMR spectra of all three compounds show low-field resonances for the NH and carbene CH (see Table I), as observed previously for compounds of this type;[14-16] both resonances appear as doublets, with considerable broadening of the NH protons. Addition of D_2O to NMR samples of **3a** and **3c** removes the NH resonance and reduces the methine proton to a singlet in each case. The carbene carbon resonances also appear at low field, but quite a bit higher than in the corresponding methoxycarbene complexes (see Table I).

Single-crystal X-ray data were obtained for **3a** under the conditions summarized in Table II; the unit cell was found to be monoclinic. Refinement, described in the Experimental Section, included the location of the hydrogen

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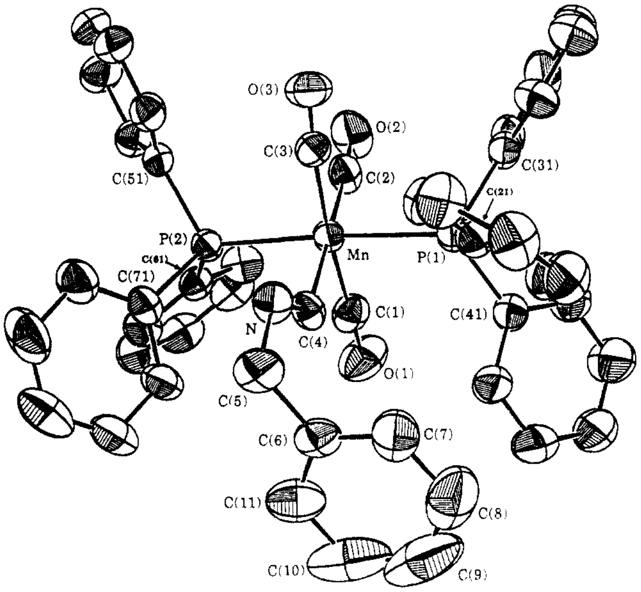

Figure 2. Molecular structure of compound **3a**. Ellipsoids are drawn at the 50% probability level.

Table V. Selected Bond Distances (Å) and Angles (deg) for Compound 3a[a]

	Bond Distances		
Mn–P1	2.342 (1)	C1–O1	1.134 (6)
Mn–P2	2.333 (1)	C2–O2	1.134 (6)
Mn–C1	1.855 (5)	C3–O3	1.133 (6)
Mn–C2	1.815 (5)	C4–N	1.284 (7)
Mn–C3	1.842 (5)	N–C5	1.493 (6)
Mn–C4	2.003 (5)	C5–C6	1.490 (8)
	Bond Angles		
P1–Mn–P2	175.02 (5)	P1–Mn–C1	90.5 (2)
P1–Mn–C2	94.7 (2)	P1–Mn–C3	86.9 (1)
P1–Mn–C4	85.9 (1)	P2–Mn–C1	89.2 (2)
P2–Mn–C2	90.2 (2)	P2–Mn–C3	94.0 (2)
P2–Mn–C4	89.2 (1)	C1–Mn–C2	91.0 (2)
C1–Mn–C3	173.8 (2)	C1–Mn–C4	88.9 (3)
C2–Mn–C3	83.6 (2)	C2–Mn–C4	179.4 (2)
C3–Mn–C4	96.5 (2)	Mn–C1–O1	179.6 (4)
Mn–C2–O2	175.9 (5)	Mn–C3–O3	170.9 (5)
Mn–C4–N	131.6 (3)	N–C5–O6	112.6 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

atoms from a difference Fourier map. An ORTEP representation of **3a** is shown in Figure 2; bond distances and bond angles are compiled in Table V. Positional parameters are given in Table VI. Again, structural analysis confirms the trans relationship of the triphenylphosphine ligands about the manganese atom. As shown in Figure 2, the complex exists in the solid state as the anti isomer with trans geometry about the carbene carbon to heteroatom (nitrogen in **3a**) bond, as does the methoxy derivative **2a**. The carbene carbon–nitrogen bond distance is 1.284 Å, and the metal–carbene carbon–nitrogen bond angle is 131.6°. This bond distance is within the range (1.26–1.29 Å) found for other secondary aminocarbene complexes; the metal–carbene carbon–nitrogen angle varies quite a bit depending upon steric factors around the aminocarbene ligand.[12e,13] There is significant shortening of the manganese–carbon bond to the CO ligand that is trans to the carbene carbon (C2) in **3a**; this does not occur for **2a**, which indicates that there is substantially more back-bonding from manganese when the carbene heteroatom is nitrogen and reflects greater electron donation from nitrogen than from oxygen to the carbene carbon.

Table VI. Positional Parameters and Their Estimated Standard Deviations for Compound 3a[a]

atom	*x*	*y*	*z*	*B*, Å^2	occ
Mn	0.37730 (5)	0.24120 (4)	0.05940 (3)	2.68 (1)	
S	0.0638 (1)	0.22439 (9)	0.17832 (8)	5.50 (4)	
P1	0.27820 (8)	0.24620 (7)	−0.04190 (6)	2.94 (3)	
P2	0.46910 (8)	0.24656 (7)	0.16211 (6)	2.75 (2)	
F1	0.1629 (4)	0.1865 (3)	0.2874 (3)	14.3 (2)	
F2	0.0419 (3)	0.2639 (3)	0.2855 (2)	13.2 (2)	
F3	0.1667 (3)	0.3115 (3)	0.2674 (3)	11.1 (2)	
O1	0.5179 (3)	0.3579 (2)	0.0248 (2)	6.4 (1)	
O2	0.4894 (3)	0.0948 (3)	0.0391 (2)	5.8 (1)	
O3	0.2484 (2)	0.1052 (2)	0.0796 (2)	4.8 (1)	
O4	0.1496 (3)	0.2095 (3)	0.1561 (2)	7.9 (1)	
O5	0.0139 (3)	0.2990 (3)	0.1543 (2)	7.5 (1)	
O6	0.0026 (3)	0.1546 (2)	0.1783 (3)	8.8 (2)	
N	0.2330 (2)	0.3456 (3)	0.1039 (2)	3.56 (9)	
C1	0.4643 (3)	0.3137 (3)	0.0378 (3)	3.8 (1)	
C2	0.4471 (3)	0.1525 (3)	0.0451 (3)	3.7 (1)	
C3	0.2944 (3)	0.1611 (3)	0.0750 (2)	3.3 (1)	
C4	0.3013 (3)	0.3393 (3)	0.0761 (2)	3.0 (1)	
C5	0.1822 (3)	0.4239 (3)	0.1127 (3)	4.6 (1)	
C6	0.1894 (3)	0.4890 (3)	0.0666 (3)	3.9 (1)	
C7	0.1263 (4)	0.4887 (3)	0.0084 (3)	5.8 (2)	
C8	0.1346 (5)	0.5471 (4)	−0.0358 (4)	9.1 (2)	
C9	0.2093 (6)	0.6064 (4)	−0.0190 (4)	11.6 (2)	
C10	0.2714 (4)	0.6066 (4)	0.0382 (5)	9.6 (2)	
C11	0.2613 (3)	0.5486 (4)	0.0819 (4)	5.9 (2)	
C12	0.1105 (4)	0.2466 (4)	0.2580 (4)	7.6 (2)	
C21	0.1500 (3)	0.2732 (3)	−0.0520 (2)	3.4 (1)	
C22	0.0996 (3)	0.2490 (3)	−0.0094 (3)	4.0 (1)	
C23	0.0027 (4)	0.2671 (3)	−0.0184 (3)	5.0 (1)	
C24	−0.0451 (3)	0.3104 (3)	−0.0699 (3)	5.1 (1)	
C25	0.0030 (3)	0.3346 (3)	−0.1134 (3)	5.2 (1)	
C26	0.0996 (3)	0.3171 (3)	−0.1051 (3)	4.5 (1)	
C31	0.2689 (3)	0.1474 (3)	−0.0841 (2)	3.6 (1)	
C32	0.3522 (4)	0.1110 (3)	−0.0932 (3)	4.4 (1)	
C33	0.3475 (4)	0.0352 (3)	−0.1235 (3)	5.9 (2)	
C34	0.2588 (4)	−0.0044 (4)	−0.1439 (3)	6.4 (2)	
C35	0.1756 (4)	0.0305 (3)	−0.1349 (3)	5.9 (2)	
C36	0.1806 (4)	0.1068 (3)	−0.1049 (3)	4.7 (1)	
C41	0.3146 (3)	0.3228 (3)	−0.0932 (2)	3.5 (1)	
C42	0.3149 (4)	0.4060 (3)	−0.0782 (3)	4.7 (1)	
C43	0.3372 (4)	0.4669 (3)	−0.1159 (3)	5.5 (2)	
C44	0.3601 (4)	0.4450 (3)	−0.1699 (3)	5.3 (1)	
C45	0.3624 (4)	0.3627 (4)	−0.1851 (3)	6.4 (2)	
C46	0.3396 (4)	0.3010 (3)	−0.1470 (3)	5.0 (1)	
C51	0.4716 (3)	0.1501 (3)	0.2059 (2)	3.2 (1)	
C52	0.5578 (3)	0.1082 (3)	0.2315 (3)	4.0 (1)	
C53	0.5570 (4)	0.0328 (3)	0.2620 (3)	5.1 (1)	
C54	0.4710 (4)	−0.0014 (4)	0.2668 (3)	5.5 (2)	
C55	0.3841 (4)	0.0410 (3)	0.2423 (3)	5.1 (1)	
C56	0.3839 (3)	0.1158 (3)	0.2121 (3)	3.8 (1)	
C61	0.5993 (3)	0.2701 (3)	0.1737 (2)	3.2 (1)	
C62	0.6477 (3)	0.3210 (3)	0.2212 (3)	4.1 (1)	
C63	0.7456 (4)	0.3384 (4)	0.2293 (3)	5.3 (2)	
C64	0.7963 (3)	0.3033 (3)	0.1910 (3)	5.2 (1)	
C65	0.7492 (3)	0.2507 (4)	0.1446 (3)	5.1 (1)	
C66	0.6508 (3)	0.2338 (3)	0.1344 (3)	4.4 (1)	
C71	0.4353 (3)	0.3267 (3)	0.2108 (2)	3.3 (1)	
C72	0.4065 (4)	0.3097 (3)	0.2643 (3)	5.0 (1)	
C73	0.3881 (4)	0.3761 (4)	0.3002 (3)	6.9 (2)	
C74	0.3995 (4)	0.4576 (3)	0.2836 (3)	6.2 (2)	
C75	0.4285 (4)	0.4740 (3)	0.2308 (3)	5.1 (1)	
C76	0.4449 (3)	0.4098 (3)	0.1944 (3)	4.3 (1)	
C13	0.6797 (8)	0.0751 (7)	0.9696 (7)	7.8 (3)*	0.7
Cl1	0.6222 (3)	0.0739 (3)	0.8933 (3)	10.5 (1)*	0.5
Cl2	0.7259 (4)	0.1689 (5)	0.9951 (4)	12.9 (2)*	0.4
Cl6A	0.570 (1)	0.558 (1)	0.523 (1)	16.0 (5)*	0.2
Cl6	0.5056 (6)	0.4553 (5)	0.5514 (6)	13.6 (3)*	0.3
Cl3	0.6156 (9)	0.1888 (8)	0.9508 (8)	12.5 (4)*	0.2
Cl2A	0.787 (2)	0.146 (1)	0.991 (1)	9.8 (6)*	0.1
Cl5	0.9538 (6)	0.0412 (5)	0.9472 (5)	12.3 (3)*	0.3
C16	1.027 (2)	0.029 (2)	0.992 (2)	14 (1)*	0.3

[a] Starred values denote atoms refined isotropically with the listed occupancies. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

Iminomethyl Complexes. There are several reports of syntheses of iminomethyl (formimidoyl) complexes via insertion reactions of isonitriles into metal–hydrogen bonds.[18] Also, compounds of this type have been prepared by deprotonation of aminocarbene cations formed by aminolysis of thiocarbene complexes.[16]

Deprotonations of **3b** and **3c** were accomplished by aqueous NaOH in CH_2Cl_2/ethanol; the reactions occurred cleanly to provide **4a** and **4b**, respectively, in nearly quantitative yields. Both compounds are stable at room temperature and have been characterized by elemental analysis as well as by IR and ^1H and ^{13}C NMR spectroscopy. Both compounds show weak- to medium-intensity bands for ν_{CN} at about 1540 cm^{-1} and medium-intensity bands at about 2710 cm^{-1}, which are assigned to ν_{CH} of the iminomethyl ligand; these absorptions are in the same regions reported by Clark[18] and Roper[16] for related compounds. The ^1H NMR spectra show the iminomethyl protons at 9.3–9.8 ppm; the values for iminomethyl compounds reported previously fall in the range 9.0–11.0 ppm. The ^{13}C NMR spectra show the imino carbon resonances at lowest field (see Table I); the chemical shifts depend greatly on the nature of the metal center. Under the conditions we have used to examine their spectral properties, there is no evidence for syn–anti isomerism in **4a,b** as seen for some of the iminomethyl complexes studied previously.[16b,18a] Both compounds react with strong protonic acids to re-form the corresponding aminocarbene complexes.

Experimental Section

General Data. Hexane and pentane were dried over concentrated H_2SO_4 and fractionally distilled. Reagent grade dichloromethane, absolute ethanol, and absolute ether were used as received. Benzylamine, CD_3CN, C_6D_6, D_2O, $CH_3SO_3CF_3$, $HBF_4{\cdot}(CH_3)_2O$, $(CH_3)_3O^+BF_4^-$, CD_2Cl_2, and $CDCl_3$ were obtained from Aldrich and used directly. p-$CH_3C_6H_4SO_3H{\cdot}H_2O$ was obtained from Aldrich and recrystallized from ether. Spectroscopic measurements were obtained on the following instruments: ^1H NMR, Varian XL-300 and EM-390; ^{13}C and ^{31}P NMR, Varian XL-300; IR, Perkin-Elmer 599B and Nicolet SX-170. ^1H and ^{13}C NMR chemical shifts were referenced to tetramethylsilane; ^{31}P chemical shifts were referenced to external H_3PO_4. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All reactions were performed under an atmosphere of prepurified nitrogen.

***mer,trans*-$\mathbf{Mn(CO)_3(PPh_3)_2(CHOH)^+(}$*p*$\mathbf{\text{-}CH_3C_6H_4SO_3)^-}$ (1a).** To a slurry of *p*-toluenesulfonic acid hydrate (0.045 g, 0.24 mmol) in 6 mL of CH_2Cl_2 at room temperature was added *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$[6] (0.10 g, 0.14 mmol) in six additions over the course of 3 min. The reaction was complete after 10 min, and the mixture was filtered through a glass pad into 75 mL of hexane at room temperature. The mixture was allowed to stand for 5 min; the yellow precipitated product was collected by filtration and dried in vacuo for 2 h. The yield was 0.12 g (94%). IR (CH_2Cl_2): ν_{CO} 2045 (w), 1960 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2, 38 °C): δ 13.09 (s), 12.35 (s, br), 7.55 (m), 2.32 (s). ^1H NMR (CD_2Cl_2, 17 °C); δ 12.86 (s), 12.70 (s, br), 7.39 (m), 2.38 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 335.32 (s), 219.64 (t, J_{PC} = 17.5 Hz), 216.75 (t, J_{PC} = 17.8 Hz), 141.96 (s), 137.75 (s), 132.75 (d, J_{PC} = 46.4 Hz), 132.27 (t, J_{PC} = 5.1 Hz), 132.15 (d, J_{PC} = 44.2 Hz), 130.73 (s), 128.85 (s), 128.77 (t, J_{PC} = 4.9 Hz), 126.17 (s), 65.80 (s).

***mer,trans*-$\mathbf{Mn(CO)_3(PPh_3)_2(CHOH)^+BF_4^-}$ (1b).** To 20 mL of CH_2Cl_2 containing $HBF_4{\cdot}(CH_3)_2O$ (0.28 g, 2.10 mmol) at −78 °C was added *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$[6] (1.00 g, 1.44 mmol) with stirring. After 10 min, 20 mL of hexane was added. The mixture was filtered through a low-temperature crystallizer[19] maintained at −78 °C; the yellow product was washed with 2 × 20 mL of hexane and then dried for 2 h before being stored in a Schlenk tube. The yield was 1.04 g (93%). IR (CH_2Cl_2): ν_{CO} 2045 (w), 1950 (s, br) cm^{-1}. IR (Nujol): ν_{CH} 2747 (w–m) cm^{-1}. ^1H NMR (CD_2Cl_2, −25 °C): δ 12.62 (s, br), 7.45 (m). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −25 °C): δ 330.94 (s), 220.30 (t, J_{PC} = 15.9 Hz), 217.62 (t, J_{PC} = 19.2 Hz), 133.77 (d, J_{PC} = 45.8 Hz), 132.75 (t, J_{PC} = 5.7 Hz), 130.70 (s), 128.93 (t, J_{PC} = 4.7 Hz).

***mer,trans*-$\mathbf{Re(CO)_3(PPh_3)_2(CHOH)^+(}$*p*$\mathbf{\text{-}CH_3C_6H_4SO_3)^-}$ (1c).** To 8 mL of a 3:1 mixture of CH_2Cl_2/ether containing *p*-toluenesulfonic acid hydrate (0.058 g, 0.30 mmol) at room temperature was slowly added *mer,trans*-$Re(CO)_3(PPh_3)_2CHO$[6] (0.25 g, 0.30 mmol) in small portions. Each portion was allowed to dissolve before the next addition was made. After the final addition, the solution was stirred for 5 min and then chilled to 0 °C. Pentane (40 mL) was then added a few milliliters at a time with stirring to precipitate the white product, which was collected by filtration; the yield was 0.29 g (96%). The compound does not have a sharp melting point; it begins to discolor at 155 °C and melts completely by 208 °C. Anal. Calcd for $C_{47}H_{39}O_7P_2ReS$: C, 56.68; H, 3.95. Found: C, 56.11; H, 3.90. IR (CH_2Cl_2): ν_{CO} 2055 (w), 1960 (s, br) cm^{-1}. No evidence for ν_{CH} or ν_{OH} was seen in the DRIFTS spectrum or in a very concentrated Fluorolube mull. ^1H NMR (CD_2Cl_2, 16 °C): δ 13.60 (s), 7.40 (m), 2.37 (s). ^1H NMR (CD_2Cl_2, 38 °C): δ 13.82 (s), 13.19 (br, s), 7.35 (m), 2.32 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 16 °C): δ 298.86 (br, s), 195.86 (t, J_{PC} = 8.7 Hz), 192.69 (t, J_{PC} = 8.2 Hz), 142.23 (s), 140.51 (s), 134.03 (t, J_{PC} = 25.3 Hz), 133.11 (t, J_{PC} = 5.8 Hz), 131.17 (s), 129.11 (t, J_{PC} = 5.0 Hz), 128.90 (s), 126.20 (s), 21.36 (s).

***mer,trans*-$\mathbf{Mn(CO)_3(PPh_3)_2(CHOCH_3)^+SO_3CF_3^-{\cdot}0.2CH_2Cl_2}$ (2a).** To 20 mL of CH_2Cl_2 containing $CH_3SO_3CF_3$ (0.12 g, 0.70 mmol) was slowly added *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$[6] (0.50 g, 0.70 mmol) with stirring. The reaction was complete in 5 min, and the solvent was evaporated, leaving a yellow residue. The residue was dissolved in CH_2Cl_2/hexane (4:1) and the solution cooled to −5 °C. Yellow crystals formed, which were collected, washed with 2 × 5 mL of hexane, and dried, in vacuo, to afford 0.60 g (98%) of the product, mp 127–129 °C. Anal. Calcd for $C_{42.2}H_{34.4}O_7F_3P_2SMnCl_{0.4}$: C, 58.02; H, 3.97. Found: C, 58.02; H, 3.93. IR (CH_2Cl_2): ν_{CO} 2050 (w), 1965 (s) cm^{-1}. IR (Nujol): ν_{CH} 2717 cm^{-1}. ^1H NMR ($CDCl_3$): δ 12.67 (s, br), 7.70 (m), 3.80 (s) (the proton resonance for the CH_2Cl_2 molecule appeared at 5.30). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 338.64 (s), 219.94 (t, J_{PC} = 17.7 Hz), 216.63 (t, J_{PC} = 17.9 Hz), 133.31 (d, J_{PC} = 45.9 Hz), 132.76 (t, J_{PC} = 4.9 Hz), 131.52 (s), 129.58 (t, J_{PC} = 4.9 Hz), 77.25 (s), CF_3SO_3 not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 60.88 (s).

***mer,trans*-$\mathbf{Mn(CO)_3(PPh_3)_2(CHOCH_3)^+BF_4^-}$ (2b).** To 20 mL of CH_2Cl_2 containing $(CH_3)_3O^+BF_4^-$ (0.21 g, 1.40 mmol) was slowly added *mer,trans*-$Mn(CO)_3(PPh_3)_2CHO$[6] (1.00 g, 1.44 mmol) with stirring. The reaction was complete after 45 min, and solvent was then evaporated, leaving a yellow residue. The residue was redissolved in CH_2Cl_2/hexane (4:1) and the solution chilled to −20 °C. The resulting yellow crystals were collected, washed with 2 × 5 mL of hexane, and then dried, in vacuo, to afford 1.10 g (89% yield) of the product, mp 215–218 °C. IR (CH_2Cl_2): ν_{CO} 2059 (w), 1965 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 12.60 (s, br), 7.65 (m), 3.62 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 60.73 (s).

***mer,trans*-$\mathbf{Re(CO)_3(PPh_3)_2(CHOCH_3)^+SO_3CF_3^-}$ (2c).** To 8 mL of CH_2Cl_2 containing $CH_3SO_3CF_3$ (0.045 g, 0.27 mmol) and maintained at 0 °C was slowly added *mer,trans*-$Re(CO)_3(PPh_3)_2CHO$[6] (0.22 g, 0.27 mmol) with stirring. The reaction was complete after 2 min, 30 mL of pentane was added, and the solution was chilled to −20 °C for several hours. Pale yellow crystals were collected by filtration, washed with 5 mL of pentane, and dried, in vacuo, to give 0.26 g (96%) of product, mp 157 °C dec. Anal. Calcd for $C_{42}H_{34}F_3O_7P_2ReS$: C, 51.06; H, 3.47. Found: C, 50.91; H, 3.22. IR (CH_2Cl_2): ν_{CO} 2070 (vw), 2000 (sh), 1968 (s) cm^{-1}. IR (neat, DRIFTS): ν_{CH} 2672 (vw) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 12.42 (s), 7.48 (m), 3.55 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 303.97 (s, br), 195.04 (t, J_{PC} = 9.0 Hz), 191.16 (t, J_{PC} = 7.9 Hz), 133.75 (t, J_{PC} = 25.9 Hz), 132.93 (t, J_{PC} = 5.8 Hz), 131.68 (s), 129.55 (t, J_{PC} = 5.2 Hz), 77.21 (s), $CF_3SO_3^-$ not observed.

***mer,trans*-$\mathbf{Mn(CO)_3(PPh_3)_2(CHNHCH_2Ph)^+CF_3SO_3^-}$ (3a).** To 20 mL of CH_2Cl_2 containing **2a** (0.10 g, 0.17 mmol) and maintained at −78 °C was added, dropwise, a solution of benzylamine (13 μL, 0.17 mmol) in 2 mL of CH_2Cl_2 while stirring was maintained. The reaction was complete after 5 min, and the mixture was warmed to room temperature. The solution was concentrated to 10 mL, pentane (15 mL) was added, and the

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solution was chilled to −20 °C overnight. The pale yellow product was collected, washed with 5 mL of pentane, and then dried, in vacuo, to afford 0.09 g (80% yield) of product, mp 138–140 °C dec. Anal. Calcd for $C_{48}H_{39}F_3MnNO_6P_2S$: C, 61.87; H, 4.22; N, 1.50. Found: C, 61.69; H, 4.14; N, 1.54. IR (CH_2Cl_2): ν_{CO} 2040 (w), 1955 (s), 1940 (sh, s) cm^{-1}. IR (neat, DRIFTS): ν_{NH} 3244 (m) cm^{-1}; ν_{CH} 2677 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 10.26 (d, J_{HH} = 21.4 Hz), 9.98 (d, br, J_{HH} = 21.4 Hz), 7.00 (m), 3.88 (s). When the ^1H NMR spectrum was recorded in CD_3CN containing a drop of D_2O, the lower field doublet collapsed to a singlet and the other low-field doublet disappeared. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 255.33 (t, J_{PC} = 17.2 Hz), 220.27 (t, J_{PC} = 15.4 Hz), 217.69 (t, J_{PC} = 18.2 Hz), 133.70 (d, J_{PC} = 42.7 Hz), 133.10 (s), 133.03 (s), 132.96 (s), 132.79 (s), 131.11 (s), 129.46 (t, J_{PC} = 5.6 Hz), 129.33 (t, J_{PC} = 5.6 Hz), 128.89 (s), 62.75 (s).

***mer,trans*-Mn(CO)$_3$(PPh$_3$)$_2$(CHNHCH$_2$Ph)$^+$BF$_4^-$ (3b).** To 25 mL of CH_2Cl_2 containing **2b** (0.50 g, 0.63 mmol) and maintained at −78 °C was added benzylamine (69 μL, 0.63 mmol) with stirring. The reaction was complete after 2 min, and the mixture was warmed to room temperature. Solvent was evaporated, leaving a pale yellow residue. The residue was dissolved in CH_2Cl_2/hexane (1:1) and the solution chilled to −5 °C to effect crystallization. The white product was collected, washed with 5 mL of ethanol followed by 5 mL of hexane, and then dried, in vacuo; 0.47 g (86% yield) of product was obtained, mp 194–196 °C. Anal. Calcd for $C_{47}H_{39}NO_3P_2BF_4Mn$: C, 64.92; H, 4.52, N, 1.61. Found: C, 64.61; H, 4.50; N, 1.60. IR (CH_2Cl_2): ν_{CO} 2040 (w), 1952 (s), 1940 (s, sh), cm^{-1}. IR (Nujol): ν_{NH} 3290 (w–m) cm^{-1}; ν_{CH} 2720 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 10.60 (d, J_{HH} = 21.2 Hz), 9.29 (d, br, J_{HH} = 21.2 Hz), 7.6 (m), 4.01 (d, J_{HH} = 2.3 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 256.26 (t, J_{PC} = 16.3 Hz), 220.23 (t, J_{PC} = 16.5 Hz), 217.71 (t, J_{PC} = 19.1 Hz), 133.97 (s), 133.61 (d, J_{PC} = 44.0 Hz), 133.01 (t, J_{PC} = 5.3 Hz) 131.15 (s), 129.53 (s), 129.41 (s), 129.35 (t, J_{PC} = 4.8 Hz), 128.80 (s), 63.38 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.73 (s).

***mer,trans*-Re(CO)$_3$(PPh$_3$)$_2$(CHNHCH$_2$Ph)$^+$CF$_3$SO$_3^-$·CH$_2$Cl$_2$ (3c).** To 10 mL of CH_2Cl_2 containing **2c** (0.22 g, 0.22 mmol) and maintained at 0 °C was added benzylamine (24 μL, 0.22 mmol) with stirring. The reaction was complete within 2 min. The solution was warmed to room temperature, pentane (20 mL) was added, and the solution was chilled at −20 °C overnight. The white crystals that formed were collected, washed with 5 mL of pentane, and dried, in vacuo, to give 0.23 g (92% yield) of product, mp 199–200 °C dec, which crystallized as the methylene chloride solvate. Anal. Calcd for $C_{49}H_{41}Cl_2F_3NO_6P_2ReS$: C, 51.27; H, 3.60; N, 1.22. Found: C, 51.34; H, 3.52; N, 1.17. IR (CH_2Cl_2): ν_{CO} 2060 (vw), 1960 (s), 1940 (sh) cm^{-1}. IR (neat, DRIFTS): ν_{NH} 3249 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 10.50 (d, br, J_{HH} = 20.9 Hz), 10.10 (d, J_{HH} = 20.9 Hz), 7.01 (m), 3.84 (s). When the ^1H NMR spectrum was recorded in CD_3CN, the two low-field doublets changed places, with the resonance assigned to the methine proton occurring at lower field. When a drop of D_2O was added to the NMR sample, the lower field doublet collapsed to a singlet and the other low-field doublet disappeared. The proton resonance for the CH_2Cl_2 solvent molecule appeared at 5.43 ppm in CD_3CN. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 227.68 (t, J_{PC} = 9.1 Hz), 194.72 (t, J_{PC} = 7.0 Hz), 191.34 (t, J_{PC} = 8.3 Hz), 133.86 (t, J_{PC} = 24.8 Hz), 133.10 (t, J_{PC} = 5.6 Hz), 132.83 (s), 131.14 (s), 129.71 (s), 129.27 (t, J_{PC} = 4.9 Hz), 128.77 (s), 61.81 (s).

***mer,trans*-Mn(CO)$_3$(PPh$_3$)$_2$CHNCH$_2$Ph (4a).** To 50 mL of 4:1 CH_2Cl_2/ethanol containing **3b** (0.50 g, 0.60 mmol) was added 10 mL of water containing 0.12 g (5.70 mmol) of NaOH. The mixture was stirred for 2 h and then concentrated on a rotary evaporator; pale yellow crystals formed, which were collected and washed with 2 × 10 mL of ethanol. The crystals were redissolved in 1:1 CH_2Cl_2/ethanol, and the solution was chilled to −5 °C. Off-white crystals formed, which were collected, washed with 2 × 10 mL of ethanol, and then dried, in vacuo, to yield 0.43 g (96%) of the product, mp 130–131 °C. Anal. Calcd for $C_{47}H_{38}NO_3P_2Mn$: C, 72.22; H, 4.90; N, 1.79. Found: C, 72.25; H, 4.72; N, 1.63. IR (CH_2Cl_2): ν_{CO} 2020 (w), 1926 (s), 1890 (m) cm^{-1}; IR (CH_2Cl_2): ν_{CN} 1535 (m) cm^{-1}. IR (neat, DRIFTS): ν_{CH} 2712 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.34 (s, br), 7.22 (m), 3.63 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 30 °C): δ 221.92 (s, br), 221.57 (s, br), 211.35 (s, br), 141.85 (s), 136.22 (d, J_{PC} = 39.0 Hz), 133.77 (t, J_{PC} = 4.8 Hz), 129.76 (s), 128.59 (s), 128.32 (t, J_{PC} = 4.5 Hz), 128.02 (s), 125.82 (s), 74.46 (s). In deuteriobenzene, several of these resonances appear differently: δ 223.08 (t, J_{PC} = 17.2 Hz), 222.08 (t, J_{PC} = 19.6 Hz), 211.48 (t, J_{PC} = 22.2 Hz), 136.58 (d of d, J_{PC} = 43.2, 4.0 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 71.56 (s).

***mer,trans*-Re(CO)$_3$(PPh$_3$)$_2$CHNCH$_2$Ph (4b).** To 10 mL of a 4:1 mixture of CH_2Cl_2/ethanol containing **3c** (0.20 g, 0.18 mmol) was added with stirring 2 mL of water containing 0.04 g (1.00 mmol) of NaOH. After 2 h, the mixture was extracted with 2 × 15 mL of water and the organic layer was separated and dried over $MgSO_4$. After filtration through Celite, the volume of solvent was reduced to 6 mL, pentane (15 mL) was added, and the solution was chilled to −20 °C overnight to effect crystallization. White crystals of the product were collected and dried, in vacuo: yield 0.16 g, 93%; mp 148–149 °C. Anal. Calcd for $C_{47}H_{38}NO_3P_2Re$: C, 61.83; H, 4.20; N, 1.53. Found: C, 61.96; H, 4.30; N, 1.44. IR (CH_2Cl_2): ν_{CO} 2040 (vw), 1935 (s), 1898 (m) cm^{-1}. IR (CH_2Cl_2): ν_{CN} 1545 (vw) cm^{-1}. IR (neat, DRIFTS): ν_{CH} 2706 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 9.78 (s), 7.16 (m), 3.68 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 199.02 (t, J_{PC} = 11.0 Hz), 197.09 (t, J_{PC} = 6.2 Hz), 195.68 (t, J_{PC} = 9.1 Hz), 141.66 (s), 135.82 (t, J_{PC} = 24.7 Hz), 133.81 (t, J_{PC} = 5.5 Hz), 130.09 (s), 128.38 (t, J_{PC} = 4.8 Hz), 128.21 (s), 128.04 (s), 125.85 (s), 76.85 (s).

X-ray Crystal Structure of 2a. A suitable single crystal of **2a** was grown by layering a CH_2Cl_2 solution of the compound with hexane. Data were collected on an Enraf-Nonius CAD4 diffractometer as outlined in Table II. Of 7866 unique reflections, 5129 had $I > 3\sigma(I)$ and were used in the final cycles of refinement. The manganese position was obtained from a three-dimensional Patterson map. Several cycles of least-squares refinement and difference Fourier synthesis yielded the positions of the remaining non-hydrogen atoms. The hydrogen atoms were included in calculated positions with thermal parameters set to 1.2 times the temperature factors of the carbons to which they are bonded; hydrogen parameters were not refined. The triflate anion and the CH_2Cl_2 solvate were found to be disordered. The triflate was modeled as two groups of half-occupancy overlapping and sharing the C, S, two F, and two O atoms (with large thermal parameters). CH_2Cl_2 showed random rotational disorder and was modeled with a single C atom having occupancy 0.8 and seven Cl atoms having occupancies ranging from 0.1 to 0.4. All non-hydrogen atoms were refined with anisotropic thermal parameters except the atoms of the disordered solvate, which were refined isotropically. The model converged except for some movement of the disordered atoms with final agreement factors of R = 0.068 and R_w = 0.059 for 442 variables.

X-ray Crystal Structure of 3a. A suitable single crystal of **3a** was grown from a CH_2Cl_2/hexane solution of the compound. Of 9027 unique reflections, 5523 had $I > 3\sigma(I)$ and were used in the final cycles of refinement. The manganese position was obtained with use of Patterson techniques, and the remaining non-hydrogen atoms were located with use of a series of least-squares cycles and difference Fourier maps. Hydrogen atoms were included in calculated positions with thermal parameters set to 1.2 times the temperature factors of the carbon atoms to which they are bonded; hydrogen parameters were not refined. The CH_2Cl_2 solvate was found to be severely disordered over two sites; each site was modeled with overlapping "CCl_2" fragments of varying occupancies. All non-hydrogen atoms were refined with anisotropic thermal parameters, with the exceptions of some atoms of disordered groups. The final agreement factors were R = 0.061 and R_w = 0.062 for 596 variables.

Acknowledgment. Support of this work by the National Science Foundation (Grant RII-8610671) and the Commonwealth of Kentucky (EPSCoR Program) is gratefully acknowledged. Partial support of this work by the Department of Energy, Division of Chemical Sciences (Office of Basic Energy Sciences), is also gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, and all bond distances and bond angles in **2a** and **3a** (19 pages); tables of structure factor amplitudes (52 pages). Ordering information is given on any current masthead page.