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New Forms of Coordinated Carbon: Wirelike Cumulenic C_3 and C_5 sp Carbon Chains that Span Two Different Transition Metals and Mediate Charge Transfer

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Abstract: Reactions of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3)(\text{C}\equiv\text{CLi})$ with W(CO)_6, Fe(CO)_5, or $\text{Mn(CO)}_3(\eta^5\text{-C}_5\text{H}_n\text{Cl}_{5-n})$, followed by $\text{Me}_3\text{O}^+\ \text{BF}_4^-$, give the heterobimetallic C_3OMe complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3)$-$(\text{C}\equiv\text{CC(OMe)}{=})\text{M(CO)}_x(\eta^5\text{-C}_5\text{H}_n\text{Cl}_{5-n})_y$ ($M/x/y/n$ = **3**, W/5/0/−; **4**, Fe/4/0/−; **5**, Mn/2/1/5; **6**, Mn/2/1/4; **7**, Mn/2/1/0). Spectroscopic and crystallographic (**3**) data indicate contributions by $^+\text{Re}{=}\text{C}{=}\text{C}{=}\text{C(OMe)}{-}\text{M}^-$ resonance forms. Reactions of **4**−**7** and BF_3 gas give the title compounds $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)}$-$\text{(PPh}_3)\text{(CCC)M(CO)}_x(\eta^5\text{-C}_5\text{H}_n\text{Cl}_{5-n})_y$ ($M/x/y/n$ = **9**, Mn/2/1/5; **10**, Mn/2/1/4; **11**, Mn/2/1/0; **12**, Fe/4/0/−). Spectroscopic and crystallographic (**9**) data indicate dominant contributions by fully cumulated $^+\text{Re}{=}\text{C}{=}\text{C}{=}\text{C}{=}\text{Mn}$ resonance forms. Reactions of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3)(\text{C}\equiv\text{CC}\equiv\text{CLi})$ with $\text{Mn(CO)}_3(\eta^5\text{-C}_5\text{Cl}_5)$, $\text{Mn(CO)}_3(\eta^5\text{-C}_5\text{Br}_5)$, or Fe(CO)_5, followed by $\text{Me}_3\text{O}^+\ \text{BF}_4^-$, give the C_5OMe complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3)$-$(\text{C}\equiv\text{CC}\equiv\text{CC(OMe)}{=})\text{M(CO)}_x(\eta^5\text{-C}_5\text{X}_5)_y$ ($M/x/y/X$ = **16**, Mn/2/1/Cl; **19**, Mn/2/1/Br; **20**, Fe/4/0/−). However, $\text{Mn(CO)}_3(\eta^5\text{-C}_5\text{H}_5)$ does not react. Reaction of **16** and BF_3 gives the C_5 complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re(NO)(PPh}_3)\text{(CCCCC)Mn(CO)}_2(\eta^5\text{-C}_5\text{Cl}_5)]^+\ \text{BF}_4^-$ (**21**) as a light-sensitive deep brown powder of >94% purity. IR and NMR data show a dominant $^+\text{Re}{=}\text{C}{=}\text{C}{=}\text{C}{=}\text{C}{=}\text{C}{=}\text{Mn}$ resonance form. UV−visible spectra of **9**−**11** and **21** show intense absorptions at 392, 396, 414, and 480 nm (ϵ 55 800, 50 900, 49 100, 60 500 $M^{-1}\ cm^{-1}$), respectively, and weaker longer wavelength bands. These are believed to have appreciable rhenium-to-manganese charge-transfer character.

Transition metals and elemental carbon fragments (C_x) can combine in a variety of fascinating motifs.[1] Of these, complexes in which sp carbon chains span two metals, $[\text{L}_n\text{MC}_x\text{M}'\text{L}'_{n'}]^{z+}$ (**I**), are attracting particular attention.[1−8] The unsaturated bridges can potentially mediate numerous types of charge-transfer processes involving the metal termini.[9] Closely related assemblies are actively being investigated for applications in nonlinear optics[10] and as molecular devices such as wires, switches, and digital circuits.[11] Furthermore, the classical sp^3 and sp^2 polymeric carbon allotropes, diamond and graphite, require capping endgroups that differ from their repeat units. Thus, complexes of the type **I** can, at very high values of x, analogously be viewed as sp polymeric carbon allotropes. In work to date, adducts with chains as long as 20 carbons have been isolated.[7c]

There is now an extensive literature for complexes **I** that contain even-carbon chains. Compounds with two carbon chains are very common,[3] and there are increasing numbers of examples with four carbon chains.[6] Species with longer even-carbon chains have been prepared by ourselves, Lapinte, Bruce, and Akita.[7] This series of compounds is limited to the symmetrical valence structures $\text{M}{-}(\text{C}\equiv\text{C})_y{-}\text{M}'$, $\text{M}{=}(\text{C}{=}\text{C})_y{=}\text{M}'$, and $\text{M}\equiv(\text{C}{-}\text{C})_y\equiv\text{M}'$ and variants associated with intermediate

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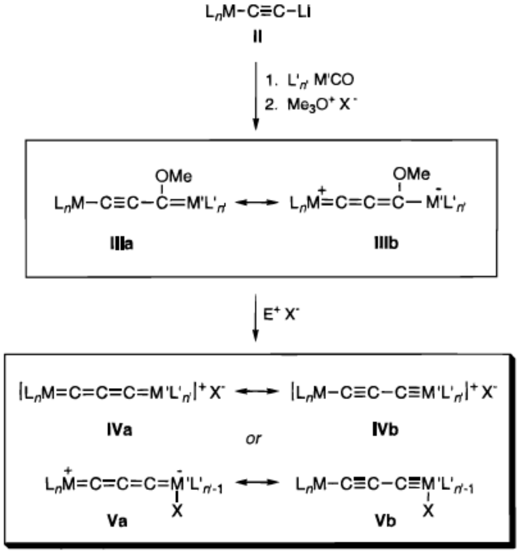
10.1021/ja981927q CCC: \$15.00

Scheme 1. Bimetallic C_3 Complexes: Synthetic Strategy



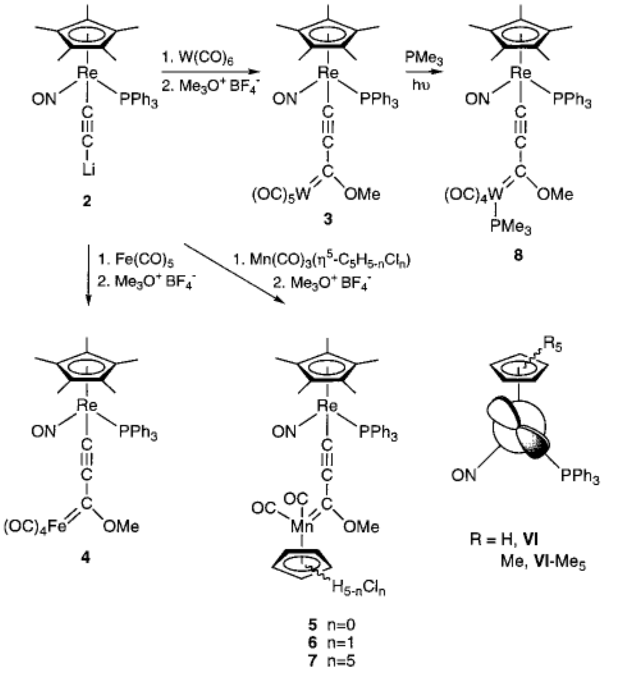
redox states. The first and third structures feature polyalkynyl chains, whereas the second features a cumulenic chain.

In contrast, there are far fewer complexes **I** that contain odd-carbon chains.[2,4,5,8] In fact, prior to the efforts described herein, none were known with a length greater than one.[2] One contributing factor is that chains assembled solely from $(C{\equiv}C)_y$ building blocks are restricted to even numbers of carbons. Thus, more sophisticated synthetic strategies are required. Such complexes can have two valence structures: (1) a symmetrical cumulenic form, $M{=}C{=}(C{=}C)_y{=}M'$, or (2) an unsymmetrical polyalkynyl form $M{\equiv}C{-}(C{\equiv}C)_y{-}M'$. The latter is distinguished by a metal−carbon single bond on one end and a triple bond or carbyne linkage on the other.

We sought to access such species by the initial deprotonation of transition metal ethynyl complexes, $L_nMC{\equiv}CH$, or higher homologues, to lithiated conjugate bases $L_nMC{\equiv}CLi$ (**II**). Previously, a variety of organic lithium acetylides, $RC{\equiv}CLi$, had been shown to attack carbon monoxide ligands in metal carbonyl complexes, $L'_{n'}M'CO$.[12] This constitutes a one-carbon homologation. The anionic adducts can then be methylated to give Fischer alkynyl carbene complexes $RC{\equiv}CC(OMe){=}M'L'_{n'}$.[12] Importantly, alkoxy groups can be abstracted from carbene complexes with electrophilic agents. This gives, depending upon the metal fragment and recipe, either cationic or neutral carbyne complexes.[13]

As shown in Scheme 1, a similar sequence with **II** would give bimetallic bridging C_3OMe complexes $L_nMC{\equiv}CC(OMe){=}M'L'_{n'}$ (**IIIa**). Carbene complexes can exhibit a variety of resonance forms, and one other possibility, zwitterion **IIIb**, is also depicted in Scheme 1. Reactions of **III** and suitable electrophiles (E^+X^-) would then give either the cationic C_3 complexes **IV** or the neutral counterparts **V**.[14] These differ in the disposition of X^-. The resonance forms **IVb** and **Vb** have carbyne linkages, whereas **IVa** and **Va** have cumulated chains. The dominant form will be a function of the relative π donor strengths of the L_nM- and $=M'L'_{n'}$ termini.

Scheme 2. Syntheses of C_3OMe Complexes



We recently reported the generation of ReC_2Li and ReC_4Li species with the chiral rhenium endgroup $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$ (**VI**-Me_5).[6b,15] This strongly π-donating fragment has (as a 16-valence-electron cation) the d orbital HOMO shown in Scheme 2. The ReC_xLi species are readily derivatized by a variety of electrophiles and have been elaborated to a number of complexes **I** with even-carbon chains.[6b,7c] In this paper, we describe the successful implementation of the methodology in Scheme 1 with these compounds, and the isolation and remarkable properties of heretofore unprecedented complexes with C_3 and C_5 chains.[4]

Results

1. C_3OMe Complexes. The ethynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CH)$ (**1**) and *n*-BuLi were combined in THF at −80 °C to generate the ReC_2Li species $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CLi)$ (**2**).[15] As shown in Scheme 2, the carbonyl complexes $W(CO)_6$, $Fe(CO)_5$, $Mn(CO)_3(\eta^5\text{-}C_5H_5)$, $Mn(CO)_3(\eta^5\text{-}C_5H_4Cl)$,[16] and $Mn(CO)_3(\eta^5\text{-}C_5Cl_5)$[17] were added. The solutions were warmed and then added to solid $Me_3O^+BF_4^-$ at −80 °C. Workups gave the heterobimetallic alkynyl carbene complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})ML_n$ (**3**−**7**) as orange-red or red powders in 73−41% yields. These were stable for weeks in air as solids and were characterized by IR, NMR (^1H, ^{13}C, ^{31}P), and mass spectroscopy as summarized in the

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(11) Ward, M. D. *Chem. Ind.* **1997**, 640 and refs 1 and 2 therein. (b) Harriman, A.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1707. (c) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690. (d) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383.

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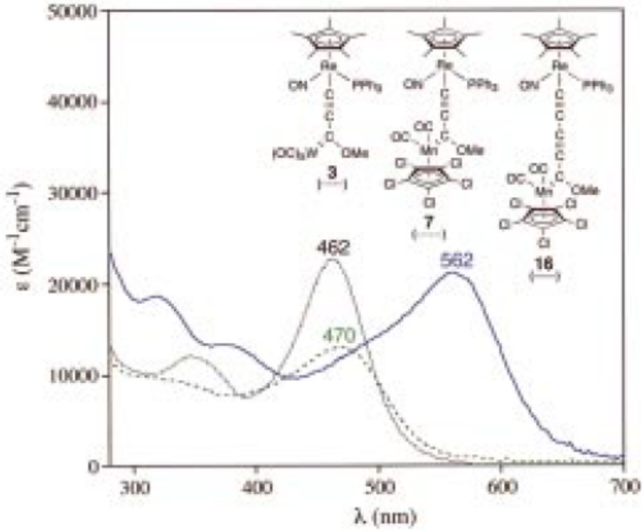

Figure 1. Representative UV−visible spectra of C_3OMe and C_5OMe complexes (CH_2Cl_2, ambient temperature).

Experimental Section. Complexes **3**−**5** also gave correct microanalyses. Some purifications were complicated by high product solubilities (**6**, **7**) and a THF polymer byproduct.

The structures of **3**−**7** were supported by numerous spectroscopic features. For example, mass spectra exhibited molecular ions. The IR spectra showed ν_{CO} absorptions similar to those of analogous Fischer carbene complexes.[12,18] By careful comparisons, $\nu_{C\equiv C}$ bands could be assigned (cm^{-1}, s−m: **3**, 1913; **4**, 1920; **5**, 1862; **6**, 1871; **7**, 1904). As expected, ^{13}C NMR spectra showed downfield ***C***═M signals (253.2, 256.6, 283.9, 282.1, 273.5 ppm). However, the Re***C*** signals (204.9, 204.0, 166.8, 171.3, 186.8; d) were intermediate between those of the neutral alkynyl complexes (η^5-C_5Me_5)Re(NO)(PPh_3)-(C≡CR) (98−86 ppm)[15] and cationic vinylidene complexes [(η^5-C_5Me_5)Re(NO)(PPh_3)(═C═CHR)]$^+X^-$ (330−329 ppm).[15,19] The $^2J_{CP}$ values showed a similar trend (12.3, 13.3, 13.8, 13.5, 11.6 vs 16−18 or 10−11 Hz), as did the IR ν_{NO} values (1674−1648 vs 1637−1629 or 1728−1681 cm^{-1}). These and other data (below) indicate significant contributions by both the neutral and zwitterionic resonance forms **IIIa**,**b** in Scheme 1.

The UV−visible spectra of **3**−**7** showed intense bands at 240−232 nm and accompanying shoulders, characteristic of all adducts of the rhenium fragment (η^5-C_5Me_5)Re(NO)(PPh_3) (**VI**-Me_5). New bands occurred at 306−382 and 446−470 nm (ϵ 9500−12 100 and 7400−22 800 M^{-1} cm^{-1}), and representative traces are given in Figure 1. Alkylidene and vinylidene complexes of **VI**-Me_x do not exhibit analogous absorptions, although aryl-substituted termini (i.e., ═CHAr) give rise to a single band (360−400 nm, ϵ 7600−13 000 M^{-1} cm^{-1}).[6a,19,20] Solvent effects were probed with representative complexes (hexane/CH_2Cl_2/acetonitrile: **3**, 350/346/348 and 464/464/464; **7**, 332/336/332 and 464/468/468). The positions of the maxima varied only slightly with polarity.

Table 1. Summary of Crystallographic Data for (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC(OMe)═)W(CO)$_5$ (**3**) and [(η^5-C_5Me_5)Re(NO)(PPh_3)(CCC)Mn(CO)$_2$(η^5-C_5H_5)]$^+$ BF_4^-·(CH_2Cl_2)$_{0.5}$ (**9**·(CH_2Cl_2)$_{0.5}$)

	3	**9**·(CH_2Cl_2)$_{0.5}$
formula	$C_{37}H_{33}NO_7PReW$	$C_{77}H_{72}B_2Cl_2F_8N_2Mn_2O_6P_2Re_2$[a]
formula weight	1004.702	1910.18
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
cell dimensions		
a, Å	13.125(2)	8.732(1)
b, Å	13.837(3)	15.248(4)
c, Å	10.880(2)	28.850(5)
α, deg	109.16(2)	84.68(2)
β, deg	92.48(2)	97.01(1)
γ, deg	77.80(2)	102.40(2)
V, Å^3	1823.55	3714.80
Z	2	2
temp of collection (°C)	16	−125
d_{calc}, g/cm^3	1.830	1.71
d_{found}, g/cm^3 (22 °C)	1.805	1.701
reflections measured	6765	12 998
total unique data	6394	12 051
observed data, $I > 3\sigma(I)$	5207	8935
no. of variables	433	928
goodness of fit	0.90	2.04
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.029	0.054
$R_w = \Sigma\|\|F_o\| - \|F_c\|\|w^{1/2}/\Sigma\|F_o\|w^{1/2}$	0.033	0.072

[a] For two independent molecules in the unit cell.

In view of the many syntheses of tungsten carbyne complexes from Fischer carbene complexes,[13] reactions of **3** were investigated first. However, repeated attempts to abstract the methoxy group from **3** were unsuccessful. For example, the traditional reagent BBr_3 (1 equiv) gave no reaction in CH_2Cl_2 at low temperature. Excess BBr_3, or Me_3SiI/THF, gave several species at room temperature. When **3** and BCl_3 were combined in CD_2Cl_2 at −80 °C, ^1H and ^{31}P NMR spectra showed at least four products. When the sample was warmed to room temperature, only one new compound, and unreacted **3**, remained. Attempts to isolate the new species failed.

Tungsten carbyne complexes have also been prepared by reactions of the anionic intermediates in syntheses of Fischer carbene complexes (RC(O^-)═M′L′$_{n'}$) with appropriate electrophiles.[21] Also, nitrogen donor ligands such as TMEDA appear to stabilize some species. Following literature precedent,[21] the ReC_2Li complex **2** was treated with W(CO)$_6$ and then (a) (ClCO)$_2$, (b) (ClCO)$_2$/TMEDA, and (c) (CF_3CO)$_2$O/TMEDA. However, numerous products were obtained. We speculated that a phosphine ligand might be beneficial. Accordingly, the photolysis of **3** and PMe_3 in THF (Scheme 2) gave the substitution product *cis*-(η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC-(OMe)═)W(PMe_3)(CO)$_4$ (**8**, 65%). The stereochemistry followed from the IR and ^{13}C NMR absorption patterns of the CO ligands. However, reactions of **8** and BBr_3 also gave a multitude of products.

These unsuccessful efforts prompted us to check for underlying structural problems. Thus, the crystal structure of **3** was determined as outlined in Table 1 and the Experimental Section. Selected bond lengths and angles are given in Table 2, and the molecular structure is shown in Figure 2. The rhenium−carbon bond length (1.973(7) Å) is between those in two redox-related complexes derived from **VI**-Me_5 with ReC≡CC≡CRe and

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[18] (a) For alkynyl carbene complexes of Fe(CO)$_4$, see: Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10*, 3413; *J. Korean Chem. Soc.* **1992**, *36*, 770. (b) For carbene complexes of (η^5-C_5H_5)Mn(CO)$_2$, see: Fischer, E. O.; Chen, J.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231 and references therein.

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Table 2. Key Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **3** and **9**·$(CH_2Cl_2)_{0.5}$

	3		
Re−P	2.398(2)	C42−W	2.200(8)
Re−N	1.763(6)	C42−O2	1.353(9)
N−O	1.178(8)	O2−C43	1.44(1)
Re−C1	2.334(8)	W−C50	2.02(1)
Re−C2	2.269(8)	W−C51	2.05(1)
Re−C3	2.251(8)	W−C52	2.05(1)
Re−C4	2.307(7)	W−C53	2.04(1)
Re−C5	2.370(7)	W−C54	2.01(1)
P−C11	1.825(7)	C50−O3	1.15(1)
P−C21	1.825(7)	C51−O4	1.12(1)
P−C31	1.841(7)	C52−O5	1.12(1)
Re−C40	1.973(7)	C53−O6	1.12(1)
C40−C41	1.23(1)	C54−O7	1.14(1)
C41−C42	1.38(1)		
C40−Re−P	94.4(2)		
C40−Re−N	98.5(3)	C42−W−C51	88.9(3)
P−Re−N	90.8(2)	C42−W−C52	87.9(4)
Re−N−O1	173.7(6)	C42−W−C53	87.1(4)
Re−C40−C41	172.3(7)	C42−W−C54	176.4(4)
C40−C41−C42	174.5(8)	W−C50−O3	177(1)
C41−C42−O2	116.5(7)	W−C51−O4	178(1)
C42−O2−C43	119.7(6)	W−C52−O5	177(1)
W−C42−C41	128.1(6)	W−C53−O6	179(1)
C42−W−C50	93.6(3)	W−C54−O7	178(1)
C41−C42−O2−C43	1.7(0.9)	W−C42−O2−C43	−178.3(0.5)
	9·$(CH_2Cl_2)_{0.5}$		
Re−P	2.410(3)	Re′−P′	2.402(3)
Re−N	1.763(9)	Re′−N′	1.750(9)
N−O1	1.18(1)	N′−O1′	1.21(1)
Re−C40	1.91(1)[b]	Re′−C40′	1.93(1)[b]
C40−C41	1.28(2)[c]	C40′−C41′	1.27(2)[c]
C41−C42	1.31(2)[d]	C41′−C42′	1.28(2)[d]
Mn−C42	1.75(1)[a]	Mn′−C42′	1.76(1)[a]
Mn−C50	2.16(1)	Mn′−C50′	2.12(2)
Mn−C51	2.13(1)	Mn′−C51′	2.12(2)
Mn−C52	2.12(1)	Mn′−C52′	2.16(1)
Mn−C53	2.17(1)	Mn′−C53′	2.17(2)
Mn−C54	2.13(1)	Mn′−C54′	2.13(2)
Mn−C60	1.82(1)	Mn′−C60′	1.81(1)
Mn−C61	1.81(2)	Mn′−C61′	1.82(2)
O2−C60	1.12(2)	O2′−C60′	1.17(1)
O3−C61	1.15(2)	O3′−C61′	1.15(2)
Re−C1	2.24(1)	Re′−C1′	2.28(1)
Re−C2	2.26(1)	Re′−C2′	2.31(1)
Re−C3	2.32(1)	Re′−C3′	2.32(1)
Re−C4	2.34(1)	Re′−C4′	2.32(1)
Re−C5	2.28(2)	Re′−C5′	2.32(1)
P−C11	1.82(1)	P′−C11′	1.81(1)
P−C21	1.82(1)	P′−C21′	1.82(1)
P−C31	1.81(1)	P′−C31′	1.84(1)
P−Re−N	88.5(3)	P′-Re′−N′	92.5(3)
P−Re−C40	92.3(4)	P′-Re′−C40′	85.6(3)
N−Re−C40	98.8(5)	N′-Re′−C40′	102.2(4)
Re−N−O1	175(1)	Re′−N′−O1′	169.0(7)
Re−C40−C41	173(1)[e]	Re′−C40′−C41′	176.1(9)[e]
C40−C41−C42	176(1)[f]	C40′−C41′−C42	171(1)[f]
Mn−C42−C41	180(1)[g]	Mn′−C42′−C41′	175(1)[g]
C42−Mn−C60	92.8(6)	C42′-Mn′−C60′	92.2(5)
C42−Mn−C61	93.2(6)	C42′-Mn′−C61′	90.8(5)
C60−Mn−C61	93.1(7)	C60′-Mn′−C61′	91.9(6)
Mn−C60−O2	178(1)	Mn′−C60′−O2′	177(1)
Mn−C61−O3	179(1)	Mn′−C61′−O3′	178(1)

[a] 1.75(2), 1.75(2) in 16 °C structure. [b] 1.92(1), 1.93(1) in 16 °C structure. [c] 1.26(2), 1.28(2) in 16 °C structure. [d] 1.32(2), 1.28(2) in 16 °C structure. [e] 173(1), 175(1) in 16 °C structure. [f] 175(2), 170(2) in 16 °C structure. [g] 178(1), 178(2) in 16 °C structure.

$^+Re{=}C{=}C{=}C{=}C{=}Re^+$ linkages (2.037(5), 1.93(1)−1.91(1) Å).[6a,22] The Re*C*≡*C* bond length (1.23(1) Å) is close to the mean for alkynyl complexes (1.210(13) Å),[23] but the ReC≡*CC*= bond length (1.38(1) Å) is short for sp−sp^2 junctions (1.43 Å).[23b]

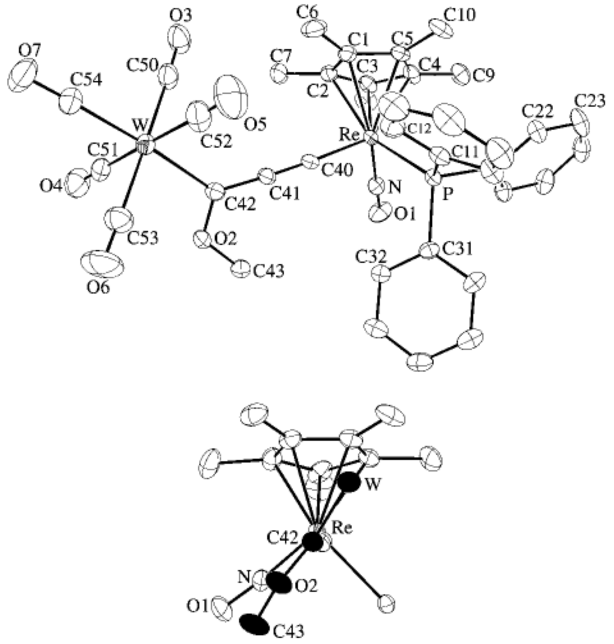

Figure 2. Views of the molecular structure of **3** (top) and Newman-type projection down the C42−Re linkage (bottom).

The carbon−tungsten bond length (2.200(8) Å) is closer to those in analogous Fischer carbene complexes ($(RC(OR'){=})W(CO)_5$, 2.191(9) Å)[24] than anionic alkyl complexes ($[RW(CO)_5]^-$, 2.31−2.34 Å).[25,26]

Adducts of **VI**-Me_x and unsaturated ligands commonly exhibit conformations that maximize overlap of ligand acceptor orbitals with the d orbital HOMO shown in Scheme 2. Accordingly, the P−Re=C planes of alkylidene and vinylidene complexes make ca. 90° and 0° angles, respectively, with the planes of the =CRR′ termini.[6a] As shown in the bottom view in Figure 2, the P−Re−C40 plane of **3** is nearly orthogonal to the W−C42−O2 plane (∠99.6(2)°). This geometry is consistent with a propadienylidene or $^+Re{=}C{=}C{=}C(OMe){-}W^-$ formulation. On the basis of all the preceding structural and spectroscopic data, we conclude that the electronic ground states of **3**−**8** are nearly halfway between those represented by resonance forms **IIIa** and **IIIb** (Scheme 1).

2. C_3 Complexes. Previous studies have shown that cyclopentadienyl manganese carbene complexes ($(RC(OR'){=})Mn(CO)_2(\eta^5\text{-}C_5H_5)$) and excess BF_3 gas react to give cationic carbyne complexes $[(RC{\equiv})Mn(CO)_2(\eta^5\text{-}C_5H_5)]^+BF_4^-$.[18b,27] Thus, as depicted in Scheme 3, the rhenium/manganese C_3OMe complex **5** and BF_3 were combined in

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[22] A rhenium/triosmium C_3OMe complex, $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Os_3(CO)_{11}$, has been structurally characterized as part of another investigation.[8b] The ReC, Re*C*≡*C*, and ReC≡*CC* bond lengths are very close to those of **3** (1.983(7), 1.238(9), and 1.364(10) Å).

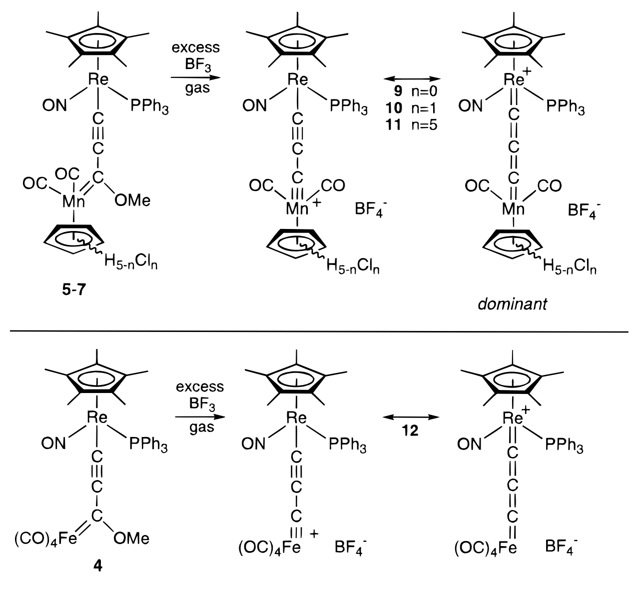
[23] (a) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; pp 21−22.

[24] This represents the average for 32 such complexes (R, R′ restricted to carbon substituents) in the January 1997 Cambridge Crystallographic Data Base (range 2.275(8)−2.10(2) Å).

[25] (a) Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045. (b) Darensbourg, D. J.; Bauch, C. G.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 977.

[26] All Fischer carbene complexes have zwitterionic resonance forms of the type $(RC({=}O^+R'))M(CO)_5^-$. Hence, the introduction of a donor-substituted alkynyl group might be expected to have a relatively small effect upon the carbon−metal bond order. Accordingly, the $^1J(^{183}W{-}^{13}C)$ value of **3** (93.2 Hz) is much closer to those of $(R\mathit{C}(OR'){=})\mathit{W}(CO)_5$ (92.8−102.5 Hz; Köhler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* **1976**, *113*, 11) than that of $[PhCH_2\mathit{C}H_2\mathit{W}(CO)_5]^-$ (48.2 Hz; Darensbourg, D. J.; Grötsch, G. *J. Am. Chem. Soc.* **1985**, *107*, 7473).

Scheme 3. Syntheses of C$_3$ Complexes



toluene/hexane at −45 °C. A precipitate formed, and workup gave the target ReC$_3$Mn complex [(^{5}-C$_5$Me$_5$)Re(NO)(PPh$_3$)(CCC)Mn(CO)$_2$(^{5}-C$_5$H$_5$)]$^+$BF$_4^-$ (**9**) as an analytically pure red-brown powder in 95% yield. The chlorocyclopentadienyl complexes **6** and **7** were similarly converted to the corresponding C$_3$ complexes [(^{5}-C$_5$Me$_5$)Re(NO)(PPh$_3$)(CCC)Mn(CO)$_2$(^{5}-C$_5$H$_{5-n}$Cl$_n$)]$^+$BF$_4^-$ (**10**, n = 1; **11**, n = 5) in 53−58% yields.

Complexes **9**−**11** were characterized analogously to **3**−**7**. FAB mass spectra exhibited intense parent ions for the cations. The rhenium IR $_{NO}$ bands (**9**/**10**/**11** 1701/1711/1717 cm^{-1}) were in the region noted above for cationic vinylidene complexes of **VI**-Me$_5$. The values increased as the number of chlorine substituents on the manganese cyclopentadienyl ligand increased. The two manganese IR $_{CO}$ bands shifted analogously (2037/2039/2047 and 1987/1991/2007 cm^{-1}). The values were lower than those of the corresponding cationic carbyne complexes [(RC≡)Mn(CO)$_2$(^{5}-C$_5$H$_5$)]$^+$ X$^-$ (2084−2096 and 2043−2054 cm^{-1}).[18b,27b] Also, intense new IR bands appeared at 1889, 1892, and 1899 cm^{-1}. They were assigned as $_{CCC}$ absorptions—a feature diagnostic of cumulated compounds. These data show that **9**−**11** are best described by cumulated $^+$Re=C=C=C=Mn resonance forms, as opposed to alkynyl carbyne Re−C≡C−C≡Mn$^+$ resonance forms (see **IVa**,**b**, Scheme 1).

The dominance of the $^+$Re=C=C=C=Mn resonance forms was also supported by ^{13}C NMR data. The Re*C*C signals of **9**−**11** (194.9/201.0/221.1 ppm) were ca. 30 ppm downfield from those of precursors **5**−**7**, and the $^2J_{CP}$ values shifted closer to those of the corresponding vinylidene complexes (12.3/11.2/11.8 Hz). The C*C*Mn signals (286.4/287.4/287.8) were nearer to those of the propadienylidene complexes (R$_2$C=C=C=)Mn(CO)$_2$(^{5}-C$_5$H$_5$) (305−331)[28] than carbyne complexes [(RC≡)Mn(CO)$_2$(^{5}-C$_5$H$_5$)]$^+$ X$^-$ (345−357).[29] The *C*CC signals (169.4/169.4/168.9) were also closer to those of the propadienylidene complexes (140−170 ppm).

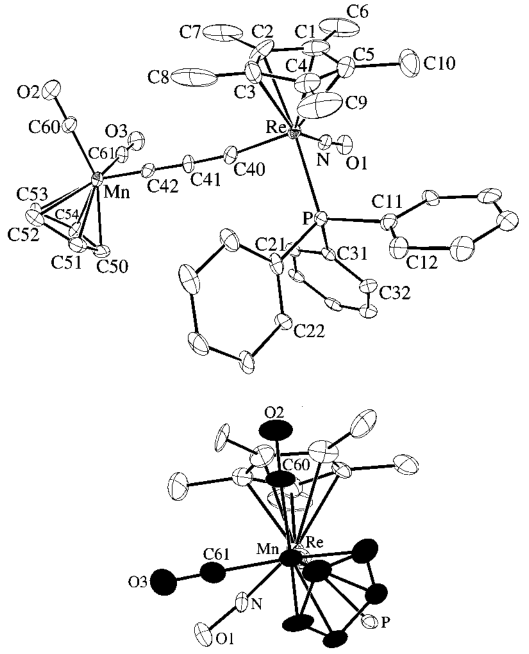


Figure 3. Structure of the cation of **9** (CH$_2$Cl$_2$)$_{0.5}$ (top) and Newman-type projection down the manganese−rhenium linkage (bottom).

Considering the novelty of and scant precedent for **9**−**11**, a crystal structure was sought. X-ray data were collected on a hemisolvate of **9** at −125 °C, as described in Table 1 and the Experimental Section. Two independent cations were present in the unit cell, and the structure of one is shown in Figure 3. Selected bond lengths and angles for both are given in Table 2. A second crystal structure was determined at room temperature, as detailed in a communication.[4a] This gave comparable metrical parameters and esd values (R = 0.048; R_w = 0.057; goodness of fit = 0.661). Since the second structure constitutes a statistically meaningful independent determination, selected data are given in a footnote to Table 2.

The six MCC and CCC bond angles in the two independent cations ranged from 171(1)° to 180(1)°, for essentially linear ReCCCMn linkages. A Newman-type projection illustrating this feature is given in Figure 3 (bottom). The C=C bond lengths ranged from 1.27(2) to 1.31(2) Å, bracketing those of allene and butatriene (1.28−1.31 Å).[23b] The Re=C bonds (1.91(1)−1.93(1) Å) and the C=C bonds were nearly identical with those in a related $^+$Re=C=C=C=C=Re$^+$ compound (1.909(7)−1.916(7) and 1.260(10)−1.305(10) Å).[6a] The C=Mn bonds (1.75(1)−1.76(1) Å) were closer to those in the propadienylidene and vinylidene complexes (Cy$_2$C=C=C=)Mn(CO)$_2$(^{5}-C$_5$H$_5$) (1.806(6) Å)[30] and (Me$_2$C=C=)Mn(CO)$_2$(^{5}-C$_5$H$_4$CH$_3$) (1.79(2) Å)[31] than the vinyl-substituted carbyne complex [(R$_2$C=CHC≡)Mn(CO)$_2$(^{5}-C$_5$H$_5$)]$^+$BF$_4^-$ (1.665(5) Å).[32] Furthermore, the ReCCCMn conformation corresponded to that which would be predicted from the HOMO of **VI**-Me$_5$ and the R$_2$CC$_x$Mn conformations of the propadienylidene and vinylidene complexes.

Of all of the properties of **9**−**11**, the UV−visible spectra were the most striking. As shown in Figure 4, very intense

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(27) (a) Handwerker, B. M.; Garrett, K. E.; Nagle, K. L.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 1562. (b) Terry, M. R.; Mercando, L. A.; Kelley, C.; Geoffroy, G. L.; Nombel, P.; Lugan, N.; Mathieu, R.; Ostrander, R. L.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1994**, *13*, 843.

(28) (a) Berke, H. *Chem. Ber.* **1980**, *113*, 1370. (b) Kolobava, N. E.; Ivanov, L. L.; Zhvanko, O. S. *Izv. Akad. Nauk SSSR*, *Ser. Khim.* **1980**, *478*, 2646.

(29) (a) Fischer, E. O.; Meineke, E. W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1140. (b) Fischer, E. O.; Postonov, V. N.; Kreissl, F. R. *J. Organomet. Chem.* **1982**, *231*, C73.

(30) Berke, H.; Huttner, G.; Seyerl, J. v. *Z. Naturforsch.*, *B*: *Anorg. Chem.*, *Org. Chem.*, **1981**, *36*, 1277.

(31) Berke, H.; Huttner, G.; Seyerl, J. v. *J. Organomet. Chem* **1981**, *218*, 193.

(32) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *262*, 39.

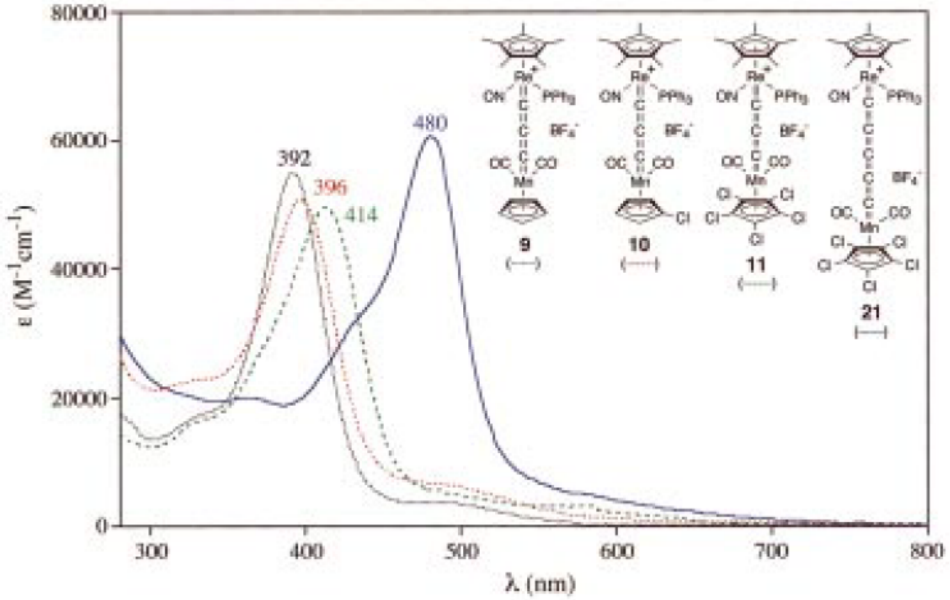


Figure 4. Representative UV−visible spectra of C_3 and C_5 complexes (CH_2Cl_2, ambient temperature).

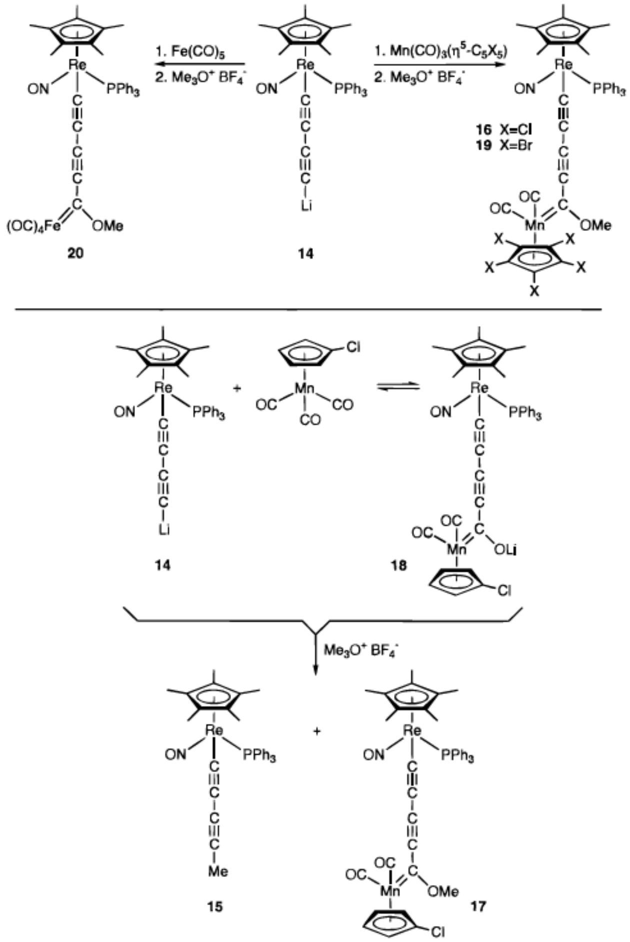
absorptions occurred near the onset of the visible region (nm, ϵ (M^{-1} cm^{-1}), CH_2Cl_2: 392, 55 800; 396, 50 900; 414, 49 100). Such extinction coefficients are rare in organometallic compounds. Weaker bands were also present further into the visible (484, 3700; 490, 6500; 554, 2700). All maxima shifted to longer wavelengths as the number of cyclopentadienyl chlorine substituents increased. To help characterize these transitions, spectra of **9** were also recorded in acetone and acetonitrile. These showed only slightly shifted maxima (390/388 and 486/486 nm).

Finally, the reaction of the rhenium/iron C_3OMe complex **4** and BF_3 was also examined (Scheme 3). Workup gave the target ReC_3Fe complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CCC)Fe(CO)_4]^+BF_4^-$ (**12**; 81%), as supported by a FAB mass spectrum that gave an intense parent ion for the cation. NMR spectra showed broadened peaks but a high degree of purity (>96%). A ^{13}C NMR spectrum exhibited Re***CCC***M signals close to those of **9**−**11** (254.5 d ($^2J_{CP}$ = 13.4 Hz), 172.2, 251.9 ppm). Metathesis with $Na^+SbF_6^-$ gave a blue powder that was nearly analytically pure. However, crystals suitable for X-ray analysis could not be grown. Since alkylidene or vinylidene complexes of the $Fe(CO)_4$ fragment do not appear to be known,[33] a crystal structure would be desirable. Nonetheless, the cationic carbyne complex $[((i\text{-}Pr)_2NC{\equiv})Fe(CO)_3(PPh_3)]^+CF_3CO_2^-$ has been isolated.[34] As with **12**, a cumulated resonance form ($R_2N^+{=}C{=}Fe$) is likely favored. Accordingly, the ***C***Fe ^{13}C NMR signal (266.5 ppm) is very close to that of **12**.

3. C_5OMe and C_5 Complexes. We sought to extend the preceding chemistry to longer carbon chains. Thus, the butadiynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CH)$ (**13**) and *n*-BuLi were combined in THF at −80 °C to generate the ReC_4Li complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CLi)$ (**14**).[6b] Then $Mn(CO)_3(\eta^5\text{-}C_5H_5)$ and Me_3O^+ BF_4^- were added under various conditions. However, the target rhenium/manganese C_5OMe complex was never detected. Rather, the major product was the 1,3-pentadiynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CMe)$ (**15**),[6b] derived from the methylation of **14**.

More electrophilic or acidic manganese tricarbonyl complexes were investigated. As shown in Scheme 4, the pentachlorocyclopentadienyl complex $Mn(CO)_3(\eta^5\text{-}C_5Cl_5)$ gave the desired, dark purple C_5OMe complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC(OMe){=})Mn(CO)_2(\eta^5\text{-}C_5Cl_5)$ (**16**) in 77% yield after workup. However, the monochlorocyclopentadienyl complex $Mn(CO)_3(\eta^5\text{-}C_5H_4Cl)$ gave a ca. 60:40 mixture of the C_5OMe complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC(OMe){=})Mn(CO)_2(\eta^5\text{-}C_5H_4Cl)$ (**17**) and 1,3-pentadiynyl complex **15**. Procedures were varied in efforts to reduce the amount

Scheme 4. Syntheses of C_5OMe Complexes



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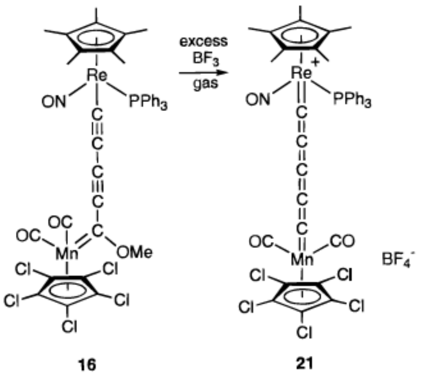
[33] The most closely related compounds would be $Ph_3P{=}C{=}C{=}Fe(CO)_4 \leftrightarrow Ph_3P^+C{\equiv}CFe(CO)_4^-$ and $RC(OR'){=}C{=}C{=}Fe(CO)_4$: (a) Petz, W.; Weller, F. *Z. Naturforsch.* **1996**, *51b*, 1598. (b) Berke, H.; Grössmann, U.; Huttner, L.; Zsolnai, L. *Chem. Ber.* **1984**, *117*, 3432.

[34] Anderson, S.; Hill, A. F. *Organometallics* **1995**, *14*, 1562.

Scheme 5. Synthesis of a C_5 Complex



of **15**. However, these and all separation attempts were unsuccessful. We presume that the anionic addition product **18** shown in Scheme 4 remains in equilibrium with **14** and that both are competitively methylated by $Me_3O^+ BF_4^-$.

The data in Schemes 2 and 4 show that the ReC_4Li complex **14** is less basic and/or nucleophilic than the ReC_2Li complex **2**. Organic terminal acetylides exhibit parallel trends.[35] A similar reaction of **14** with the pentabromocyclopentadienyl complex $Mn(CO)_3(\eta^5\text{-}C_5Br_5)$[17] and $Me_3O^+BF_4^-$ gave the dark blue C$_5$OMe complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC(OMe){=})Mn(CO)_2(\eta^5\text{-}C_5Br_5)$ (**19**) in 55% yield. However, when the pentaiodocyclopentadienyl complex $Mn(CO)_3(\eta^5\text{-}C_5I_5)$[17] was employed, no adduct was detected. An analogous sequence with $Fe(CO)_5$ gave the dark blue C$_5$OMe complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC(OMe){=})Fe(CO)_4$ (**20**) in 77% yield.

Most spectroscopic properties of the C$_5$OMe complexes were similar to those of the C$_3$OMe complexes. However, as illustrated in Figure 1, the longest wavelength visible absorption of **16** was red-shifted from that of the lower homologue **7** and more intense (562 vs 470 nm; ϵ 21 300 vs 13 000 M^{-1} cm^{-1}). Also, the IR $\nu_{C\equiv C}$ values of **16**, **17**, and **20** were 100−180 cm^{-1} greater than those of **7**, **6**, and **4**. Several features suggested slightly lower contributions from zwitterionic resonance forms. For example, the IR ν_{NO} values of **16**, **17**, and **20** were 5−10 cm^{-1} less than those of **7**, **6**, and **4**. Similarly, the ***C***=M ^{13}C NMR signals shifted 9−17 ppm *down*field (288.9, 291.9, 273.6), while the Re*C*C signals shifted 16−20 ppm *up*field (167.1, 155.6, 183.6; $^2J_{CP}$ = 1−3 Hz greater). The remaining RеC***CCC*** ^{13}C signals fell into two ranges, 127.6−116.3 (2 s) and 88.1−82.4 (1 s) ppm.

In a procedure analogous to that employed for the C$_3$ complexes in Scheme 3, toluene/hexane solutions of the pentachlorocyclopentadienyl C$_5$OMe complex **16** were treated with excess BF_3 gas. A product precipitated. As shown in Scheme 5, workup gave the C$_5$ complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CCCCC)Mn(CO)_2(\eta^5\text{-}C_5Cl_5)]^+BF_4^-$ (**21**) as a dark brown powder of ca. 94% purity in 52% yield. A FAB mass spectrum showed a parent ion for the cation. However, several unusual properties were immediately apparent. These have, to date, precluded further purification.

For example, **21** was extremely sensitive to ambient room lighting, both in solution and in the solid state. A CH_2Cl_2 solution was >60% decomposed after 0.5 h and >90% decomposed after 1 h, as assayed by UV−visible spectroscopy. A control solution that was kept in the dark showed <10% decomposition after 15 h. Consequently, all manipulations were performed in subdued light. Also, more concentrated solutions gave more rapid thermal decomposition (e.g., >80% after 10 h). Black precipitates formed that gave broad NMR signals and broad IR ν_{NO} and ν_{CO} bands (1726, 1974, 2043 cm^{-1}). A sextet ESR signal was detected ($g = 2.02$), indicating at least small amounts of a monorhenium radical ($I = {}^5/_2$). The coupling ($A_{iso,Re} = 97$ G) showed the spin to be much more delocalized from rhenium than in the cation radical $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)]^{\bullet+}PF_6^-$ (190−195 G).[6a,b]

Carbon, hydrogen, and chlorine analyses of the decomposition products (42.71−42.64, 3.49−3.54, and 12.51%, respectively) remained close to the theoretical values for **21** (43.33, 2.73, and 15.99%). However, FAB mass spectra did not show ions of mass higher than $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)]^+$. The pentachlorocyclopentadienyl C$_3$ complex **11** did not exhibit analogous photochemical or thermal lability. Hence, the chlorine substituents in **21** are not an intrinsic source of instability. Similar reactions of **19** and **20** with BF_3 were investigated but gave much less stable products.

The ^{13}C NMR spectrum of **21** showed downfield Re***C***C (218.4 ppm, $^2J_{CP}$ = 12.5 Hz) and ***C***Mn (296.2 ppm) signals that were close to those of the C$_3$ analogue **11** (221.1 ppm, $^2J_{CP}$ = 11.8 Hz; 287.8 ppm). The remaining C***CCCC*** signals were clustered at 119.1−107.0 ppm (3 s). The IR ν_{NO} and ν_{CO} values (1718 cm^{-1}; 2045−2042 and 2008−1996 cm^{-1}) were essentially identical with those of **11**. The strong ν_{CCC} band was shifted from that of **11** (1953 vs 1899 cm^{-1}). These data indicate that a cumulated $^+Re{=}C{=}C{=}C{=}C{=}C{=}Mn$ resonance form dominates. A UV−visible spectrum of **21** (Figure 4) showed a very intense absorption at 480 nm, with a shoulder at 442 nm (ϵ 60 500 and 33 000 M^{-1} cm^{-1}) and a weaker, longer wavelength band at 634 nm (ϵ 4800). These are red-shifted 65−80 nm from the corresponding absorptions of **11**—a trend that is analyzed below.

Efforts were made to prepare stable derivatives of **21**. However, no reactions occurred with TCNE (1.5 equiv), ethylene (1 atm), or dimethyl sulfide (5 equiv) in CH_2Cl_2 at ambient temperature. In contrast, **21** and PMe_3 immediately reacted at −80 °C. An aliquot showed two broad ν_{NO} bands (1689, 1721 cm^{-1}) and four strong bands in the ν_{CCC} region (1900−2050 cm^{-1}). Workup gave a black powder, and a ^{31}P NMR spectrum showed many peaks between 20 and 30 ppm. Attempts to isolate a pure compound by chromatography or crystallization were unsuccessful.

Discussion

1. Synthetic Methodology. Preparative strategies for C$_3$ complexes of the type **I** can be classified by retrosynthetic analysis, in the same manner as commonly done in organic natural product synthesis. Only limited pairings of L_nM, L_nMC, L_nMCC, or L_nMCCC moieties with complementary $C_xM'L'_{n'}$ moieties, or three-component constructs (e.g., $L_nMC + C + CM'L'_{n'}$), are possible. Our syntheses (Schemes 2 and 3) join two-carbon and one-carbon building blocks, initially giving bimetallic bridging C$_3$OMe complexes. Although such carbon−carbon bond-forming reactions have precedent in monometallic systems,[12] it was first necessary to develop the synthesis and chemistry of the nucleophilic ReC_2Li complex **2**. Now that other types of $L_nMC{\equiv}CLi$ species have become available,[7d,36] the versatility of our approach is enhanced.

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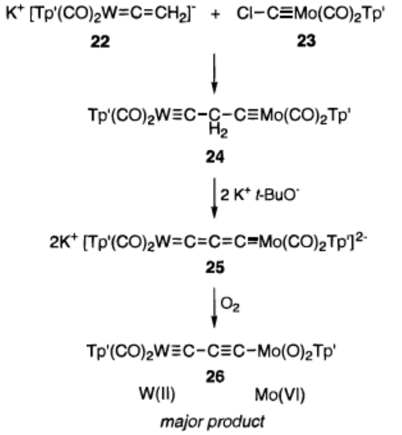
Scheme 6. Syntheses of Other C_3 Complexes of the Type **I**



Nonetheless, other strategies also hold promise. For example, C_3OMe complexes might be assembled by coupling appropriately matched L_nMX precursors and three-carbon building blocks $X'C{=}CC(OMe){=}M'L'_{n'}$. Fischer has recently explored several such approaches involving amino carbene complexes.[14] Furthermore, any bridging C_xH assembly[37] is only a proton, hydride ion, or hydrogen atom abstraction removed from a C_x complex. Although the longer chain in C_5 complexes should, in principle, allow an expanded range of preparative strategies, most are likely to be homologues of those developed for C_3 complexes.

Templeton has reported the only other C_3 complexes of type **I** known to date.[5,8] As illustrated in Scheme 6, he first condenses the two-carbon, anionic tungsten vinylidene building block **22**, and the one-carbon, molybdenum chlorocarbyne building block **23**. This yields **24**, which has a $W{\equiv}CCH_2C{\equiv}Mo$ linkage. Reaction with excess base gives the dianionic C_3 complex **25**, which has a cumulated W=C=C=C=Mo linkage and can be characterized in solution. The ^{13}C NMR spectrum shows signals at 238.4, 153.8, and 234.4 ppm, a pattern similar to that of **9** (194.9, 169.9, and 286.4 ppm). Oxidation gives the isolable C_3 complex **26**, which has an unsymmetrical $W{\equiv}C{-}C{\equiv}C{-}Mo$ valence structure and termini with distinctly different oxidation states (^{13}C NMR 246, 130, 120 ppm). Several related compounds were also characterized.[5]

Apart from the issue of target stability (below), there should be no intrinsic upper limit on our strategy with regard to chain length. For example, ReC_6Li and ReC_8Li complexes analogous to **2** and **14** have been generated and functionalized.[7c] They should be progressively less basic and nucleophilic[35] and, thereby, more prone to the type of complication illustrated at the bottom of Scheme 4. Nonetheless, they should still condense with sufficiently electrophilic metal carbonyl complexes to give, following methylation, isolable bridging C_7OMe and C_9OMe species.

2. Electronic Structure and Charge Transfer. The above structural and spectroscopic data clearly show that the ground states of the C_3 and C_5 complexes **9**−**11** and **21** are best described by the cumulated valence structures $^{+}Re{=}C{=}C{=}C{=}Mn$ and $^{+}Re{=}C{=}C{=}C{=}C{=}C{=}Mn$. However, there are hints that the rhenium is less positively charged in **21** than the C_3 homologue **11**. This is also evident with the C_5OMe and C_3OMe complexes, including systems described elsewhere.[8b] Many series of compounds are known in which donors and acceptors are linked by unsaturated bridges of varying lengths. The effects of bridge lengths upon electronic interactions are currently under intense investigation. Data generally indicate a diminution with distance, as would be intuitively expected.[38,39] Thus, as the carbon chains in **11** and **21** are further extended, ground states should acquire more $Re{-}(C{\equiv}C)_y{-}C{\equiv}Mn^{+}$ character.

All of the new complexes exhibit UV−visible absorptions that have no counterparts in the corresponding monometallic species (Figures 1 and 4). For example, alkynyl and butadiynyl complexes of **VI**-Me_x show only intense PPh_3-derived UV bands that tail into the visible.[6b] As noted above, analogous alkylidene and vinylidene complexes give unique absorptions only with aryl-substituted termini (360−400 nm, 7600−13 000 M^{-1} cm^{-1}).[19,20] The cyclopentadienyl manganese alkylidene complex $(Ph_2C{=})Mn(CO)_2(\eta^5\text{-}C_5H_5)$ exhibits bands near 380 and 625 nm (ca. 7000 and 140 M^{-1} cm^{-1}).[40] The latter is weak and of uncertain origin, but the former is believed to arise from metal-to-ligand charge transfer (manganese d_π to carbene p_π), consistent with a moderate dependence upon solvent polarity (372 vs 383 nm, acetonitrile vs cyclohexane).

We were curious about the nature of the optical transitions of the new complexes, particularly with regard to the possibility of metal-to-metal charge transfer.[41] The rhenium/manganese C_3OMe complexes **5**−**7** show progressive red-shifts of the two longest wavelength bands (306, 310, 330, and 446, 462, 470 nm) as the number of chlorine substituents on the manganese cyclopentadienyl ligand increases. This would be consistent with charge transfer from a rhenium-based orbital. Importantly, these bands move to ≥376 and 562 nm in the C_5OMe complex **16**. Such a marked chain length effect requires the involvement of orbitals with appreciable ReC_x π *or* C_xMn π^* character, as opposed to just metal character. The modest ±4-nm dependence of these bands as the solvent is varied from hexane to CH_2Cl_2 and acetonitrile (above) indicates similar ground- and excited-state polarities. This would be consistent with a large contribution of the zwitterionic resonance form **IIIb** (Scheme 1) to the ground state.

The corresponding C_3 complexes **9**−**11** also show progressive red shifts of the most intense bands (392, 396, 414 nm). The maxima of the weaker visible absorptions are not as well defined but appear to follow an analogous trend. The most intense band moves to 480 nm in the C_5 complex **21**. The chlorine substituent and chain length trends suggest that, similarly to the C_xOMe complexes, charge transfer occurs from a rhenium- or ReC_x-based orbital to one with appreciable manganese or C_xMn π^* character. The ±4-nm solvent effect (CH_2Cl_2, acetone, acetonitrile) again indicates similar ground- and excited-state polarities. One of several possible excited-state models would feature a rhenium radical cation singly bonded to a C_xMn radical assembly. However, more sophisticated experimental probes, such as resonance Raman spectroscopy,[41] will be necessary to further clarify this point.

3. Stability Trends and Prospective. The decrease in stability upon going from C_3 complex **11** to C_5 complex **21** has parallels in many other series of cumulated compounds.[42] As C_x chains are lengthened, HOMO/LUMO gaps diminish, UV−

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visible absorptions shift to longer wavelengths, and electronic coupling becomes less efficient. All of these enhance possibilities for thermal and photochemical decomposition pathways. Furthermore, the chains become sterically less shielded and amenable to external attack or coupling processes. Hence, we are pessimistic that higher homologues of **21** will be accessible in spectroscopically pure form. However, endgroup modifications, such as a more electron-releasing aryl phosphine on rhenium, may give incremental improvements.

Instructive examples of the preceding points include the following. First, Lapinte has shown that a formally cumulated $^+Fe{=}C{=}C{=}C{=}C{=}Fe^+$ complex is in thermal equilibrium with a paramagnetic, diradical $^{+\bullet}FeC{\equiv}CC{\equiv}CFe^{\bullet +}$ valence form.[43] Second, increasing numbers of pentatetraenylidene complexes, $L_nM{=}C{=}C{=}C{=}C{=}CY_2$, are being reported.[44] These feature the same number of C=C linkages as **21** but lack one C=M terminus. All are less stable than lower homologues. In unpublished work, we have isolated labile rhenium complexes of the formula $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)({=}C{=}C{=}C{=}C{=}CAr_2)]^+X^-$.[45] These exhibit many more UV−visible absorptions than analogous alkylidene and vinylidene complexes, or even **21** (nm, ϵ (M^{-1} cm^{-1}), CH_2Cl_2, CAr_2 = 2,7-dibromofluorenylidene: 350, 10 300; 412, 8400; 442, 6900; 564, 13 000; 614, 15 400). However, none approach the intensity of the 480-nm band of **21**. Finally, attempts to prepare the $W{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2$ analogue of an isolable $W{=}C{=}C{=}C{=}C(NMe_2)_2$ species gave only trapping products.[46]

We nonetheless remain cautiously optimistic that it will be possible to extend the chain lengths in other series of odd-carbon complexes beyond those described in this paper—as has already been accomplished with even-carbon complexes. Some novel approaches to enhancing thermal stabilities of C_x complexes are currently being pursued.[47] Furthermore, as will be communicated soon, we have developed facile syntheses of a fundamentally new series of complexes that are best described by polyalkynyl valence structures, $M{\equiv}C{-}(C{\equiv}C)_y{-}M'$. For the moment, this investigation has demonstrated the ready accessibility, via a rational synthetic strategy that was designed in advance, of a series of unprecedented C_3 and C_5 complexes that exhibit fascinating structural, spectroscopic, and electronic properties. Additional studies of their electronic and chemical attributes are in progress.

Experimental Section

General Data. General procedures and instrumentation were identical with those in recent papers.[6a,b] Solvents or reagents not listed earlier were used as received from commercial suppliers.

$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})W(CO)_5$ (3). A Schlenk tube was charged with $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CH)$ (**1**,[15] 0.044 g, 0.069 mmol) and THF (6 mL) and cooled to −80 °C (acetone/CO_2). Then *n*-BuLi (0.054 mL, 2.2 M in hexane) was added with stirring. After 1−2 h, a solution of $W(CO)_6$ (0.028 g, 0.080 mmol) in THF (3 mL) was added by cannula. After 1 h, the cold bath was removed. After 0.5 h, the orange solution was transferred by cannula to a Schlenk flask that had been charged with $Me_3O^+BF_4^-$ (0.026 g, 0.18 mmol) and cooled to −80 °C. The mixture was stirred for 0.8 h, and the cold bath was removed. After 0.3 h, the sample was concentrated to ca. 2 mL, and hexane (10 mL) was added. Chromatography (N_2, Florisil washed with aqueous NH_4OH; hexane → 10:1 → 3:1 v/v hexane/THF) gave a bright red band. Solvent was removed by oil pump vacuum to give **3** as an orange-red powder (0.051 g, 0.050 mmol, 73%), dec pt > 155 °C (gradual, no melting). Anal. Calcd for $C_{37}H_{33}NO_7PReW$: C, 44.23; H, 3.31. Found: C, 44.37; H, 3.55. IR (cm^{-1}, CH_2Cl_2/KBr): ν_{CO} 2058/2059 m/s, 1966/1965 m, $\nu_{CO} + \nu_{C\equiv C}$ 1913/1912 vs-br, ν_{NO} 1670/1663 m. UV−vis (4.1×10^{-5} M):[48] 348 (12 100), 462 (22 800). MS (tetraglyme/benzene):[49] 1005 (M^+, 70%), 682 ($M^+ - W(CO)_5$, 100%); no other peaks above 460 of >50%.

NMR (C_6D_6):[50] ^1H 7.59−7.39 (m, 6H of $3C_6H_5$), 7.11−6.82 (m, 9H of $3C_6H_5$), 3.21 (s, OCH_3), 1.57 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 253.2 (d, $J_{CP} = 3.0$, $J_{CW} = 93.2$, C=W), 205.1 (s, $J_{CW} = 127.3$, CO_{trans}), 204.9 (d, $J_{CP} = 12.3$, Re*C*C), 200.4 (s, $J_{CW} = 130.6$, CO_{cis}), 157.5 (s, $J_{CW} = 9.9$, ReC*C*), 133.8 (d, $J_{CP} = 10.8$, *o*-Ph), 130.9 (d, $J_{CP} = 3.0$, *p*-Ph), 128.7 (d, $J_{CP} = 10.3$, *m*-Ph), 103.6 (s, $\mathit{C}_5(CH_3)_5$), 62.2 (s, OCH_3), 9.9 (s, $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ 22.0 (s).

$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Fe(CO)_4$ (4). Complex **1** (0.064 g, 0.10 mmol), THF (5 mL), *n*-BuLi (0.065 mL, 2.46 M in hexane), $Fe(CO)_5$ (0.018 mL, 0.14 mmol), and $Me_3O^+BF_4^-$ (0.038 g, 0.26 mmol) were combined in a procedure analogous to that for **3**. Solvent was removed by oil pump vacuum, and hexane (10 mL) was added. Chromatography (N_2, Florisil washed with aqueous NH_4OH; hexane → 5:1 v/v hexane/THF) gave a bright red band. Solvent was removed by oil pump vacuum, and the residue was extracted with hexane (2 × 10 mL). The extract was passed through a medium-frit Kramer filter, concentrated to ca. 10 mL, and kept at −20 °C for 24 h. Dark red microcrystals were collected by filtration and dried by oil pump vacuum to give **4** (0.057 g, 0.067 mmol, 67%), mp 166−169 °C dec. Anal. Calcd for $C_{36}H_{33}FeNO_6PRe$: C, 50.95; H, 3.92. Found: C, 51.35; H, 4.30. IR (cm^{-1}, hexanes/KBr): ν_{CO} 2041/2035 m, 1965/− m, 1949/1931 vs/vs-br, $\nu_{C\equiv C}$ 1920/− m, ν_{NO} 1671/1674 m. UV−vis (3.1×10^{-5} M):[48] 274 sh (20 200), 382 (10 700), 466 (9300). MS (tetraglyme/benzene):[49] 849/850 ($M^+/M^+ + 1$, 15/18%), 737 ($M^+ - 4CO$, 100%); no other peaks above 225 of >25%.

NMR (C_6D_6):[50] ^1H 7.54−7.49 (m, 6H of $3C_6H_5$), 7.07−7.01 (m, 6H of $3C_6H_5$), 6.96−6.93 (m, 3H of $3C_6H_5$), 3.26 (s, OCH_3), 1.61 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 256.6 (s, C=Fe), 218.4 (s, CO), 204.0 (d, $J_{CP} = 13.3$, Re*C*C), 152.0 (s, ReC*C*), 133.8 (d, $J_{CP} = 11.0$, *o*-Ph), 130.8 (d, $J_{CP} = 2.4$, *p*-Ph), 128.7 (d, $J_{CP} = 10.3$, *m*-Ph), 103.7 (s, $\mathit{C}_5(CH_3)_5$), 63.0 (s, OCH_3), 9.7 (s, $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ 22.3 (s).

$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Mn(CO)_2(\eta^5\text{-}C_5H_5)$ (5). Complex **1** (0.064 g, 0.10 mmol), THF (5 mL), *n*-BuLi (0.060 mL, 2.46 M in hexane), $Mn(CO)_3(\eta^5\text{-}C_5H_5)$ (0.028 g, 0.14 mmol; in 3 mL THF; 3-h interval after cold bath removal), and $Me_3O^+BF_4^-$ (0.068 g, 0.46 mmol) were combined in a procedure analogous to that for **3**. The sample was concentrated to ca. 0.5 mL, and hexane (10 mL) was added. Chromatography (N_2, Florisil washed with aqueous NH_4OH; hexane → 4:1 v/v hexane/THF) gave a red-orange band. Solvent was removed by oil pump vacuum to give **5** as a red-orange powder (0.062 g, 0.072 mmol, 72%), mp 81−84 °C dec. Anal. Calcd for $C_{39}H_{38}MnNO_4PRe$: C, 54.67; H, 4.47. Found: C, 54.77; H, 4.63. IR (cm^{-1}, CH_2Cl_2/KBr): ν_{CO} 1968/1969 m, 1921/1920 vs, $\nu_{C\equiv C}$ 1862/1862 s, ν_{NO} 1653/1648 s. UV−vis (3.9×10^{-5} M):[48] 274 sh (14 100), 288 sh (12 000), 306 (10 500), 446 (9700). MS (tetraglyme/benzene):[49] 857 (M^+, 65%), 826 ($M^+ - OMe$, 43%), 801 ($M^+ - 2CO$, 100%), 698 ($M^+ - Mn(CO)(C)(C_5H_5)$, 50%), 682 ($M^+ - Mn(CO)_2(C_5H_5)$, 34%); no other peaks above 225 of >32%.

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(48) The UV−visible spectra were recorded in CH_2Cl_2 unless noted, and absorbances are in nm (ϵ, M^{-1} cm^{-1}).

(49) Positive FAB, *m/z* for most intense peak of isotope envelope; relative intensities are for the specified mass range.

(50) The ^1H, ^{13}C, and ^{31}P NMR chemical shifts are in δ, ppm, and ppm, respectively, and *J* values are in Hz. In some cases, the *i*-Ph ^{13}C signals are not observed.

NMR (C_6D_6):[50] ^{1}H 7.69−7.62 (m, 6H of $3C_6H_5$), 7.13−6.96 (m, 9H of $3C_6H_5$), 4.67 (s, C_5H_5), 3.51 (s, OCH_3), 1.67 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 283.9 (s, C=Mn), 235.6 (s, CO), 235.5 (s, CO), 166.8 (d, J_{CP} = 13.8, Re***C***C), 146.2 (s, ReC***C***), 134.7 (d, J_{CP} = 52.7, *i*-Ph), 134.2 (d, J_{CP} = 10.8, *o*-Ph), 130.4 (s, *p*-Ph), 128.5 (d, J_{CP} = 10.1, *m*-Ph), 102.2 (s, ***C***$_5(CH_3)_5$), 86.5 (s, C_5H_5) 61.0 (s, OCH_3), 10.1 (s, C_5(***C***$H_3)_5$); $^{31}P\{^1H\}$ 22.2 (s).

$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Mn(CO)_2(\eta^5\text{-}C_5H_4Cl)$ (6). Complex **1** (0.064 g, 0.10 mmol), THF (5 mL), *n*-BuLi (0.060 mL, 2.46 M in hexane), $Mn(CO)_3(\eta^5\text{-}C_5H_4Cl)$ (0.024 g, 0.10 mmol;[16] in 3 mL THF; 4 h interval after cold bath removal), and $Me_3O^+BF_4^-$ (0.068 g, 0.46 mmol) were combined in a procedure analogous to that for **3**. The mixture was stirred for 0.5 h, and the cold bath was removed. After 0.3 h, Florisil (2 g) was added, and the solvent was removed by oil pump vacuum. The dry powder was placed at the top of a Florisil column. Chromatography (N_2, hexane to elute a light yellow $Mn(CO)_3(\eta^5\text{-}C_5H_4Cl)$ band, then 1:1 v/v hexane/ether) gave a red band. Solvent was removed by oil pump vacuum to give **6** as red powder (0.036 g, 0.041 mmol, 41%), mp 110−113 °C dec. Anal. Calcd for $C_{39}H_{37}ClMnNO_4PRe$: C, 52.55; H, 4.18. Found: C, 51.80; H, 4.11. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 1967 m, 1926 vs, $\nu_{C\equiv C}$ 1871 s, ν_{NO} 1653 s. UV−vis (6.7 × 10^{-5} M):[48] 268 sh (14 500), 310 (10 100), 462 (7400). MS (3-NBA/benzene):[49] 891 (M^+, 18%), 835 (M^+ − 2CO, 65%), 614 ($(C_5Me_5)Re(NO)(PPh_3)^+$, 100%); no other peaks above 300 of >25%.

NMR (C_6D_6):[50] ^{1}H 7.79−7.54 (m, 6H of $3C_6H_5$), 7.22−6.87 (m, 9H of $3C_6H_5$), 4.78 (br d, J_{HH} = 18.0, 2H of C_5H_4Cl), 4.45 (br s, 2H of C_5H_4Cl), 3.48 (s, OCH_3), 1.65 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 282.1 (s, C=Mn), 234.2 (s, CO), 234.1 (s, CO), 171.3 (d, J_{CP} = 13.5, Re***C***C), 146.8 (s, ReC***C***), 134.1 (d, J_{CP} = 10.7, *o*-Ph), 130.5 (s, *p*-Ph), 128.6 (d, J_{CP} = 9.9, *m*-Ph), 102.3 (s, ***C***$_5(CH_3)_5$), 85.7, 85.6, 85.5, 85.2 (4 s, 4 CH of C_5H_4Cl),[51] 58.3 (s, OCH_3), 10.1 (s, C_5(***C***$H_3)_5$); $^{31}P\{^1H\}$ 24.3 (s).

$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Mn(CO)_2(\eta^5\text{-}C_5Cl_5)$ (7). Complex **1** (0.064 g, 0.10 mmol), THF (5 mL), *n*-BuLi (0.060 mL, 2.46 M in hexane), $Mn(CO)_3(\eta^5\text{-}C_5Cl_5)$ (0.038 g, 0.10 mmol;[17] in 3 mL of THF; 4 and 0.25 h before and after cold bath removal), and $Me_3O^+BF_4^-$ (0.068 g, 0.46 mmol) were combined in a procedure analogous to that for **3**. The mixture was stirred for 0.5 h, and the cold bath was removed. After 0.3 h, Florisil (2 g) was added, and the solvent was removed by oil pump vacuum. The dry powder was placed at the top of a Florisil column. Chromatography (N_2, hexane to elute a yellow $Mn(CO)_3(\eta^5\text{-}C_5Cl_5)$ band, then 4:1 v/v hexane/THF) gave an orange band. Solvent was removed by oil pump vacuum to give crude **7** as an orange-brown oil (0.059 g, 0.057 mmol, 57%). Hexane (15 mL) was added. The mixture was filtered through a Celite pad (2 cm) and kept at −100 °C. After 24 h, the orange-red powder was collected by filtration at −80 °C and dried by oil pump vacuum to give **7** (0.034 g, 0.041 mmol, 41%), mp 104−106 °C dec. IR (cm^{-1}, THF): ν_{CO} 1972 vs, 1934 s, $\nu_{C\equiv C}$ 1904 s, ν_{NO} 1661 vs UV−vis (3.1 × 10^{-5} M):[48] 270 sh (14 300), 330 (9500), 470 (13 000).

NMR (C_6D_6):[50] ^{1}H 7.35−7.05 (m, $3C_6H_5$), 3.47 (s, OCH_3), 1.57 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 273.5 (s, C=Mn), 230.1 (s, 2CO), 186.8 (d, J_{CP} = 11.6, Re***C***C), 150.2 (s, ReC***C***), 133.9 (d, J_{CP} = 10.4, *o*-Ph), 130.7 (s, *p*-Ph), 128.7 (d, J_{CP} = 10.6, *m*-Ph), 102.9 (s, ***C***$_5(CH_3)_5$), 95.5 (s, ***C***$_5Cl_5$), 63.3 (s, OCH_3), 9.9 (s, C_5(***C***$H_3)_5$); $^{31}P\{^1H\}$ 22.1 (s).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CCC)Mn(CO)_2(\eta^5\text{-}C_5H_5)]^+\ BF_4^-$ (9). A Schlenk tube was charged with **5** (0.086 g, 0.10 mmol), toluene (10 mL), and hexane (5 mL) and cooled to −45 °C (CH_3CN/CO_2). For 2 min, BF_3 gas was bubbled through the solution. A dark red solid precipitated. Solvent was removed by syringe. The solid was washed with hexane (2 × 5 mL), dried by oil pump vacuum, and dissolved in a minimum of CH_2Cl_2 (1 mL). The solution was passed through a medium frit into rapidly stirred ether (15 mL). The red-brown powder was collected by filtration, washed with ether (2 × 2 mL), and dried by oil pump vacuum to give **9** (0.087 g, 0.095 mmol, 95%), mp 182−187 °C, slow dec. Anal. Calcd for $C_{38}H_{35}BF_4MnNO_3PRe$: C, 50.01; H, 3.87. Found: C, 49.81; H, 3.98. IR (cm^{-1}, CH_2Cl_2/KBr): ν_{CO} 2037/2033 m, 1987/1980 m, ν_{CCC} 1889/1881 vs, ν_{NO} 1701/1684 m. UV−vis (3.0 × 10^{-5} M):[48] 268 (19 200), 286 sh (16 500), 328 sh (17100), 392 (55 800), 484 (3700). MS (3-NBA/CH_2Cl_2):[49] 826 (M^+, 18%), 770 (M^+ − 2CO, 33%), 614 ($(C_5Me_5)Re(NO)(PPh_3)^+$, 100%); no other peaks above 320 of >15%.

NMR (CD_2Cl_2):[50] ^{1}H 7.61−7.42 (m, $3C_6H_5$), 5.13 (s, C_5H_5), 1.90 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 286.4 (s, C=Mn), 221.8 (s, 2CO), 221.6 (s, CO), 194.9 (d, J_{CP} = 12.3, Re***C***C), 169.4 (s, ReC***C***), 133.7 (d, J_{CP} = 11.0, *o*-Ph), 132.2 (s, *p*-Ph), 131.1 (d, J_{CP} = 56.9, *i*-Ph), 129.4 (d, J_{CP} = 11.1, *m*-Ph), 106.5 (s, ***C***$_5(CH_3)_5$), 90.2 (s, C_5H_5), 10.0 (s, C_5(***C***$H_3)_5$); $^{31}P\{^1H\}$ 18.9 (s).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CCC)Mn(CO)_2(\eta^5\text{-}C_5H_4Cl)]^+BF_4^-$ (10). Complex **6** (0.089 g, 0.10 mmol), toluene (10 mL), hexane (10 mL), and BF_3 gas (5 min) were combined in a procedure analogous to that for **9**. A dark brown oil precipitated. Solvent was removed by syringe. The residue was extracted with CH_2Cl_2 (3 mL). The extract was added to ether (30 mL). Solvent was removed from the oily precipitate by syringe, which was washed with ether (10 mL) to give **10** as a dark brown oil that solidified over the course of 24 h under oil pump vacuum (0.050 g, 0.053 mmol, 53%). IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2039 m, 1991 m, ν_{CCC} 1892 vs, ν_{NO} 1711 m. UV−vis (4.0 × 10^{-5} M):[48] 270 sh (32 100), 326 sh (22 700), 396 (50 900), 490 (6500). MS (3-NBA/benzene):[49] 861 (M^+, 100%), 805 (M^+ − 2CO, 41%), 614 ($(C_5Me_5)Re(NO)(PPh_3)^+$, 68%); no other peaks above 400 of >45%.

NMR (CD_2Cl_2):[50] ^{1}H 7.65−7.35 (m, $3C_6H_5$), 5.28−5.22 (m, 2H of C_5H_4Cl), 5.10−5.05 (m, 2H of C_5H_4Cl) 1.90 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 287.4 (s, C=Mn), 221.2 (s, CO), 221.1 (s, CO), 201.0 (d, J_{CP} = 11.2, Re***C***C), 169.4 (s, ReC***C***), 133.9 (d, J_{CP} = 11.1, *o*-Ph) 132.5 (s, *p*-Ph), 130.0 (d, J_{CP} = 56.7, *i*-Ph), 129.7 (d, J_{CP} = 10.9, *m*-Ph), 107.0 (s, ***C***$_5(CH_3)_5$), 89.6, 87.9, 87.7 (3 s, 2:1:1, 4 CH of C_5H_4Cl),[51] 10.3 (s, C_5(***C***$H_3)_5$); $^{31}P\{^1H\}$ 18.9 (s).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CCC)Mn(CO)_2(\eta^5\text{-}C_5Cl_5)]^+\ BF_4^-$ (11). Complex **7** (0.051 g, 0.050 mmol), toluene (10 mL), hexane (10 mL), and BF_3 gas (5 min) were combined in a procedure analogous to that for **9**. A dark brown solid precipitated. Solvent was removed by syringe. The residue was extracted with CH_2Cl_2 (3 mL). The extract was filtered through a Celite pad (2 cm). Solvent was removed from the filtrate by oil pump vacuum to give an oily solid, which was dissolved in ether (3 mL). Hexane (30 mL) was added, and the mixture was kept at −100 °C. After 24 h, the yellow-brown powder was collected by filtration and dried by oil pump vacuum to give **11** (0.031 g, 0.029 mmol, 58%), mp 101−106 °C dec. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 2047 m, 2007 w, ν_{CCC} 1899 vs, ν_{NO} 1717 m. UV−vis (2.3 × 10^{-5} M):[48] 266 sh (16 800), 334 sh (16 200), 414 (49 100), 554 sh (2700). MS (3-NBA/benzene):[49] 998 (M^+, 100%); no other peaks above 200 of >25%.

NMR (CD_2Cl_2):[50] ^{1}H 7.57−7.46 (m, $3C_6H_5$), 1.93 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 287.8 (s, C=Mn), 221.1 (d, J_{CP} = 11.8, Re***C***C), 218.2 (s, CO), 218.0 (s, CO), 168.9 (s, ReC***C***), 133.5 (d, J_{CP} = 11.3, *o*-Ph), 132.6 (s, *p*-Ph), 129.7 (d, J_{CP} = 11.1, *m*-Ph), 108.0 (s, ***C***$_5(CH_3)_5$) 100.1 (s, C_5Cl_5), 10.1 (s, C_5(***C***$H_3)_5$); $^{31}P\{^1H\}$ 19.7 (s).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CCC)Fe(CO)_4]^+BF_4^-$ (12). Complex **4** (0.052 g, 0.061 mmol), toluene (5 mL), hexane (5 mL), and BF_3 gas were combined in a procedure analogous to that for **9** (−80 °C). A dark red-brown solid precipitated. Solvent was removed via syringe. The solid was washed with hexane (2 × 5 mL), dried by oil pump vacuum, and dissolved in a minimum of CH_2Cl_2 (1 mL). The solution was passed through a medium frit into rapidly stirred ether (10 mL). The blue-gray precipitate was collected by filtration, washed with ether (2 × 2 mL), and dried by oil pump vacuum to give **12** (0.045 g, 0.050 mmol, 81%), mp 128−134 °C slow dec. IR (cm^{-1}, CH_2Cl_2/KBr): ν_{CO} 2105/2106 s, 2043/2054 vs/s sh, 2029/2035 s/vs, ν_{CCC} 1877/1871 s, ν_{NO} 1715/1699 s. UV−vis (3.4 × 10^{-5} M):[48] 270 sh (21 500), 296 sh (17 800), 364 (32 900), 468 sh (8500), 560 sh (3000). MS (3-NBA/CH_2Cl_2):[49] 818 (M^+, 100%), 706 (M^+ − 4CO, 40%), 614 ($(C_5Me_5)Re(NO)(PPh_3)^+$, 30%); no other peaks above 400 of >25%.

NMR (CD_2Cl_2):[50] ^{1}H 7.75−7.50 (m, 9H of $3C_6H_5$), 7.50−7.35 (m, 6H of $3C_6H_5$), 1.94 (br s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ (−30 °C) 254.5 (d, J_{CP} = 13.4, Re***C***C), 251.9 (s, C=Fe), 204.6 (s, CO), 172.2 (s, ReC***C***), 133.1

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(51) The rhenium stereocenter renders all $\eta^5\text{-}C_5H_4Cl$ carbons inequivalent, and the weak CCl signal could not confidently be assigned. For comparison, the ^{13}C NMR spectrum of $Mn(CO)_3(\eta^5\text{-}C_5H_4Cl)$,[16] which has not been previously reported, was independently determined ($CDCl_3/CD_2Cl_2$): 224.0/224.7 (s, CO), 103.5/103.7 (s, CCl), 81.7/82.4, 80.6/81.3 (2 s, CH).

(d, J_{CP} = 10.1, *o*-Ph), 132.3 (s, *p*-Ph), 129.4 (d, J_{CP} = 11.5, *m*-Ph), 108.7 (s, $\mathit{C}_5(CH_3)_5$), 9.8 (s, $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ 20.5 (br s).

A Schlenk flask was charged with **12** (0.016 g, 0.018 mmol), $Na^+SbF_6^-$ (0.047 g, 0.18 mmol), and THF (10 mL). The mixture was stirred (0.5 h), and the solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2. The extract was filtered and concentrated (1 mL). Then ether (10 mL) was added. Solvent was removed by oil pump vacuum to give the SbF_6^- salt of **12** as a blue powder (0.015 g, 0.014 mmol, 82%), mp 127−130 °C dec. IR (cm^{-1}, CH_2Cl_2) ν_{CO} 2105 s, 2041 vs, 2028 s, ν_{CCC} 1875 s, ν_{NO} 1713 vs.

NMR (CD_2Cl_2):[50] ^1H 7.63−7.50 (m, 6H of $3C_6H_5$), 7.44−7.26 (m, 9H of $3C_6H_5$), 1.96 (s, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ 20.4 (s).

(η^5-C_5Me_5)Re(NO)(PPh_3)($C{\equiv}CC{\equiv}CC(OMe){=}$)Mn$(CO)_2$($\eta^5$-$C_5Cl_5$) (16). A Schlenk tube was charged with (η^5-C_5Me_5)Re(NO)(PPh_3)($C{\equiv}CC{\equiv}CH$) (**13**;[6b] 0.048 g, 0.072 mmol) and THF (5 mL) and cooled to −80 °C. Then *n*-BuLi (0.036 mL, 2.3 M in hexane) was added with stirring. After 1 h, a solution of $Mn(CO)_3$(η^5-C_5Cl_5) (0.028 g, 0.075 mmol) in THF (3 mL) was added by cannula. After 1 h, the cold bath was removed. After 1 h, the red-orange solution was transferred by cannula to a Schlenk flask that had been charged with $Me_3O^+BF_4^-$ (0.050 g, 0.32 mmol) and cooled to −80 °C. The mixture was stirred for 0.5 h, and the cold bath was removed. After 0.5 h, the sample was concentrated to ca. 2 mL, and hexane (10 mL) was added. Chromatography (N_2, Florisil washed with aqueous NH_4OH; hexane → 3:1 v/v hexane/THF) gave a deep purple band. Solvent was removed by oil pump vacuum to give **16** as a dark purple powder (0.059 g, 0.056 mmol, 77%), mp 114−116 °C. Anal. Calcd for $C_{41}H_{33}Cl_5MnNO_4PRe$: C, 46.76; H, 3.16. Found: C, 46.36; H, 3.67. IR (cm^{-1}, CH_2Cl_2/KBr): $\nu_{C\equiv C}$ 2057/2054 m, 2046/2044 m sh, ν_{CO} 1965/1962 vs, 1925/1922 m, ν_{NO} 1655/1657 s. UV−vis (3.9×10^{-5} M):[48] 264 sh (29 000), 318 (18 700), 376 (13 300), 502 sh (14 600) 562 (21 300). MS (3-NBA/benzene):[49] 1053 (M^+, 3%), 690 ((C_5Me_5)Re(NO)(PPh_3)$(C_5O)^+$, 100%), 614 ((C_5Me_5)Re(NO)$(PPh_3)^+$, 78%); no other peaks above 320 of >20%.

NMR (C_6D_6):[50] ^1H 7.65−7.55 (m, 6H of $3C_6H_5$), 7.12−6.95 (m, 9H of $3C_6H_5$), 3.53 (s, OCH_3), 1.55 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 288.9 (s, C=Mn), 228.2 (s, CO), 228.1 (s, CO), 167.1 (d, J_{CP} = 14.8, Re*C*C), 134.2 (d, J_{CP} = 52.4, *i*-Ph), 134.0 (d, J_{CP} = 10.8, *o*-Ph), 130.7 (s, *p*-Ph), 128.6 (d, J_{CP} = 10.3, *m*-Ph), 127.4, 116.3, 82.4 (3 s, ReC*CCC*), 102.1 (s, $\mathit{C}_5(CH_3)_5$), 97.0 (s, C_5Cl_5), 63.3 (s, OCH_3), 9.9 (s, $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ 20.6 (s).

(η^5-C_5Me_5)Re(NO)(PPh_3)($C{\equiv}CC{\equiv}CC(OMe){=}$)Mn$(CO)_2$($\eta^5$-$C_5H_4Cl$) (17). Complex **13** (0.066 g, 0.10 mmol), THF (5 mL), *n*-BuLi (0.055 mL, 2.3 M in hexane), $Mn(CO)_3$(η^5-C_5H_4Cl) (0.030 g, 0.125 mmol; in 3 mL THF), and $Me_3O^+BF_4^-$ (0.044 g, 0.30 mmol) were combined in a procedure analogous to that for **16**. An identical workup gave a dark sticky residue, which solidified over the course of 24 h under oil pump vacuum (0.059 g). A ^{31}P NMR spectrum showed a ca. 60:40 mixture of **17** (39%) and (η^5-C_5Me_5)Re(NO)(PPh_3)($C{\equiv}CC{\equiv}CMe$).[6b] IR (cm^{-1}, CH_2Cl_2/KBr): $\nu_{C\equiv C}$ 2064/2058 m, ν_{CO} 1950/1947 vs, 1896/1895 m, ν_{NO} 1648/1647 s.

NMR (C_6D_6):[50] ^1H 7.81−7.59 (m, 6H of $3C_6H_5$), 7.10−6.95 (m, 9H of $3C_6H_5$), 3.59 (s, OCH_3), 1.56 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ (partial) 291.9 (s, C=Mn), 232.5 (s, 2CO), 155.6 (d, J_{CP} = 15.3 Hz, Re*C*C), 134.5 (d, J_{CP} = 11.1 Hz, *o*-Ph), 131.0 (s, *p*-Ph), 118.3 (s, one of ReC*CCC*), 102.1 (s, $\mathit{C}_5(CH_3)_5$), 88.3, 88.2, 88.0 (3 s, 2:1:1, 4 CH of C_5H_4Cl),[51] 62.5 (s, OCH_3), 10.4 (s, $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ 21.2 (s).

(η^5-C_5Me_5)Re(NO)(PPh_3)($C{\equiv}CC{\equiv}CC(OMe){=}$)Fe$(CO)_4$ (20). Complex **13** (0.064 g, 0.096 mmol), THF (5 mL), *n*-BuLi (0.056 mL, 2.35 M in hexane), $Fe(CO)_5$ (20 mL, 0.15 mmol), and $Me_3O^+BF_4^-$ (0.038 g, 0.31 mmol) were combined in a procedure analogous to that for **16**. The mixture was stirred for 30 min, and the cold bath was removed. After 10 min, a dark blue-purple solution had formed. Solvent was removed by oil pump vacuum, and hexane (10 mL) was added. Chromatography (N_2, Florisil; hexane → 1:1 v/v hexane/THF) gave a blue-purple band. Solvent was removed by oil pump vacuum to give **20** as a dark blue powder (0.065 g, 0.074 mmol, 77%), mp >150 °C dec. IR (cm^{-1}, CH_2Cl_2/KBr): ν_{CO} 2062/2060 m/s, 1965/1962 vs/vs-sh, 1945/1940 s, $\nu_{C\equiv C}$ 2018/2014 vs, ν_{NO} 1664/1662 s.

NMR (C_6D_6):[50] ^1H 7.58−7.50 (m, 6H of $3C_6H_5$), 7.07−6.92 (m, 9H of $3C_6H_5$), 3.36 (s, OCH_3), 1.51 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ 273.6 (s, C=Fe), 217.1 (s, CO), 183.6 (d, J_{CP} = 14.1, Re*C*C), 133.9 (d, J_{CP} = 10.9, *o*-Ph), 133.6 (d, J_{CP} = 53.1, *i*-Ph), 130.9 (s, *p*-Ph), 128.7 (d, J_{CP} = 11.0, *m*-Ph), 127.4, 119.6, 88.1 (3 s, ReC*CCC*), 102.8 (s, $\mathit{C}_5(CH_3)_5$), 64.2 (s, OCH_3), 9.8 (s, $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ 21.0 (s).

[(η^5-C_5Me_5)Re(NO)(PPh_3)(CCCCC)Mn$(CO)_2$(η^5-C_5Cl_5)]$^+BF_4^-$ (21). This procedure was carried out in the dark. A Schlenk tube was charged with **16** (0.094 g, 0.089 mmol), toluene (10 mL), and hexane (8 mL) and cooled to −60 °C. For 1 min, BF_3 gas was bubbled through the solution. A dark solid precipitated. The solvent was removed via syringe. The solid was washed with hexane (3 × 5 mL), dried by oil pump vacuum, and extracted with CH_2Cl_2 (2 × 2 mL). The extract was filtered through a Celite pad (1 cm), and hexane (10 mL) was added. The dark brown precipitate was collected by filtration, washed with hexane (2 × 2 mL), and dried by oil pump vacuum to give **21** (0.051 g, 0.046 mmol, 52%). IR (cm^{-1}, CH_2Cl_2/KBr): ν_{CO} 2045/2042 s, 2008/1996 m, ν_{CCCCC} 1953/1948 vs, ν_{NO} 1718/1705 s. UV−vis (2.4×10^{-5} M):[48] 262 sh (19 000), 370 (12 500), 442 sh (33 000), 480 (60 500), 634 (4800). MS (3-NBA/CH_2Cl_2):[49] 1022 (M^+, 4%), 690 ((C_5Me_5)Re(NO)(PPh_3)$(C_5O)^+$, 12%), 614 ((C_5Me_5)Re(NO)$(PPh_3)^+$, 100%); no other peaks above 425 of >12%.

NMR (CD_2Cl_2):[50] ^1H 7.64−7.49 (m, 9H of $3C_6H_5$), 7.48−7.36 (m, 6H of $3C_6H_5$), 1.95 (s, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ (−20 °C) 296.2 (s, C=Mn), 220.8 (s, CO), 220.2 (s, CO), 218.4 (d, J_{CP} = 12.5, Re*C*C), 133.2 (d, J_{CP} = 10.9, *o*-Ph), 132.4 (s, *p*-Ph), 129.5 (d, J_{CP} = 10.6, *m*-Ph), 119.1, 110.6, 107.0 (3 s, C*CCC*C), 108.5 (s, $\mathit{C}_5(CH_3)_5$), 100.4 (s, C_5Cl_5), 10.0 (s, $C_5(\mathit{C}H_3)_5$); $^{31}P\{^1H\}$ 20.5 (s).

Crystallography. A hexane/CH_2Cl_2 solution of **3** was slowly concentrated by evaporation. A concentrated CH_2Cl_2 solution of **9** was layered with hexane. Dark red prisms of **3** and **9**·$(CH_2Cl_2)_{0.5}$ formed. Data were collected on a CAD4 diffractometer as outlined in Table 1. Cell constants were obtained from 25 reflections with $30° < 2\theta < 40°$ and $10° < 2\theta < 30°$, respectively. The space groups were determined from systematic absences (none) and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (Ψ scans) corrections were applied. The structures were solved by standard heavy-atom techniques with the SDP/VAX package.[52] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions for **3** were calculated and added to the structure factor calculations but were not refined. Hydrogen atom positions were not calculated for **9**. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[53] Other data are given in the Supporting Information (−125 °C structure of **9**·$(CH_2Cl_2)_{0.5}$) and that of a communication (16 °C structures of **3** and **9**·$(CH_2Cl_2)_{0.5}$).[4a]

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Supporting Information Available: Experimental details for **8** and **19** and tables of atomic coordinates and anisotropic thermal parameters (−125 °C) for **9**·$(CH_2Cl_2)_{0.5}$ (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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