2008 *Organometallics* **1997,** *16,* 2008−2015

Articles

Synthesis, Structure, and Reactivity of Polymetallic C_3OMe Complexes of the Formula $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})M_m(CO)_n$ ($M/m/n$ = Re/2/9, Os/3/11): A New Form of Coordinated Carbon in Which a C_3 Chain Links Two Metals and Spans a Third

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Received January 27, 1997⊗

Reaction of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CLi)$ with $Re_2(CO)_{10}$ and then $Me_3O^+BF_4^-$ gives the trirhenium C_3OMe complex *cis*-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Re(CO)_4Re(CO)_5$ (**3**, 92%). An analogous reaction with $Os_3(CO)_{12}$ gives heterotetrametallic $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Os_3(CO)_{11}$ (**4**, 87%). NMR, IR, and crystallographic data (**4**) show substantial contributions by $^+Re{=}C{=}C{=}C(OMe){-}M^-$ resonance forms. Reaction of **3** and excess BF_3 gas in toluene precipitates $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CCC)(Re(CO)_4)Re(CO)_5]^+BF_4^-$ (**5**, 64%). A crystal structure shows a slightly bent C_3 moiety (152(4)°) that binds a rhenium on each end and spans a third. NMR, IR, and bond length data show that **5** is best viewed as a completely metalated π propargyl or $PRe{=}\boldsymbol{C}\boldsymbol{C}{\equiv}\boldsymbol{C}{-}Re(CO)_5$ adduct of $Re(CO)_4$. It is likely derived by initial methoxide abstraction from **3** to give a ReCCCReRe species, followed by rearrangement. Reaction of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CLi)$ with $Re_2(CO)_{10}$ and then $Me_3O^+BF_4^-$ gives the C_5OMe complex *cis*-$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC(OMe){=})Re(CO)_4Re(CO)_5$ (**8**, 44%). When **4** or **8** are treated with BF_3 gas, C_x complexes are not detected.

Transition metals and elemental carbon (C_x) exhibit numerous, structurally diverse binding modes, the coordination chemistry of which has become the focus of particular attention. Major classes of complexes include metal cluster carbides,[1,2] C_x chains that link two metals,[2,3] *cyclo*carbon adducts,[4] and fullerene derivatives.[5] These compounds exhibit many fascinating properties and have the potential for practical applications as materials and in catalysis.

Metal cluster carbides were the first class of C_x complexes to be recognized.[6] The pioneering efforts of Shriver and Bradley established that unique reactivity modes are associated with clusters that bear *exposed* carbon atoms.[1,7,8] Furthermore, such complexes provide homogeneous models for surface-bound intermediates in heterogeneously catalyzed commodity chemical transformations. Indeed, some interstitial carbides are themselves effective catalysts.[9] Thus, we sought to develop new approaches to polymetallic complexes containing unusual types of chemically accessible C_x fragments.

We have discovered that certain transition metal ethynyl and butadiynyl complexes, $L_nMC{\equiv}CH$ and $L_nMC{\equiv}CC{\equiv}CH$, can be lithiated to give the C_2Li and C_4Li species $L_nMC{\equiv}CLi$ (**I**) and $L_nMC{\equiv}CC{\equiv}CLi$.[10] These have proven to be valuable synthons that can be derivatized by carbon, main-group element, and transition metal electrophiles in high yields.[10,11] Thus, as sketched in Scheme 1, we sought to gain access to polynuclear C_3 adducts by first elaborating **I** to Fischer carbene complexes derived from polymetallic carbonyl compounds (**II**). This has abundant precedent with

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

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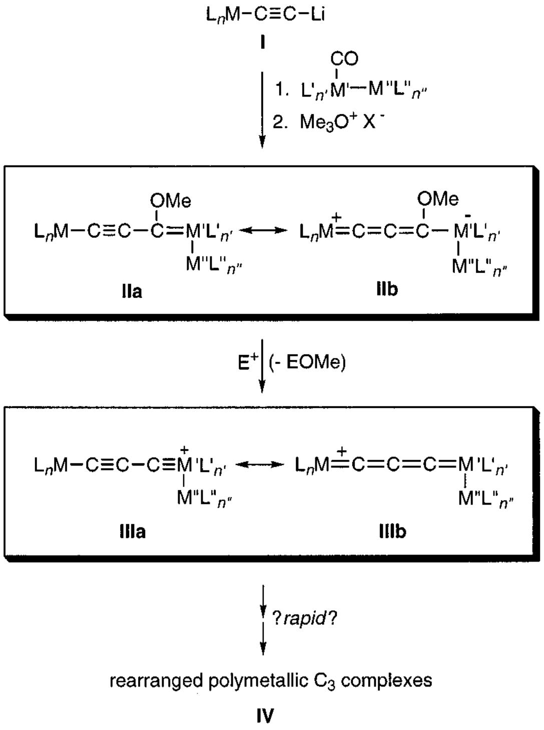
S0276-7333(97)00055-1 CCC: $14.00

Scheme 1. Planned Route to Polymetallic C_3 Complexes

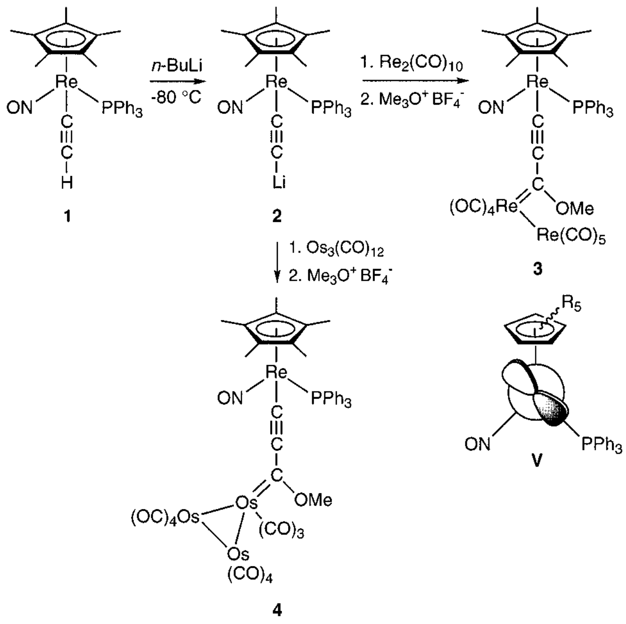


organic lithium acetylides, RC≡CLi, many of which have been similarly converted to monometallic alkynyl carbene complexes RC≡CC(OMe)=M′L′$_{n'}$.[12] Carbene complexes can exhibit a variety of resonance forms, two types of which are illustrated in Scheme 1 (**IIa**,**b**).

The alkoxy groups in many Fischer carbene complexes can be abstracted by electrophiles, giving Fischer carbyne complexes.[13] Depending upon the recipe, either cationic or neutral products are obtained. In the case of **II**, loss of a methoxide anion would initially give the C_3 complex **III**. At the outset of this study, C_3 complexes of any description were unknown.[14] As described in separate reports, this protocol has been reduced to practice with monometallic carbonyl complexes, giving isolable $[L_nMCCCM'L'_{n'}]^+$ species.[11]

Although **III** can also exhibit more than one resonance form (**IIIa**,**b**), the MCC***C***M′ carbon should in all cases be electrophilic. We thought that the proximity of this carbon and the third metal center (M″) should facilitate further chemistry—such as isomerization to give a μ_2 terminus. In this paper, we report that additional reactions indeed ensue. In one instance, this strategy affords a complex in which a C_3 chain is bound to a metal on each end and spanned by a third. A portion of this work has been communicated previously.[15]

Scheme 2. Syntheses of C_3OMe Complexes



Results

C_3OMe Complexes. As shown in Scheme 2, the ethynyl complex (η^5-C_5Me_5)Re(NO)(PPh$_3$)(C≡CH) (**1**) and *n*-BuLi were combined in THF at −80 °C to generate the ReC_2Li species (η^5-C_5Me_5)Re(NO)(PPh$_3$)(C≡CLi) (**2**) reported earlier.[10a] Then $Re_2(CO)_{10}$ was added. The mixture was allowed to warm and was subsequently added to Me_3O^+ BF_4^- at −80 °C. A chromatographic workup gave the orange trirhenium alkynyl carbene complex *cis*-(η^5-C_5Me_5)Re(NO)(PPh$_3$)(C≡CC(OMe)=)Re(CO)$_4$Re(CO)$_5$ (**3**) in 92% yield. Complex **3** and other new compounds described below were characterized by microanalysis and NMR (^{1}H, ^{13}C, ^{31}P), IR, UV−vis, and mass spectroscopies. Data are summarized in the Experimental Section. Many properties of **3** were similar to those of the dirhenium carbene complexes RC(OMe)=Re(CO)$_4$Re(CO)$_5$, which have been analogously prepared by Fischer.[16]

The structure of **3** was supported by a variety of data. The mass spectrum gave a strong molecular ion. The IR spectrum exhibited a strong band at 2097 cm^{-1} that had no counterpart in Fischer's dirhenium carbene complexes. Hence, this was assigned as the $\nu_{C\equiv C}$ absorption. A ^{13}C NMR spectrum (−50 °C, C_7D_8) showed one signal for the four equivalent CO ligands of the Re(CO)$_5$ moiety (196.6 ppm) and four signals for the remaining CO ligands (200.7, 200.2, 196.1, 192.1; 1:2:1:1). This requires a *cis* C=Re-Re stereochemistry. The Re***C***≡***CC***=Re resonances were located at 202.7 (d, J_{CP} = 11.2 Hz), 156.4, and 240.5 ppm, respectively. However, the ***C***=Re signal was not as far downfield as in Fischer's complexes (377−318 ppm).[16b,c] Also, the Re***C***≡ signal and IR ν_{NO} value (1664 cm^{-1}) were between those of neutral alkynyl complexes (η^5-C_5Me_5)Re(NO)(PPh$_3$)(C≡CR) (98−86 (d, J_{CP} = 16−18 Hz); 1629−1637 cm^{-1})[10a] and cationic vinylidene complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(=C=CHR)]^+$ BF_4^- (329−330

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[12] (a) For an extensive reference list, see refs 2−7 in Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Pertierra, P. *J. Am. Chem. Soc.* **1996**, *118*, 695. (b) Aumann, R.; Meyer, A. G.; Fröhlich, R. *Organometallics* **1996**, *15*, 5018 and references therein.

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(d, J_{CP} = 10−11 Hz); 1681−1728 cm^{-1}).[10a,17] These trends suggest a significant structural contribution by a zwitterionic $^{+}Re{=}C{=}C{=}C(OMe){-}Re^{-}$ resonance form, as shown with **IIb** in Scheme 1. Accordingly, the 16 valence electron fragment $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)]^+$ is a strong π donor, with the d orbital HOMO shown in **V** (Scheme 2).[17]

Analogs with increased metal nuclearities were sought next. Thus, as shown in Scheme 2, the ReC_2Li complex **2** was similarly treated with $Os_3(CO)_{12}$ and then Me_3O^+ BF_4^-. Workup gave the orange heterotetrametallic C_3-OMe complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Os_3(CO)_{11}$ (**4**) in 87% yield. The structure was again supported by NMR, IR, and mass spectrometric data. A ^{13}C NMR spectrum showed $Re\boldsymbol{C}{\equiv}\boldsymbol{C}\boldsymbol{C}{=}Os$ signals at 198.8 (d, J_{CP} = 11.9 Hz), 154.9, and 209.4 ppm. However, the IR $\nu_{C\equiv C}$ band overlapped with the many ν_{CO} absorptions and could not be assigned. As with **3**, the $Re\boldsymbol{C}{\equiv}$ ^{13}C NMR signal and IR ν_{NO} value (1666 cm^{-1}) were in an intermediate range, suggesting an appreciable ground state contribution by a zwitterionic $^{+}Re{=}C{=}C{=}C(OMe){-}(Os_3)^{-}$ resonance form.

Interestingly, simple Fischer carbene complexes of $Os_3(CO)_x$ fragments have proved elusive and to our knowledge unknown for $x = 11$. In particular, the oxygen alkylation step appears to be susceptible to a variety of complications.[18] In view of the scant synthetic precedent and the two possible neutral and zwitterionic valence formulations, the crystal structure of **4** was determined as outlined in Table 1 and the Experimental Section. Key bond lengths and angles are listed in Table 2. The molecular structure, shown in Figure 1, confirms the assignment. The carbene ligand occupies an equatorial position analogous to the majority of structurally characterized $Os_3(CO)_{11}(L)$ complexes.[19]

Importantly, the ReC bond (1.983(7) Å) is shorter than those in other neutral complexes of the formula $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CX)$ (2.079(9), 2.037(5), 2.032(7) Å; X = $Pd(PEt_3)_2Cl$,[10b] $C{\equiv}C(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)$,[20] $C{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$[21]) but longer than those in the cationic cumulenic C_x complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)({=}C{=}C{=}C{=})Mn(CO)_2(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (1.91(1)−1.93(1) Å)[11a,c] and $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)({=}C{=}C{=}C{=}C{=})(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]^{2+}(PF_6^-)_2$ (1.909(7)−1.916(7) Å).[20,22] Also, a *bi*metallic rhenium/tungsten C_3OMe complex, $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})W(CO)_5$, has been structurally characterized as part of another investigation.[11a,c] It exhibits ReC, $Re\boldsymbol{C}{\equiv}\boldsymbol{C}$, and $ReC{\equiv}\boldsymbol{C}\boldsymbol{C}$ bond lengths very close to those of **4** (1.973(7) vs 1.983(7) Å; 1.23(1) vs 1.238(9) Å; 1.38(1) vs 1.364(10) Å). The $Re\boldsymbol{C}{\equiv}\boldsymbol{C}$ distances are slightly long for triple bonds, whereas the $ReC{\equiv}\boldsymbol{C}\boldsymbol{C}$ distances are slightly short for sp/sp^2 single bonds.[20,21]

Unsaturated ligands commonly adopt conformations that maximize overlap of their acceptor orbitals with the rhenium fragment d orbital HOMO shown in **V** (Scheme 2). Thus, in alkylidene and vinylidene complexes, the planes of the =CRR′ termini define ca. 90° and 0° angles, respectively, with the P−Re=C plane. Importantly, the P−Re−C(41) plane of **4** is nearly orthogonal to the Os(1)−C(43)−O(2) plane (80.7(2)°). Analogous conformations would be expected of =C=C=

Table 1. Summary of Crystallographic Data for $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Os_3(CO)_{11}$ (4) and $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu_3\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CCC)(Re(CO)_4)Re(CO)_5]^+BF_4^-$ (5)

compound	**4**	**5**
mol formula	$C_{43}H_{33}NO_{13}Os_3PRe$	$C_{40}H_{30}BF_4NO_{10}PRe_3$
mol wt	1559.47	1361.06
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
cell dimens (16 °C)		
a, Å	9.060(2)	12.241(3)
b, Å	15.275(5)	11.921(2)
c, Å	18.699(3)	29.797(6)
α, deg	111.01(2)	
β, deg	96.26(2)	93.08(2)
γ, deg	100.58(2)	
V, Å^3	2331.1(10)	4341.7(11)
Z	2	4
d_{calcd}, g/cm^3	2.222	2.082
d_{found}, g/cm^3 (22 °C)		2.105
cryst dimens, mm	0.36 × 0.29 × 0.22	0.16 × 0.15 × 0.05
diffractometer	CAD4	CAD4
radiation (Å)	Mo Kα (0.709 30)	Mo K_α (0.709 30)
data collection method	$\theta{-}2\theta$	$\theta{-}2\theta$
scan speed, deg/min	variable	variable
no. of reflns measd	7837	8337
range/indices (*h*,*k*,*l*)	+1 to +10, −17 to 17, −21 + 21	0 to +14, 0 to +14, −32 to +32
2θ limit, deg	4.0−48.0	4.0−50.0
total unique data	7309	7947
abs coeff, cm^{-1}	10.83	85.65
min transmission, %	59.4	49.4
max transmission, %	99.9	99.9
no. of variables	565	542
goodness of fit	1.083	0.766
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0280	0.0425
$R_w = \sum\|\|F_o\| - \|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$	0.0439	0.0485
Δ/σ (max)	0.000	0.010
Δρ (max), e/Å^3	1.065, −1.125	0.810, 0.846

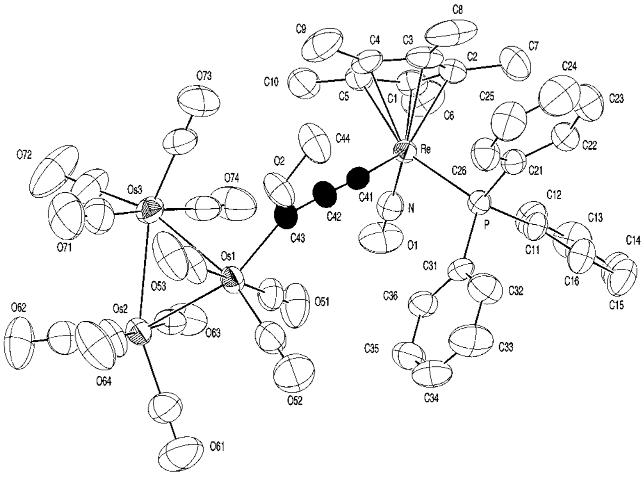

Figure 1. Molecular structure of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC(OMe){=})Os_3(CO)_{11}$ (**4**).

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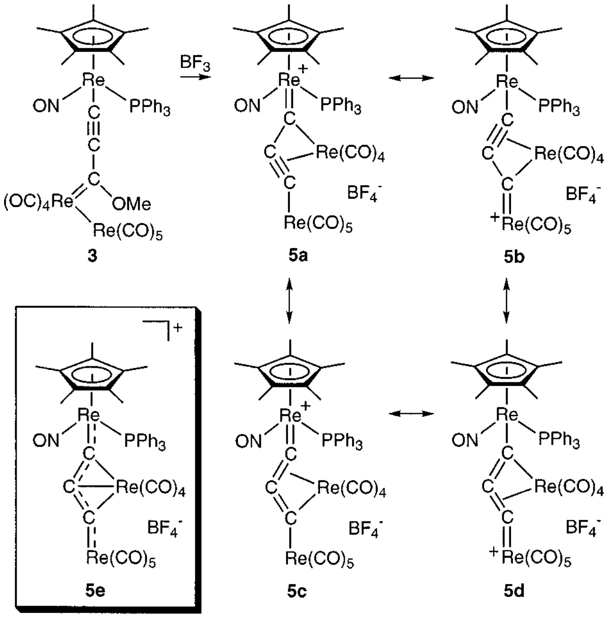
[21] Bartik, B.; Dembinski, R.; Bartik, T.; Arif, A. M.; Gladysz, J. A. *New J. Chem.* **1997**, in press.

[22] The rhenium−carbon bond lengths in two *cyclopentadienyl* alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CRR')]^+PF_6^-$ are 1.945(4) and 1.949(6) Å. See: Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 729 and references therein.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

Re−N	1.756(7)	Os(1)−Os(3)	2.8682(6)
Re−P	2.382(2)	Os(1)−Os(2)	2.8985(7)
N−O(1)	1.196(8)	Os(2)−Os(3)	2.8854(8)
Re−C(41)	1.983(7)	Re−C(1)	2.302(7)
Os(1)−C(43)	2.042(7)	Re−C(2)	2.311(7)
C(41)−C(42)	1.238(9)	Re−C(3)	2.329(8)
C(42)−C(43)	1.364(10)	Re−C(4)	2.323(8)
O(2)−C(43)	1.347(9)	Re−C(5)	2.292(7)
O(2)−C(44)	1.449(10)	C−O(avg)	1.135
N−Re−P	93.2(2)	C(43)−Os(1)−Os(2)	155.5(2)
Re−N−O(1)	171.5(6)	C(43)−O(2)−C(44)	119.2(6)
P−Re−C(41)	86.9(2)	O(2)−C(43)−C(42)	118.8(7)
N−Re−C(41)	97.8(3)	O(2)−C(43)−Os(1)	116.9(5)
C(41)−C(42)−C(43)	174.2(8)	Os(1)−Os(3)−Os(2)	60.50(2)
Re−C(41)−C(42)	174.5(6)	Os(3)−Os(1)−Os(2)	60.04(2)
C(42)−C(43)−Os(1)	124.2(6)	Os(3)−Os(2)−Os(1)	59.46(2)
C(43)−Os(1)−Os(3)	96.4(2)	Os−C−O(avg)	177.8

Scheme 3. Synthesis of a Re_3C_3 Complex



CRR′ adducts of **V**. On the basis of all the preceding structural and spectroscopic data, we conclude that the electronic ground state of **4** is almost halfway between those represented by neutral and zwitterionic resonance forms **IIa** and **IIb**.

C_3, C_5OMe, and Other Complexes. Fischer found that the dirhenium carbene complexes RC(OMe)=Re(CO)$_4$Re(CO)$_5$ and Al_2X_6 react to give cationic carbyne complexes $[(RC{\equiv})Re(CO)_4Re(CO)_5]^+AlX_4^-$.[16c] These also exhibit downfield ***C***≡Re ^{13}C NMR signals (e.g., 356 ppm). We sought to similarly abstract the methoxide group from **3**. As shown in Scheme 3, a toluene solution of **3** was treated with excess BF_3 gas.[23] A precipitate formed, and workup gave a yellow powder (**5**) in 67% yield that was thermally stable to 145−150 °C. Microanalytical and mass spectrometric data were consistent with a PReC≡CC≡ReRe species such as **IIIa**. A ^{13}C NMR spectrum showed three signals that could be attributed to the C_3 moiety (297.1 (d, J_{CP} = 10 Hz), 146.6 (s), 95.1 (s)). However, the downfield signal was a *doublet*, with a phosphorus coupling diagnostic of a carbon bonded to the cyclopentadienyl rhenium moiety.

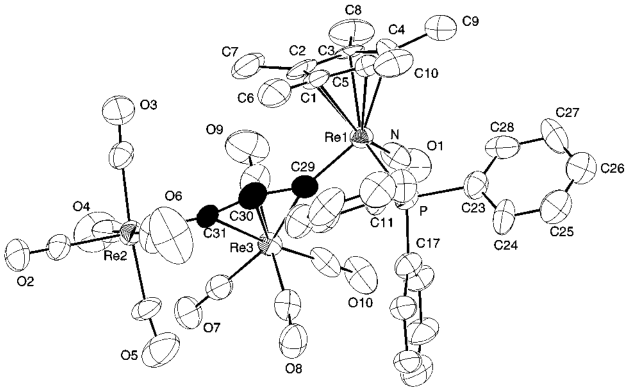


Figure 2. Structure of the cation of $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-CCC})(Re(CO)_4)Re(CO)_5]^+BF_4^-$ (**5**).

The other signals were too far upfield for a ReC≡C***C***≡ReRe carbon.

Thus, reddish-brown plates of **5** were grown, and the crystal structure was determined as outlined in Table 1 and the Experimental Section. Key bond lengths, bond angles, and torsion angles are given in Table 3, and the cation is shown in Figure 2. Accordingly, **5** can be represented by the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-CCC})(Re(CO)_4)Re(CO)_5]^+BF_4^-$. It features a C_3 chain that is bent at a 152(4)° angle, anchored by a $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$ moiety on one end, a Re(CO)$_5$ moiety on the other end, and spanned by a Re(CO)$_4$ group. Possible mechanisms of formation are discussed below.

The structure of **5** can be analyzed in terms of two resonance forms with $^+$Re=C−C≡C−Re backbones, as illustrated by **5a**,**b** in Scheme 3. Since the $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$ fragment is a much stronger π donor than Re(CO)$_5$, the former would be expected to dominate. The pattern of rhenium−carbon and carbon−carbon bond lengths is indeed best modeled by **5a** (Re(1)−C(29) vs Re(2)−C(31), 1.94(3) vs 2.09(4) Å; C(29)−C(30) vs C(31)−C(30), 1.41(6) vs 1.28(5) Å). The Re(1)−C(29) and Re(2)−C(31) distances are also very close to the reference values for double and single bonds given above. However, the estimated standard deviations are large, despite the good *R* values in Table 1. This diminishes the significance of the differences. Regardless, the dominance of **5a** is also supported by the IR ν_{NO} value (1692−1681 cm^{-1}), which indicates a much more cationic $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)$ terminus than in the above C_3OMe complexes, as well as the downfield PRe***C*** NMR signal.

It is also possible to formulate **5** with $^+$Re=C=C=C−Re backbones, as shown by resonance forms **5c**,**d** in Scheme 3. On the basis of the π donor strengths of the rhenium fragments, **5c** would be expected to dominate. However, substantial contributions by **5c** or **5d** would be evidenced by more nearly equal carbon−carbon bond lengths. Additional structures in which the Re(CO)$_4$ π bond is replaced by two σ bonds, as well as the delocalized representation **5e**, may also be written. The P−Re(1)−C(29)−C(30) torsion angle (−103(2)°) is similar to that in alkylidene complexes of **V**, consistent with the frontier orbital interactions discussed above and dominant PRe=C double bond character.

We sought to extend the preceding chemistry to longer carbon chains. Thus, as shown in Scheme 4, the butadiynyl complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CH)$

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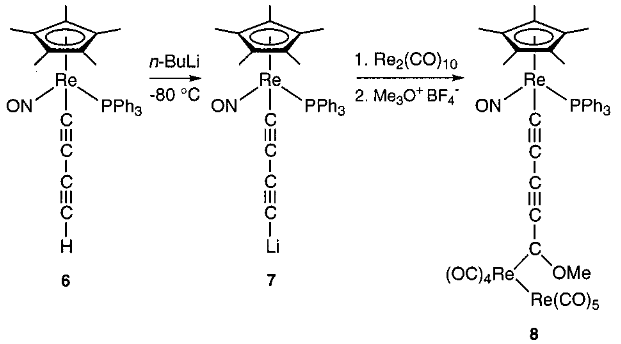
[23] For an earlier reference to a similar recipe, see: Handwerker, B. M.; Garrett, K. E.; Nagle, K. L.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 1562.

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in 5

Re(1)–P	2.440(9)	C(29)–C(30)	1.41(6)
Re(1)–N	1.73(3)	C(30)–C(31)	1.28(5)
N–O(1)	1.19(5)	Re(1)–C(1)	2.30(4)
Re(1)–C(29)	1.94(3)	Re(1)–C(2)	2.31(4)
Re(2)–C(31)	2.09(4)	Re(1)–C(3)	2.29(4)
Re(2)–C(32)	1.99(4)	Re(1)–C(4)	2.30(4)
Re(3)–C(29)	2.24(3)	Re(1)–C(5)	2.39(4)
Re(3)–C(30)	2.27(4)	C–O(avg)	1.14
Re(3)–C(31)	2.43(4)		
P–Re(1)–N	94(1)	Re(3)–C(29)–C(30)	73(2)
Re(1)–N–O(1)	169(3)	Re(3)–C(30)–C(29)	71(2)
P–Re(1)–C(29)	92(1)	Re(3)–C(30)–C(31)	81(2)
N–Re(1)–C(29)	94(2)	Re(3)–C(31)–C(30)	67(2)
Re(1)–C(29)–C(30)	140(3)	C(31)–Re(2)–C(32)	177(2)
C(29)–C(30)–C(31)	152(4)	C(29)–Re(3)–C(30)	36(2)
Re(1)–C(29)–Re(3)	145(2)	C(29)–Re(3)–C(31)	68(1)
Re(2)–C(31)–Re(3)	138(2)	C(30)–Re(3)–C(31)	31(1)
Re(2)–C(31)–C(30)	155(3)		
Re(1)–C(29)–C(30)–C(31)	−159(3)	C(29)–C(30)–C(31)–Re(2)	−178(2)
Re(1)–C(29)–C(30)–Re(3)	−164(2)	Re(3)–C(30)–C(31)–Re(2)	−173(3)
N–Re(1)–C(29)–C(30)	163(2)	P–Re(1)–C(29)–C(30)	−103(2)

Scheme 4. Synthesis of a C_5OMe Complex



(**6**) and *n*-BuLi were combined to generate the ReC_4Li species (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CLi) (**7**).[10b] Then, $Re_2(CO)_{10}$ and Me_3O^+ BF_4^- were added, as in the synthesis of the C_3OMe complex **3**. Workup gave the dark purple trirhenium butadiynyl carbene complex *cis*-(η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CC(OMe)=)Re(CO)$_4$-Re(CO)$_5$ (**8**) in 44% yield. Complex **8** was characterized analogously to **3**. The ^{13}C NMR pattern of the carbonyl ligands was identical, and IR spectra now showed two medium $\nu_{C\equiv C}$ bands (2101–2100, 2069–2073 cm^{-1}).

The IR ν_{NO} value of **8** was similar to that of **3** (1663–1662 vs 1664–1666 cm^{-1}), consistent with comparable rhenium charges and resonance form contributions. However, the PRe***C***≡ ^{13}C NMR signal was further upfield (182.1 vs 243.1 ppm) and the ***C***=Re signal was further downfield (263.7 vs 243.1 ppm), suggesting slightly less zwitterionic character. As shown in Figure 3, the UV–vis spectrum of **8** exhibited an intense long wavelength band that was (1) responsible for the purple color and (2) markedly red-shifted from that of **3** (568 vs 464 nm). Complex **5**, which is distinguished by a bent carbon chain of lower overall bond order, gave less intense absorptions. These patterns suggest transitions with appreciable metal-to-metal charge transfer character, and investigations are in progress with related compounds.[11c]

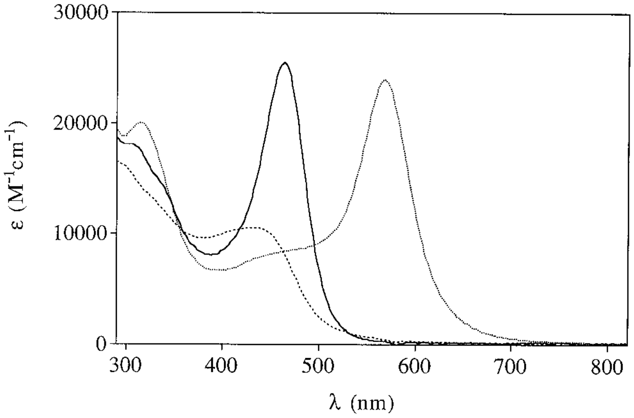
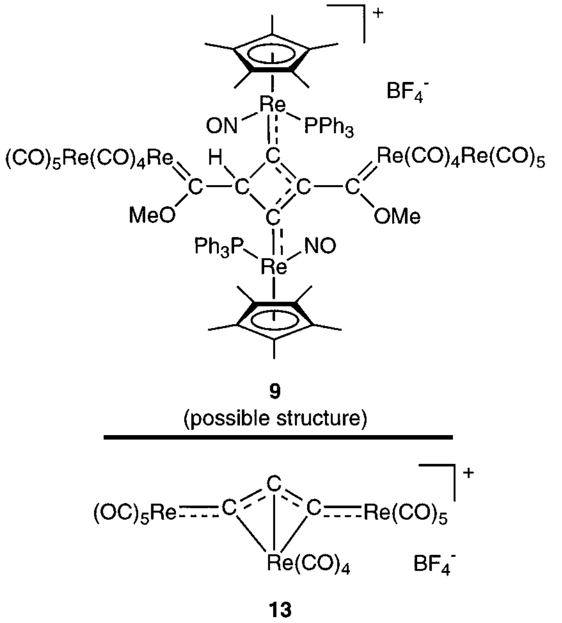


Figure 3. UV–vis spectra of **3** (—), **5** (- - -), and **8** (···) (CH_2Cl_2, 2.4–3.9 × 10^{-5} M).

Scheme 5. Other Polymetallic Products or Targets



Finally, **8** and the Re(C_3OMe)Os_3 adduct **4** were treated with BF_3 gas in toluene, analogous to the recipe used for the conversion of **3** to **5**. Powders again precipitated, but NMR analyses indicated that a multitude of products had formed. In the course of unsuccessful attempts to effect any type of clean methoxide ion abstraction, it was found that the reaction of **3** and excess $BF_3{\cdot}Et_2O$ in toluene gave an air-stable orange-red powder in high yield. Although the structure could not be definitively assigned from spectroscopic data, there were similarities with dirhenium cycloadducts previously prepared from alkynyl complexes of **V**−Me_5 and Lewis acids.[17,24] Thus, one possible formulation would be **9** (Scheme 5). This apparently quite general type of reaction,[25] the mechanism of which has been analyzed in detail,[17] could potentially complicate some efforts to implement the synthetic strategy in Scheme 1.

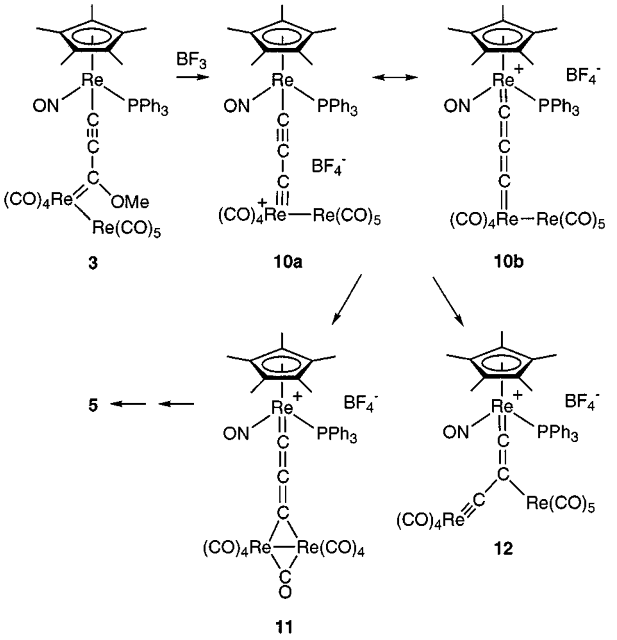
Discussion

The above C_3OMe and C_5OMe complexes represent previously unknown classes of polymetallic compounds. However, they are comprised of familiar structural components and accessed by precedented types of reactions that use newly available MC_2Li and MC_4Li building blocks (Schemes 2 and 4). The C_3 complex **5** also represents a previously unknown class of compounds but is structurally novel. Furthermore, it is accessed by a reaction with little if any precedent (Scheme 3).

We suggest that **5** forms along the general lines sketched in Scheme 6. Abstraction of the methoxide group would initially give a ReCCCReRe complex, for which resonance forms **10a** and **10b** are possible. Beck has isolated a related trimetallic C_1 complex with dirhenium and iron porphyrin termini, *trans*-(TPP)-Fe=C=Re(CO)$_4$Re(CO)$_5$.[30] Subsequently, the Re(CO)$_5$ rhenium in **10** must somehow become attached to the carbon chain. One possibility would be isomerization to a species in which the C_3 terminus bridges the rhenium−rhenium bond, such as **11**. Another would be a 1,3-sigmatropic shift of the Re(CO)$_5$ group in **10b** to give **12**. In either event, several additional steps would be required to form **5**. In our opinion, it is not possible to formulate a uniquely compelling pathway at this time.

Except for the issue of dominant resonance form, the C_3OMe and C_5OMe complexes have straightforward bonding descriptions. In the case of **5**, we favor analogies to π propargyl (RC≡C−CR′R″) complexes[26−29] or alkylidene-substituted, η^3-butenynyl derivatives (RC≡C−C=CR′R″).[29] Both exhibit resonance forms comparable to **5a−d** in Scheme 3. Thus, **5** may be viewed as an adduct of Re(CO)$_4$ and a π propargyl ligand in which all of the carbon or hydrogen substituents on the C_3 core have been replaced by the (η^5-C_5Me_5)Re(NO)(PPh$_3$) and Re(CO)$_5$ end groups.

Scheme 6. Possible Steps in the Formation of 5



Importantly, the bent C_3 linkage in **5** (152(4)°) directs all of the bonds of the central carbon to one side of a spatial plane. Such deformations have the potential for introducing considerable strain and reactivity, analogous to that associated with planar tetracoordinate carbon.[31,32] Indeed, this feature is common to all π propargyl complexes. However, it appears to have attracted little attention, even in theoretical analyses.[28] As noted in the introduction, metal carbide clusters with certain types of *exposed* carbon atoms show special reactivity, such as toward carbon monoxide.[1,7] Accordingly, nucleophiles readily attack the central carbon of cationic palladium and platinum π propargyl complexes.[26b] Hence, there would appear to be excellent prospects for addition reactions involving the central carbon of **5**.

In preliminary experiments, we combined **5** and PMe$_3$ or sodium methoxide in CH_2Cl_2 at −80 °C. When the samples were warmed to ca. −20 °C, a multitude of products formed, as assayed by ^{31}P NMR. This prompted concern that the sterically and electronically dissimilar termini in **5** might complicate or bias certain types of reactions. Thus, the fundamental chemical (and physical) properties of such trimetallic C_3 complexes would seemingly best be probed with symmetrical systems, as exemplified by the Re$_3$C$_3$ species **13** in Scheme 5.

We therefore sought to synthesize **13**. First, (CO)$_5$Re-

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(24) The product was a ca. 90:10 mixture of diastereomers, similar to the dirhenium cycloadducts.[17] IR (cm^{-1}, CH_2Cl_2): 2105 (s), 2045 (s), 1996 (vs), 1950 (s), 1741 (m), 1685 (w), 1570 (m). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2): 26.80 (s, major), 20.29 (s, minor). The mass spectrum showed ions derived from **3**, but none with six rheniums. The UV−vis spectrum showed intense bands at 400, 452, and 532 nm (CH_2Cl_2).[17]

(25) Fischer, H.; Leroux, F.; Roth, G.; Stumpf, R. *Organometallics* **1996**, *15*, 3723.

(26) Reviews: (a) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39. (b) Wojcicki, A. *New J. Chem.* **1994**, *18*, 61.

(27) The following recent full papers provide good lead references for this now-extensive literature: (a) Casey, C. P.; Selmeczy, A. D.; Nash, J. R.; Yi, C. S.; Powell, D. R.; Hayashi, R. K *J. Am. Chem. Soc.* **1996**, *118*, 6698. (b) Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164. (c) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 343.

(28) For MO analyses of π propargyl complexes see: Carfagna, C.; Deeth, R. J.; Green, M.; Mahon, M. F.; McInnes, J. M.; Pellegrini, S.; Woolhouse, C. B. *J. Chem. Soc., Dalton Trans.* **1995**, 3975.

(29) (a) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247. (b) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (c) McMullen, A. K.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1991**, *10*, 3421. (d) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T.; Bravo, M.; McKenna, C. E.; McKenna, M.-C. *J. Chem. Soc., Chem. Commun.* **1991**, 522. (e) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (f) Field, L. D.; George, A. V.; Purches, G. R.; Slip, I. H. M. *Organometallics* **1992**, *11*, 3019.

(30) Beck, W.; Knauer, W.; Robl, C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 318.

(31) For lead references to lithium-containing examples, see: Sorger, K.; Schleyer, P. v. R.; Fleischer, R.; Stalke, D. *J. Am. Chem. Soc.* **1996**, *118*, 6924.

(32) For lead references to transition metal-containing examples, see: (a) Poumbga, C. N.; Bénard, M.; Hyla-Kryspin, I. *J. Am. Chem. Soc.* **1994**, *116*, 8259. (b) Leoni, P.; Pasquali, M.; Pieri, G.; Albinati, A.; Pregosin, P. S.; Rüegger, H. *Organometallics* **1995**, *14*, 3143. (c) Erker, G.; Röttger, D. *Angew. Chem., Int. Ed. Engl.*, in press. (d) Radius, U.; Silverio, S. J.; Hoffmann, R.; Gleiter, R. *Organometallics* **1996**, *15*, 3737. (e) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1996**, 975.

($C\equiv CH$),[33] $(CO)_5Re(C\equiv CSiMe_3)$,[33b,34] and related alkynyl complexes were prepared.[35] It was hoped that these could be converted to the ReC_2Li complex $(CO)_5Re(C\equiv CLi)$, which would then (by analogy to Scheme 2) react with $Re_2(CO)_{10}$ and $Me_3O^+BF_4^-$ to give the precursor $(CO)_5Re(C\equiv CC(OMe)=)Re(CO)_4Re(CO)_5$. However, there was no practical way to monitor exploratory reactions at low temperature—in contrast to the ^{31}P NMR probe offered by the chiral rhenium endgroup. This hampered analysis, interpretation, and optimization at each stage. Consequently, the generation of $(CO)_5Re(C\equiv CLi)$ could not be definitively established, and attempts to obtain **13** were unsuccessful.[35]

Thus, a number of important reactivity issues remain to be resolved. It will also be of interest to extend the synthesis of **5** in Scheme 3 to other M_3C_3 complexes or the general strategy in Scheme 1 to new types of C_3 species. For example, the $Re(C_3OMe)Os_3$ complex **4** cannot give a product comparable to **5** but might react with an appropriate electrophile to yield another type of ReC_3Os_3 adduct. Indeed, a variety of routes to new classes of cluster-containing C_x complexes are under active investigation. Syntheses of compounds in which even-membered C_x chains span chiral rhenium and triosmium end groups have recently been developed and will be reported in the near future.[36]

Experimental Section

General Data. General procedures and instrumentation have been described previously.[10b] Any reagent or solvent not specified earlier was obtained from common commercial sources and used without purification.

***cis*-($\boldsymbol{\eta^5}$-$\mathbf{C_5Me_5}$)Re(NO)(PPh$_3$)(C≡CC(OMe)=)Re(CO)$_4$Re(CO)$_5$ (3).** A Schlenk tube was charged with $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C\equiv CH)$ (**1**;[10a] 0.096 g, 0.15 mmol) and THF (5 mL) and cooled to −80 °C (acetone/CO_2). Then *n*-BuLi (0.095 mL, 2.46 M in hexane) was added with stirring. After 1 h, a solution of $Re_2(CO)_{10}$ (0.11 g, 0.17 mmol) in THF (5 mL) was added by cannula. After 1 h, the cold bath was removed. After 0.5 h, the orange solution was transferred via cannula to a Schlenk flask that had been charged with $Me_3O^+\ BF_4^-$ (0.068 g, 0.45 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 solution was concentrated to ca. 0.5 mL. Hexane (10 mL) was added. Chromatography (N_2, Florisil washed with aqueous NH_4OH; hexane → 5:1 v/v hexane/THF) gave a yellow-orange band. Solvent was removed by oil-pump vacuum to give **3** as an orange powder (0.181 g, 0.138 mmol, 92%); mp 92−94 °C (dec). Anal. Calcd for $C_{41}H_{33}NO_{11}PRe_3$: C, 37.73; H, 2.55. Found: C, 37.67; H, 2.63.

IR (cm^{-1}, CH_2Cl_2/KBr): $\nu_{C\equiv C}$ 2097/2095 (s/s), ν_{CO} 2035/2033 (s/s), 1988/1981 (vs/vs), 1931/1927 (s/vs), ν_{NO} 1664/1666 (s/s). ^1H NMR (δ, C_6D_6): 7.50−7.43 (m, 6H of 3Ph), 7.10−6.95 (m, 9H of 3Ph), 3.33 (s, OCH_3), 1.55 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (ppm, C_6D_6): 243.1 (s, Re=C), 202.5 (d, J_{CP} = 13.6 Hz, $Re\boldsymbol{C}\equiv C$), 201.9 (s, CO), 200.0 (s, CO), 196.5 (br, CO), 195.9 (s, CO), 191.9 (s, CO), 155.8 (s, $ReC\equiv\boldsymbol{C}$), 133.8 (d, J_{CP} = 11.0 Hz, *o*-Ph), 130.9 (d, J_{CP} = 2.6 Hz, *p*-Ph), 128.7 (d, J_{CP} = 10.8 Hz, *m*-Ph), 103.5 (s, $\boldsymbol{C}_5(CH_3)_5$), 62.3 (s, OCH_3), 10.0 (s, $C_5(\boldsymbol{C}H_3)_5$).[37] $^{13}C\{^1H\}$ NMR (C_7D_8, −50 °C, partial data): 240.5 (s, Re=C), 202.7 (d, J_{CP} = 11.2 Hz, $Re\boldsymbol{C}\equiv C$), 200.7 (s, 1CO), 200.1 (s, 2CO), 196.6 (s, 4CO), 196.1 (s, 1CO), 192.1 (s, 1CO), 156.4 (s, $ReC\equiv\boldsymbol{C}$), 103.2 (s, $\boldsymbol{C}_5(CH_3)_5$), 62.3 (s, OCH_3), 9.7 (s, $C_5(\boldsymbol{C}H_3)_5$). $^{31}P\{^1H\}$ NMR (ppm, C_6D_6): 22.1 (s). UV−vis (nm (ϵ, $M^{-1}cm^{-1}$), 3.1×10^{-5} M in CH_2Cl_2): 232 (53 000), 276 (sh, 21 000), 304 (18 000), 342 (sh, 14 000), 464 (26 000). MS (positive Cs−FAB, tetraglyme/benzene):[38] 1305 (M^+, 81), 1274 ($M^+ - CO$, 35), 1246 ($M^+ -$ 2CO, 27), 952 ($M^+ - Re(CO)_6$, 45), 922 ($M^+ - Re(CO)_7$, 58), 682 ($M^+ - Re_2(CO)_9$, 100), 614 ($(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)^+$, 35); no other peaks above 225 of >30%.

($\boldsymbol{\eta^5}$-$\mathbf{C_5Me_5}$)Re(NO)(PPh$_3$)(C≡CC(OMe)=)Os$_3$(CO)$_{11}$ (4). A Schlenk flask was charged with **1** (0.035 g, 0.056 mmol), THF (15 mL) and hexane (15 mL), and cooled to −45 °C (acetonitrile/CO_2). Then *n*-BuLi (0.027 mL, 2.5 M in hexane) was added with stirring. After 20 min, a solution of $Os_3(CO)_{12}$ (0.077 g, 0.085 mmol) in THF (5 mL) was added by cannula. After 20 min, the cold bath was removed. After 3 h, the solution was cooled to −80 °C and transferred by cannula to a Schlenk flask that had been charged with $Me_3O^+\ BF_4^-$ (0.022 g, 0.150 mmol) and cooled to −80 °C. The mixture was stirred for 1 h, and the cold bath was removed. After 1 h, the solvent was removed by oil-pump vacuum. Column chromatography of the residue (Florisil washed with aqueous NH_4OH; 4:1 v/v hexane/THF) gave an orange band that was further purified by thin layer chromatography (silica gel, 2:1 v/v hexane/CH_2Cl_2). The orange band was extracted with CH_2Cl_2. The extract was concentrated (ca. 1 mL), and hexane was added (10 mL). The solvent was removed by oil-pump vacuum to give **4** as an orange powder, retaining ca. 0.3 equiv of hexane (0.075 g, 0.045 mmol, 87%). A CH_2Cl_2 solution of **4** was layered with hexane in a sealed vial. This gave orange crystals that were used for X-ray analysis; mp 184−186 °C. Anal. Calcd. for $C_{43}H_{33}NO_{13}Os_3PRe$: C, 33.11; H, 2.13; N, 0.89. Found: C, 33.20; H, 2.15; N, 0.96.

IR (cm^{-1}, CH_2Cl_2): $\nu_{C\equiv C}$ and ν_{CO} 2097 (w), 2068 (m), 2031 (s), 2010 (vs), 1974 (m), 1929 (m); ν_{NO} 1664 (w). ^1H NMR (δ, C_6D_6): 7.54−7.49 (m, 6H of 3Ph), 7.10−7.01 (m, 6H of 3Ph), 6.96−6.83 (m, 3H of 3Ph), 3.18 (s, OMe), 1.55 (s, C_5Me_5).[39] $^{13}C\{^1H\}$ (ppm, C_6D_6): 209.4 (s, Os=C), 198.8 (d, J_{CP} = 11.9 Hz, ReC), 195.8, 185.8, 183.5, 182.3, 181.5, 179.0, 178.1, 175.3, 172.6, 172.5, 171.0 (s, 11CO), 154.9 (s, $ReC\equiv\boldsymbol{C}$), 133.7 (d, J_{CP} = 10.4 Hz, *o*-Ph), 131.0 (s, *p*-Ph), 128.8 (d, J_{CP} = 10.4 Hz, *m*-Ph), 103.7 (s, $\boldsymbol{C}_5(CH_3)_5$), 62.2 (s, OCH_3), 9.8 (s, $C_5(\boldsymbol{C}H_3)_5$).[37] $^{31}P\{^1H\}$ NMR (ppm, C_6D_6): 21.6 (s). MS (positive Cs−FAB, tetraglyme/benzene):[38] 1561 (M^+, 100), 1533 ($M^+ - CO$, 20), 1530 ($M^+ - OCH_3$, 14), 1505 ($M^+ -$ 2CO, 26), 1477 ($M^+ -$ 3CO, 33), 1449 ($M^+ -$ 4CO, 19), 1421 ($M^+ -$ 5CO, 10), 1393 ($M^+ -$ 6CO, 26); no other peaks above 1000 of >10%.

[($\boldsymbol{\eta^5}$-$\mathbf{C_5Me_5}$)Re(NO)(PPh$_3$)($\boldsymbol{\mu_3}$-$\boldsymbol{\eta^1{:}\eta^3{:}\eta^1}$-CCC)Re(CO)$_4$Re(CO)$_5$]$^+BF_4^-$ (5). A Schlenk tube was charged with **3** (0.13 g, 0.10 mmol) and toluene (15 mL) and was cooled to −45 °C. Then BF_3 gas was bubbled through the solution for 2 min. A dark red solid precipitated. The toluene 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 filtered through a medium frit into rapidly stirred ether (20 mL). The yellow precipitate was collected by filtration, washed with ether (2 × 2 mL), and dried by oil-pump vacuum to give **5** (0.087 g, 0.064 mmol, 64%); mp 145−150 °C (slow dec). Anal. Calcd for $C_{40}H_{33}BF_4NO_{10}PRe_3$: C, 35.30; H, 2.22. Found: C, 35.22; H, 2.25.

IR (cm^{-1}, CH_2Cl_2/KBr): ν_{CO} 2149/2151 (m/m), 2088/2086 (s/s), 2043/2034 (vs/vs), 1996/1994 (s/vs-sh), 1946/1932 (s/s); ν_{NO} 1692/1681 (s/s). ^1H NMR (δ, CD_2Cl_2): 7.55−7.28 (m, 3Ph), 1.84 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): 297.1 (d, J_{CP} = 9.8 Hz, $PRe\boldsymbol{C}C$), 195.5 (s, 1CO), 191.6 (s, 1CO), 186.0 (s, 1CO), 184.2 (s, 1CO), 180.8 (s, 1CO), 178.5 (s, 4CO), 146.6 (s,

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(37) The *ipso* C_6H_5 resonance was not observed.

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

(39) Some hexane is also present (1.26 (m), 0.87 (t); 0.31 equiv based upon integration). The mmol/yield calculation has been adjusted.

PReCC***C***), 133.3 (d, $J_{CP} = 11.5$ Hz, *o*-Ph), 132.6 (d, $J_{CP} = 2.3$ Hz, *p*-Ph), 129.8 (d, $J_{CP} = 11.3$ Hz, *m*-Ph), 108.2 (s, $\boldsymbol{C}_5(CH_3)_5$), 95.1 (s, PReC***C***C), 9.8 (s, $C_5(\boldsymbol{C}H_3)_5$).[37] $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2): 20.9 (s). UV-vis (nm (ϵ, $M^{-1}cm^{-1}$), 2.4×10^{-5} M in CH_2Cl_2): 232 (52 000), 268 (sh, 22 000), 300 (sh, 16 000), 344 (sh, 12 000), 432 (11 000). MS (positive Cs−FAB, tetraglyme/CH_2Cl_2):[38] 1274 (M^+, 54), 1246 ($M^+ - CO$, 100), 1218 ($M^+ - 2CO$, 42); no other peaks above 225 of >35%.

***cis*-($\boldsymbol{\eta^5}$-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CC(OMe)=)Re-$(CO)_4Re(CO)_5$ (8).** A Schlenk tube was charged with (η^5-C_5Me_5)Re(NO)(PPh_3)(C≡CC≡CH) (**6**;[10b] 0.035 g, 0.053 mmol) and THF (5 mL) and was cooled to −80 °C. Then *n*-BuLi (0.028 mL, 2.5 M in hexane) was added with stirring. After 1 h, a solution of $Re_2(CO)_{10}$ (0.052 g, 0.079 mmol) in THF (3 mL) was added by cannula. After 1 h, the cold bath was removed. After 1.5 h, the orange solution was transferred via cannula to a Schlenk flask that had been charged with $Me_3O^+ BF_4^-$ (0.025 g, 0.16 mmol) and cooled to −80 °C. The mixture was stirred for 1 h, and the cold bath was removed. The solution was allowed to reach room temperature, and then concentrated to ca. 2 mL. Hexane (10 mL) was added. Chromatography (N_2, Florisil washed with aqueous NH_4OH; hexane → 2:1 v/v hexane/THF) gave a deep purple band. The solvent was removed by oil-pump vacuum to give **8** as a dark purple powder (0.031 g, 0.023 mmol, 44%); mp 194−196 °C. Anal. Calcd for $C_{43}H_{33}NO_{11}PRe_3$: C, 38.85; H, 2.48. Found: C, 38.79; H, 2.56.

IR (cm^{-1}, CH_2Cl_2/KBr): $\nu_{C≡C}$ 2101/2100 (m), 2069/2073 (m); ν_{CO} 2047/2044 (s), 2030/2029 (vs), 1990/1984 (vs), 1958/1956 (s), 1924/1922 (s); ν_{NO} 1663/1662 (s/s). ^1H NMR (ppm, C_6D_6): 7.56−7.48 (m, 6H of 3Ph), 7.08−6.99 (m, 9H of 3Ph), 3.37 (s, OCH_3), 1.50 (s, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (ppm, C_6D_6): 263.7 (s, Re=C), 203.7 (s, CO), 199.1 (s, CO), 198.9 (s, CO), 196.4 (s, CO), 190.9 (s, CO), 182.1 (d, $J_{CP} = 13.8$ Hz, Re***C***≡C), 133.9 (d, $J_{CP} = 10.8$ Hz, *o*-Ph), 130.9 (d, $J_{CP} = 2.6$ Hz, *p*-Ph), 128.7 (d, $J_{CP} = 10.8$ Hz, *m*-Ph), 120.0, 101.9, 92.2 (3s, ReC≡***CC***≡***C***), 102.8 (s, $\boldsymbol{C}_5(CH_3)_5$), 64.2 (s, OCH_3), 9.8 (s, $C_5(\boldsymbol{C}H_3)_5$).[37] $^{31}P\{^1H\}$ NMR (ppm, C_6D_6): 20.8 (s). UV−vis (nm (ϵ, $M^{-1}cm^{-1}$), 3.9×10^{-5} M in CH_2Cl_2): 232 (50 800), 262 (sh, 30 700), 314 (20 700), 476 (8 000), 568 (24 500). MS (positive Cs−FAB, 3-NBA/benzene):[38] 1329 (M^+, 20), 1244 ($M^+ - 3CO$, 55), 1216 ($M^+ - 4CO$, 100), 1188 ($M^+ - 5CO$, 63), 614 ((η^5-C_5Me_5)Re(NO)$(PPh_3)^+$, 55); no other peaks above 165 of >55%.

Crystallography. An orange prism of **4** and a dark reddish brown plate of **5** were obtained from layered CH_2Cl_2/hexane. Data were collected on a CAD4 diffractometer as outlined in Table 1. Cell constants were obtained from 25 reflections with 10° < 2θ < 25°. The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structures were solved by the standard heavy-atom techniques with the SDP/VAX package.[40] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated and added to the structure factor calculations but were not refined. The BF_4^- anion of **5** showed some disorder. Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[41] Other data are in the Supporting Information of this paper (**4**) or the Cambridge Structural Database (**5**).[15]

Acknowledgment. We thank the DOE for support of this research and T.-S. Peng and R. Lai for some preliminary observations.

Supporting Information Available: Table giving atomic coordinates for **4** (3 pages). Ordering information is given on any current masthead page.

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